Investigation into the Nature and Degradation of Leather and Leather-related Materials within a Museum-based Context

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The candidate confirms that the work submitted is his/her own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

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Abstract

The importance of preventing the degradation of museum objects is undeniable and it is connected with the knowledge available on the item to be stored. Animal skin, leather and synthetic leather are part of museum collections. Their degradation mechanisms have been studied, but that of newly developed coated leather and fabrics are less understood. Likewise, composite materials made of leather fibres and textiles have been commercialised but their degradation mechanism is mostly unknown. Therefore innovative coated substrates, leather, textiles and composites, require thorough investigations because both their identification and degradation can become a problem for museums in the near future.

Initial characterisation of natural, artificial and composite leather material with and without flame retardant was conducted using invasive and non-invasive techniques. It was found that successful identification can be carried out with non-invasive methods when both top and reverse side of the materials are accessible. In particular, visual investigation, stereo-microscopy and ATR-FTIR allowed the discrimination of the substrates. However, only the latter was able to discriminate between composites with or without flame retardant. Invasive SEM-EDX and KES-FB2 and KES-FB3 also allowed substrate identification but only EDX discriminated between the different composite materials.

Accelerated ageing was then conducted on leather and related materials. Leather-based substrates were characterised by similar degradation pathways, but only natural leather samples showed obvious signs of deterioration in appearance and mechanical properties. The composite's mechanical properties worsened in the case of substrates containing flame retardant, in particular after high heat and humidity ageing. The appearance of these materials was also partially compromised as demonstrated by the roughness results. The composite without flame retardant and synthetic leather were more stable. Synthetic leather was mainly degraded after severe heat ageing.

A list of invasive and non-invasive degradation markers was prepared and the correlation between the roughness and the bending rigidity and work for compression evaluated. In addition, the data collected during the accelerated ageing procedures were examined in the light of the current preventive conservation guidelines for museums and a revised proposal for preliminary guidelines was prepared.

Finally, the Proactive Collaborative Conservation (ProCoCo) was developed as a novel approach that has the potential to create a bridge between the knowledge of manufacturers, that of conservators and conservation scientists.

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Abbreviations

ATR-FTIR: Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy

CD: Cross-machine direction

EDX: Energy Dispersive X-ray

EL2: E-Leather® SL2

EL3: E-Leather® SL3 UL

FAST: Fabric Assurance by Simple Testing

HE: Hydroentangled fibrous face in E-Leather® samples

H+RH: High heat and humidity ageing

H115: Moderate heat ageing

H150: Severe heat ageing

H70: Mild heat ageing

KES: Kawabata Evaluation System

MD: Machine direction

PAS: Permanent Area Loss

SD: Standard deviation

SEM: Scanning Electron Microscopy

SY: Synthetic Leather

TL: Traditional Leather

UV: Light ageing using UV radiation

VML: Volatile Matter Loss

Chapter 1 Introduction

Materials degradation is an area of research which interconnects several fields. Physics, chemistry, engineering and many of their research sub-areas play a role in degradation studies and the methods used to investigate the deterioration are strictly related to the application of the product under investigation.

Normally invasive techniques are used in industry to assess properties and test resistance of products to specific parameters in the so called "quality control" procedures (Mehta, 1992). These procedures simulate, in laboratory, conditions or stresses that can occur in everyday operations. In other situations non-invasive techniques are used where sampling is not allowed or destruction of samples is not recommended (Willcox and Downes, 2002). There are other applications, along with commercial ones, that require the study of material's degradation and some of them are significant for entire communities or even whole nations.

Museums and public or private collectors have the duty of taking care of artworks and objects of social and historical significance (ICOM, 2013). Indeed it can be assumed that, when an object enters a collection, some of its intrinsic values have been recognised by a panel of experts or from a certain community (Mason, 2002). On the one side, further values are acquired by the object because of its presence in the collection. On the other side, an artwork can also reduce or lose its value as a consequence of manifold reasons. Inadequate control over environmental factors during museum exhibitions or during the storage represent some of the most overlooked causes of damage (Throsby, 2011). For this reason, preventive conservation practices have been introduced and fostered (Raphael, 2005). In fact, despite deterioration being an intrinsic feature in any material because of its chemical or physical nature, higher rates of degradation can result from incorrect storage or exhibition conditions.

To prevent the damage it is useful to put in place actions which aim at reducing the effect of harmful factors such as exposure to improper lighting sources, temperature or relative humidity fluctuations (Alcántara, 2002). However, testing the conservation state of artworks and cultural heritage often requires the use of non-invasive or non-destructive techniques. These techniques give essential information on the substrate, but sometimes they are not able to discriminate between similar materials.

Any commercial material has its own peculiarities which result from its chemical composition and manufacturing process, hence it would be risky assuming that artworks or objects made of the similar will follow the same degradation patterns. This means that the exact identification of materials in museum context is essential but it can be complex because of the difficulty of obtaining sufficient samples. One of the main consequences is the application of the wrong conservation plan, resulting in dangerous treatments on the item (Garside and Wyeth, 2003).

This difficulty is even more pronounced when new manmade or composite materials become part of museum's collections, a growing tendency in the last decades. Therefore, it is essential the development of new approaches able to address old issues, such as the simplest challenge which is the correct identification in novel and pragmatic ways.

1.1 Innovative Leather-Related Materials: Problems of Degradation and Conservation

Leather-related materials represent a good example of the identified problem. The presence of leather objects in museums is common and the variability in the state of preservation of the material is equally widespread (The Museum of Leathercraft, 2011). Nevertheless its long-term presence would suggest the availability of established conservation standards. This is partially true, however the majority of the literature on the subject is focused on vegetable tanned leather, referring to almost any object manufactured before the 1884. After this year chrome-tanning process was introduced and has been used in virtually every area of leather production, and today chrome-tanned leather remains the predominant method of tanning manufacturing (CORDIS (European Commission), 2013). Accordingly, even if the mechanism of degradation and some conservation treatments are available for leather, they are generally not addressed to the "current" chrome-tanned products.

Leather tanned with chromium, the most common form over the last hundred years, have not been the subject of extensive degradation and conservation studies. However, some research groups have started to investigate the degradation of this type of leather, often comparing its behaviour to the one of wet-white leather (Ollè *et al.*, 2011; Ollè *et al.*, 2012). To make the situation more complex, a number of concerns on the effects of chromium salts on man and environment have been brought to the attention of the public in recent years (Palop *et al.*, 2008). As a result, research in the area of more environmentally friendly tanning agents is increasing (Bacardit *et al.*, 2014; Luo and Feng, 2015) despite the continuous use of the chromium compounds. This situation makes the future of chrome-tanning uncertain.

Synthetic leather has often replaced natural leather because of two main reasons: cheaper cost of manufacturing and 'cleaner' production. Its popularity continues to grow also as a consequence of new brands and definitions like 'vegan leather' that attract specific groups of the population. Despite the questionable claim that many of these products are more environmentally friendly than "natural" leather (Chou and Chen, 2011; Christian *et al.*, 2016), synthetic substitutes have often gained the support of niche markets and general public. Synthetic leathers are designed to be very similar to natural products and it can be difficult to distinguish the two substrates, most of all in situations where the back of the material cannot be accessed and sampling is not allowed.

In addition to coated and laminated fabrics, composite products made out of leather fibres have started to be used in place of leather too. E-Leather® is one type of composite that, thanks to its properties, has found room in the transportation sector. Being quoted for three consecutive years as "one of Britain's Top 100 Fastest-Growing Private Technology Companies in the 2015 Sunday Times Tech Track Top 100", the company has demonstrated its growth potential (Fast Track, 2015). Consequently, as already happened in the past to other successful materials (Rodriguez-Mella *et al.*, 2014), the products manufactured by E-Leather can soon become part of museum collections and thus their degradation pathways need to be understood.

This flourishing of leather-like products represents a significant problem from a museum perspective, because it introduces unprecedented identification problems and new variables into the conservation equation. A proactive approach was used in this thesis to assess the possibility to overcome the issues discussed above, along with others, tackling the material's degradation from the initial production stage. The use of non-invasive and invasive techniques to detect signs of damage after accelerated ageing, along with the understanding of correlations between the two types of techniques, has been used to find possible relationships among the properties and to identify possible degradation markers.

The understanding of the typical degradation patterns associated with the specific ageing factors has potentially allowed the identification of the best preventive conservation conditions to be associated with the substrates.

1.2 Thesis Structure

This thesis is composed of seven chapters and it could be divided in three main bodies of research:

- General literature review and initial investigations;
- Development of relevant ageing simulations and ageing assessment;
- Degradation markers and remarks for preventive conservation.

The first chapter has provided an overview of the research context, presenting the close connection between conservation and development of innovative materials that is embedded in the whole thesis structure.

The second chapter gives an introduction to the concept of innovative materials and their importance in museum collections. The general characteristics of leather, synthetic leather and E-Leather® processing are reported, together with the main substrates properties that are relevant for both industries and museums. The distinction between chemical, physical and mechanical degradation is described, as well as typical methods that are adopted to investigate deterioration. The chapter ends with the elaboration of preliminary research questions, aims and objectives.

The third chapter presents materials investigated for this work and analytical techniques used to assess their properties. The instruments used to conduct the accelerated ageing procedures are also described.

The fourth chapter consists in the initial investigation of the different substrates under examination. It begins with a literature review of chemical composition and structure of the material and it continues with the study conducted on the samples. A summary of the findings concludes the chapter.

The fifth chapter is entirely concentrated on techniques of accelerated ageing and their effects on the samples under investigation. Also in this case the chapter starts with an introduction, focussed of ageing methods and parameters to be used, continues with the presentation of the results and their evaluation and concludes with a summary of the findings.

The sixth chapter provides a list of the degradation markers that can be potentially shared with museums and galleries. It then continues with the correlation analysis between three of these markers to address the need for studies that correlate non-invasive and invasive techniques. The second part of the chapter comprises an overview of past and current preventive conservation approaches, including new ideas in the field. Moreover, it suggests some preliminary remarks to help conservators in creating a safe storage and exhibition environment.

The final seventh chapter presents the main outcomes of the research and lists some important areas to be further investigated in the future. The Proactive Collaborative Conservation (ProCoCo) approach is also described and proposed as a new tool for both conservation and material development purposes. This approach consists of studying products that could become part of museum collections (alone or associated with other substrates) before they actually enter the collections. The study may be best undertaken by a team comprising manufacturers, conservation scientists and museums or private collectors.

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Chapter 2 Preliminary Concepts

The collections of items which represent artistic creativity, social testimonies and historical moments are indispensable to save traces of the past and to remember previous steps in intellectual human evolution. The history of society plays an essential role in the personal development of any individual and, even if underestimated, the same is true for the history of arts. In fact, the history of arts often comprises and represents social, historical and political issues along with developments which are meaningful for a part of certain communities or, in some cases, for a large part of the population (Europa Nostra, 2009). Therefore, society and arts are frequently intertwined and it could be challenging to define when the former influences the second and vice versa (Eccher, 2006).

The significance of any item in a collection is associated with a number of values. On the one hand, some items can hold socio-cultural values which are assigned by the society, or parts of it, because of characteristics of particular significance (Low, 2002). This represents the driving reason that guided early philanthropists in the past and often guides museums acquisitions today. On the other hand, artworks and objects can also acquire economic values and generate incomes. For example, cultural heritage is indispensable for tourism being the main stimulus to motivate people to visit a country, city or public space (Fernández-Blanco and Prieto-Rodríguez, 2011; El Beyrouty and Tessler, 2013).

The importance of preserving items that are related to historical memories of society and individuals, both in the form of artworks or objects, becomes clear and preserving items in collections acquires manifold roles. Without taking care of collections objects would become difficult to be read, lowering the effectiveness of their message; moreover in the long-term museums would experience a reduction in the number of visitors associated with the assets' deterioration. Accordingly, this would reduce the revenues (Throsby, 2011) and would make necessary to perform further conservation treatments.

Art conservation has its origin in ancient times, when Greeks and Romans artisans and craftsmen restored parts of statues or elements of paintings; renovations and adaptations have followed for centuries, becoming gradually more specialised practices (Conti, 2002). Today, despite the recognised centrality of conservation in museum contexts, it is not always straightforward to decide which is the type of approach to be used on an asset. This is valid for any object made of any material, but it is even more complex when modern and contemporary materials are involved (Chiantore and Rava, 2005).

Classic paintings and sculptures, coins, manuscripts realised before the second part of the 19th century are made of relatively well known materials and their conservation has a number of references with few exceptions. These references constitute an essential starting point for further studies on any specific field. By contrast, modern and contemporary paintings and sculptures, modern textiles, design objects and so forth can be made of countless materials often less investigated than the classic ones (Manco, 2012). They can comprise traditional and modern staples and these staples may have been subject to traditional processing methods or innovative ones. Along with them, innovative materials such as composites are often used and many of these innovative materials are characterised by unknown degradation patterns. Unfortunately, this can determine premature deterioration or the use of inappropriate conservation treatments (Hornbuckle, 2009).

Leather and textiles represent the perfect example of how classical materials have evolved from traditional to innovative performance products. They are used in countless applications, from apparel to upholstery, from medical to technical applications and it is almost impossible to live without them. Also for this reason textiles and leather can be found in many museum collections in the form of artworks, clothes, shoes, bags and so forth. This variety can be easily noticed when words like 'leather' and 'textiles' are searched in museum's catalogues (Victoria and Albert Museum, 2016). Moreover, other types of collections such as in transport museums can include these materials in the form of seats or other components (Greater Manchester Transport Society, 2016; London Transport Museum, 2016).

It is often difficult to understand the exact composition and structure of leather, synthetic and composite leather items by the naked eye and this causes confusion (Kanigel, 2011; Mirghani *et al.*, 2012). Moreover, even in those cases where it is possible to distinguish between the three materials, there is the tendency to use approaches already applied to similar items. However, there is no guarantee that the treatments applied in the past can be appropriate for the new needs and challenges. This is valid for both objects and, as pointed out by various authors, for contemporary artworks that require an understanding of the artist's thinking before the conservation can take place (Althöfer, 1991; Wharton *et al.*, 1995). Therefore, there is a necessity for modern approaches to conservation which look at introducing, presenting and conserving innovative materials in museums in a different way.

A proactive approach was experimented in this thesis to achieve the final goal of developing a flexible preventive conservation strategy for leather and leather-related materials, coming from the aviation industry, before they actually reach museum collections. The key outcome of the approach, in this and other contexts, is the achievement of social, environmental and economical values by applying treatments to prevent from the beginning the deterioration of new collection acquisitions. To do so, it is indispensable to study materials and products before their actual degradation occurs.

As already observed by Cone (2007), private companies can become crucial partners of museums and these two actors can effectively work together. If Cone proposes to use this interdisciplinarity mainly to promote innovation, a further use of this collaboration can result in the achievement of the goal of global sustainability. This approach can be crucial in specific contexts, e. g. where objects are preserved as testimonies of technological progress. However the approach can potentially be applied also in many other contexts.

An initial overview of the concepts treated in this work is essential to better understand how the different ideas have been investigated out of this thesis and why they are meaningful for this research.

2.1 Innovative Materials in Museums

As identified above, collections of modern and contemporary artworks, as well as design objects, comprise a variety of distinct materials and combinations of materials. From 300 BC onward, museums have been devoted to collect books and classic art, such as paintings and sculptures, made of well-known traditional materials (Osborne, 1985). They have gradually integrated objects considered as testimonies of the past, such as archaeological remains, transportation vehicles, design items and artworks of any kind. In the same time frame the manufacturing processes of traditional and commonly used products have been revised to encompass modern and contemporary products. The result is that today countless products are available on the market and can be chosen to become part of the object designer’s portfolio; contemporarily, they can inspire artists and be used as artworks. In the one case or in the other these items can become part of museum collections (Poli, 2005).

The shift from classic to modern materials and objects necessarily involved an increase not only in the type of exhibitions, but also on the type of conservation treatments. Remedial (active) conservation has been the most common approach for many centuries until the introduction of concepts such as the 'minimal intervention' approach. Preventive (passive) conservation gained increasing credibility in the conservation community and today it is considered an essential practice for archaeological remains (Pye, 2009) as well as for twentieth century plastic artworks and design objects (Thickett and Richardson, 2007).

These two conservation methods, remedial and preventive, appear to be much more effective on traditional materials than on the more recent, innovative multicomponent type products. New challenges have to be faced with composites and smart materials becoming part of collections. Additionally, artists become more and more aware of the importance of long-term behaviours of materials, meaning that they have certain expectations from the individual constituents they use to create their artworks. These considerations suggest that new conservation methodologies should be developed to tackle the evolving manufacturing and conservation challenges.

2.1.1 Collection Types

Museums host a variety of objects, from artworks that represent some form of expression (creative or technical ability) to items linked to social aspect, historical or technological events. The reason that determines the presence of these objects in a collection has an impact on the conservation approaches that need to be applied.

In the Fine Arts world, some of the fundamental pillars started to fall apart since the second part of the 1800. Realism moved the subject of its representations toward themes such as the working class and their struggles. Impressionists started to publicly challenge the use of well-defined lines, contours and subjects through their artworks; then followed Post-impressionism and Expressionism paving the way to Dadaism, which on its turn interacted with Cubism and avant-garde movements like Futurism (Arnason and Mansfield, 2013).

Dadaism, born as a sort of response to the World War I, has been essential to deconstruct the idea of classic art and it is probably one of the main contributors to the appearance of contemporary art movements (Ryan, 2014). However, Poli (2005) states that the introduction of everyday materials in art began in 1912-1913 thanks to Picasso and Braque. They started to use the technique called papier collé (in English, pasted paper) as an expressive mean and, in doing so, they were able to influence contemporary and future generations of artists.

Members of Abstract Expressionism, the artistic movement that in the US marks the beginning of contemporary art, used a great variety of materials many of which were not originally produced for artistic purposes. One of the most famous examples is Jackson Pollock, who often created his works by using enamel and sometimes buttons, nails, cigarettes and much more (Coddington and Hickey, 2013). Many following artistic movements have used unconventional materials because of many reasons, such as availability of that specific material, aesthetic effect of the product, suggestion of someone, best final appearance of the artwork composition or the best way to convey the message of the artist.

Innovative materials can be of any kind and they can be easily found in collections, but they are challenging and characterised by different conservation issues compared to traditional materials. For example, newly developed products might present complex ethical issues such as in the presence of genetically modified products in Eduardo Kac's Transgenic works (Kac, 2016). Consequently, any case and object has its own peculiarities that needs to be evaluated on a case-by-case basis.

If it is still quite rare to find innovative materials in more conventional art collections, they can be easily discovered in less conventional art galleries or collections of items. Despite their relatively limited presence, it is essential to know how to properly take care of these items to save them for future generations. This need becomes evident when considering specific materials as plastics. Early plastics were not developed to be used as design objects neither to become part of artworks, but they have been used by artists and designers to obtain objects that today are part of museum collections. The result is that materials used in the early years of production presented unknown degradation behaviour and, at present, some of those artefacts are in poor conditions (Keneghan, 1996).

Figure 2-1: Salvador Dalì "Lips Sofa". Courtesy of Chris Ilsley

Leather, such as fibres and textiles, effectively represents how innovation can influence and change products, markets and artist's choices (Figure 2-1). These substrates, and leather in particular, were among the first to be modified and made by man and their innovation has been continuous throughout history. For centuries manufacturing processes of leather and natural fibres have mainly changed machineries without affecting the raw materials, however the introduction of manmade polymers has revolutionised every part of these sectors (Cook, 1984). In particular the development of laminated and coated fabrics has had a revolutionary effect in many fields (Meyer *et al.*, 2008).

Leather and coated or laminated fabrics that are normally used to produce footwear, bags and clothing are already documented in the V&A collection (Victoria and Albert Museum, 2016). It is likely that many other museums and private collectors own items originally manufactured using these materials. For example, Meyer, Schulz and Stoll (2008) mentioned that automotive industries introduced nitrocellulose-coated fabrics in the 1927, therefore these materials are likely to be present in collections of cars or other transportation vehicles.

Today many textiles are manufactured with the aim of reproducing the structure and appearance of leather, generally using coating or lamination techniques. Likewise, leathers can be sometimes manufactured to simulate fabric properties. The level of innovation in these materials is very high but, being composite materials, it is rather common to come across unpredictable degradation patterns. The understanding of common deterioration patterns provides a foundation for the development of solutions to tackle the composite degradation.

For all the above reasons, the need for studies on leather-related materials focused on the correct identification of innovative materials and on ways of determining common degradation patterns becomes clear.

2.1.2 Conservation Ethics

Rarities and objects recovered from sites inhabited by early humans or past populations have always fascinated naturalists, archaeologist and anthropologists and since the late 1600 onward they became part of exhibitions and collections gradually accessible to the public (Salter and Lobel, 1954). The number of items in archaeological collections and museums of early and contemporary civilisations is incredibly varied, ranging from wood, metal and pottery to leather and textiles. Dealing with diverse collections requires a broad knowledge of the practical treatments as well as a profound awareness of social and ethical implications of the same treatments (Hoeniger, 2009).

When dealing with more recent items or artworks, the reason that determined the choice of a material over another has a great impact on the conservative approach to be used, both in terms of storage and exhibition (Chiantore and Rava, 2005; Stigter, 2009). In addition, the ephemeral nature of many modern and contemporary artworks has been brought to the centre of the discussion in online magazines (Lansroth, 2016) as well as in specialised public events (Getty Conservation Institute, 2009), indicating that this is becoming a major issue in the field. Preserving or conserving items and artworks of this kind can be an intricate puzzle with many variables. As further proof of this delicate equilibrium, and to point out the deep connection between heritage and capital value, in 2014 Emily MacDonald-Korth and James Korth defined the Art Preservation Index (APIx), which is a method for evaluating and rating an artwork's stability to provide art investors with information on the long-term stability of possible acquisitions (Art Preservation Index/APIx, 2016).

Recently, interviews with established artists have been carried out and collected in books and websites with the aim of gathering opinions and preferences with regard to conservation methods to be applied in the future on their artworks (Pugliese, 2006). However, this approach only covers a limited aspect of the problem, the one of the artist or maker, introducing the issue of who should decide how to conserve the item. In an article posted online from The Royal Academy of Arts two visions are proposed: the sculptor Phillip King thought that the artist who creates an artwork should have the final say on its conservation, whereas the art historian Alison Bracker argued that as soon as an object becomes part of a collection the artist's voice is not the most relevant anymore (King and Bracker, 2015).

This controversy does not have a definite answer or a black/white solution. However, it strongly emphasizes that artworks are composed of manifold facets that lay on different 'spaces of significance': the one of the artist, that of the gallery, that of the public and that of the conservator.

2.2 Leather and Related Materials

Leather and fabrics are two categories of materials defined by different morphological, chemical and physical characteristics. These two groups of products have also a more subtle difference. The word leather refers to the product of specific manufacturing procedures that must always comprise a tanning stage (British Standards Institution, 2015). The term fabric comprises a wide range of products among which also includes the coated fabric family. More specifically, the term leather-related materials focuses on those textiles that have been subject to treatments to make them look like leather materials. In between these two categories, hybrid composites of leather and textiles have also appeared in the last decades.

It is noticeable that only a limited number of published articles have investigated the similarities and differences between leather, synthetic substitutes and composites. For example, Sudha *et al.* (2009) compared data relating to comfort, morphology and the chemical and physical properties of leather and synthetic leather fabrics. The aim of the study was mainly to achieve an understanding of the comfort properties of the two substrates and to assess if leather and synthetic leather had similar levels of comfort. The lack of publications in this area was considered as a technical deficiency which needed further research to provide solid comparative data.

A description of the historical background concerning both materials and processes follows.

2.2.1 Traditional Materials - New Developments

Due to the obvious difficulties in material preservation it is rather uncommon to find evidence of skin and early leather objects in archaeological context, however, it is thought that man has always used skins of hunted animals (Higham, 2011; Harris, 2014). The lack of a real tanning process, which is commonly carried out to avoid skin putrefaction, has probably contributed to leather artefacts easily deteriorating. Over time, the type of treatments performed and the raw materials used have changed making leather increasingly more resistant and more versatile (Figure 2-2).

Since 1884 leather has undergone one of the most significant technological changes in its history with the introduction of the chrome-tanning process (Dirksen, 1997). This process has spread throughout the world and has brought further innovations into the sector.

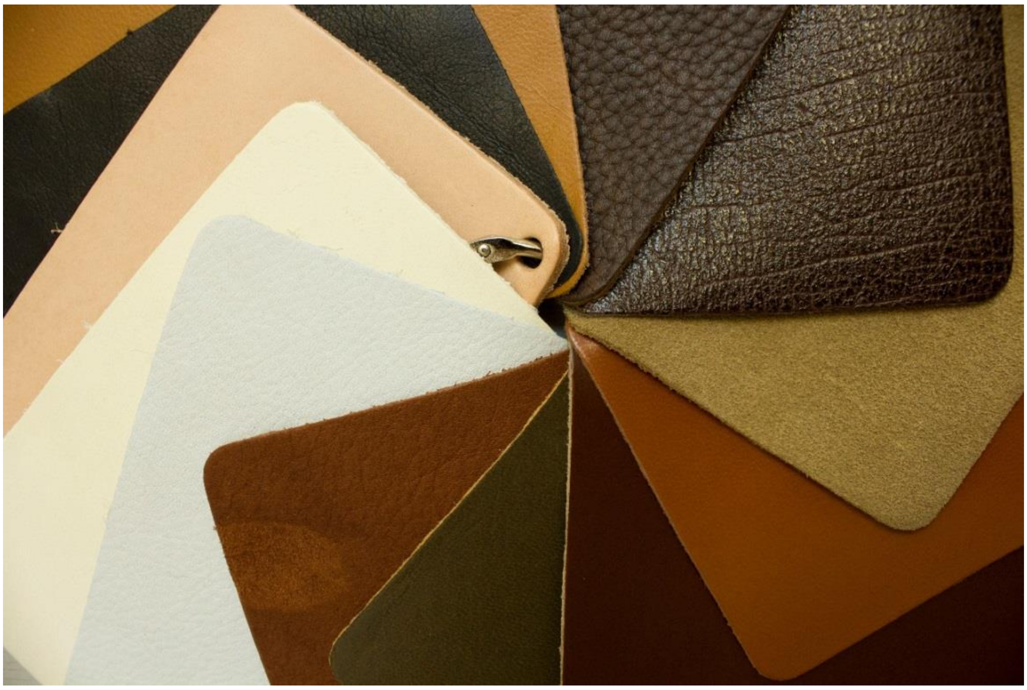

Figure 2-2: Leather samples tanned and coated in different ways

Not all these innovations have had a positive effect on the final material and, unfortunately, the major part of the issues becomes evident only when the material has started its degradation (Palop *et al.*, 2008). Detecting signs of damage at an early stage is therefore essential to preserving materials and items, but to do so one must be aware of the original manufacturing techniques and chemicals used.

2.2.1.1 Natural Leather

The historic evolution of leather manufacture has probably had its beginning with primitive man. Rock paintings dated to thirty-five thousands and twenty-five thousands years ago show humans in skin clothes (Thomson, 2011b). Despite their limited number, a few items made of animal skin have come to us due to particular conservation conditions as in the case of the Ice Man (Spindler, 2013). This has allowed archaeologists and scientists to trace back the pathway followed by early skin products and leather materials during the centuries. Probably a number of trials have been carried out before defining which agents were able to stop or decrease the rate of skin degradation and, because of the high decomposition rate of untanned materials, these trials did not withstand the passage of time.

Vegetable tanning was represented in Egyptian wall paintings and documented in Sumerian books of spiritual ceremonies (Thomson, 2011b). Both in the period of Classical Greece and with the Romans leather commerce was crucial for the development of the urban environment. However, after these initial innovations the manufacture procedures remained almost unchanged until the nineteenth century (Thomson, 2011b).

The introduction of chrome-tanning represented a significant industrial development within the overall industrial leather tanning process. Between the 1870s and the 1880s Heinzerling and Augustus Schultz made crucial steps in the understanding of the operations to optimise the tanning for industrial applications but it was not until Martin Dennis patented the one-bath method that the current commercial technology for tanning was established (Thomson, 2011b).

According to FAO (Food and Agriculture Organisation) sources, in recent years leather production has been growing weakly due to two opposing market trends. In the developing world the production shows a positive, growing trend whereas in more developed EU and American countries there is manufacturing contraction due to a number of factors. The cost of the production is higher in developed areas than in emerging countries and is considered one of the main factors for the market changes (Trade and Markets Division Food and Agriculture Organization of the United Nations, 2013). Other influential factors that are likely to contribute to the lowering of the leather production in richer areas is the price of raw hides and, to a greater extent, the number of environmental concerns and regulations which also result in high disposal costs (COTANCE & Industrial All, 2012). These considerations make the future of leather less certain than it was in the past and encourages the emergence of substitute materials into the market.

As a consequence, studying the degradation of leather products is not only important for historic objects, but it is also crucial for those materials that are produced today and will need to be preserved in the future.

2.2.1.2 Manufacturing Process

Thomson (2011b) describes the main technical innovations in skin processing from primitive men till recent innovations. A summary of common operations carried out in tanneries is shown below (Figure 2-3).

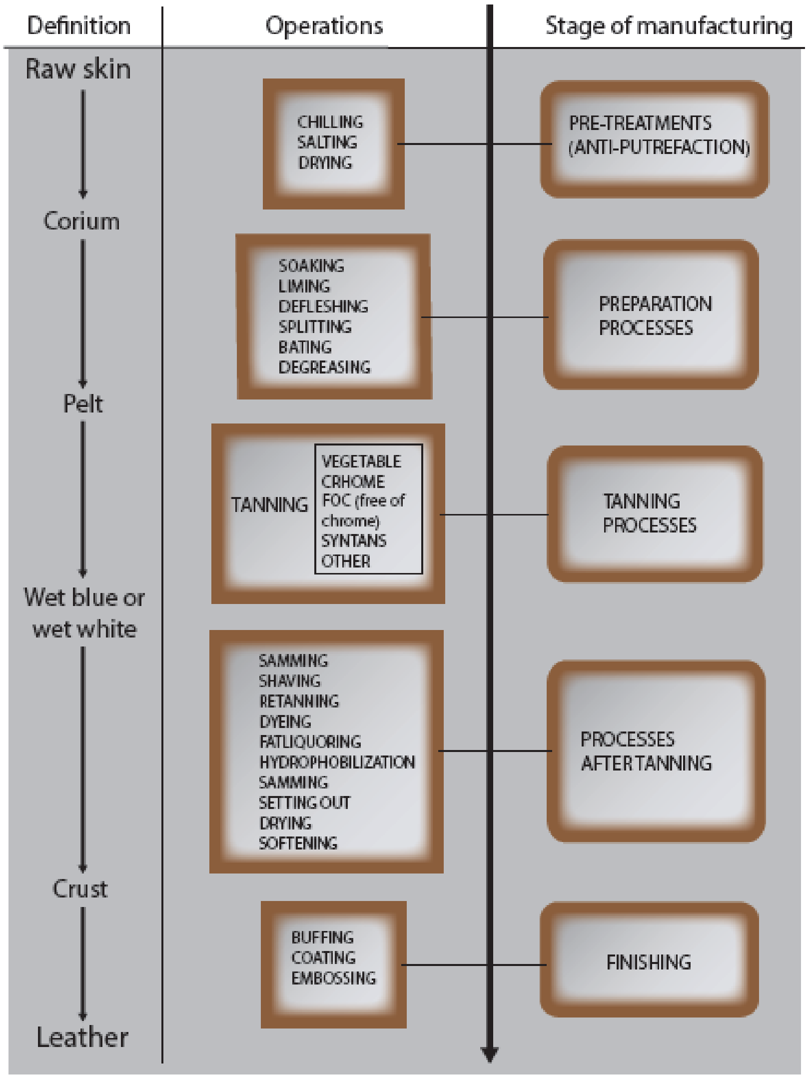

Figure 2-3: Representation of typical leather manufacturing stages with related operations and definitions

The procedures involved in today's leather manufacturing are very similar to the ones used in the past, even if the introduction of new machinery and the use of carefully selected chemical agents has increased the quality of the work environment. It is important, in fact, to point out that the conditions in which leather workers used to work in the past has dramatically improved due to factors such as environmental and health concerns. Nevertheless for reasons connected to religion, working conditions of workers still remains a problem in countries as India, Nepal and Japan (Higham, 2011).

Five main processing stages are normally carried out:

- pre-treatments, refers to processes conducted to avoid putrefaction;
- preparation, where the corium (sometimes only the grain layer is used) is prepared to receive the tanning agent;
- tanning, characterised by different steps according to the tanning procedure applied;
- post-tanning, defines the operations used to improve aesthetic qualities of the wet-blue or wet-white;
- finishing, which comprises operations like coating application and, therefore, are more common in leather produced after the 1950s.

Salting or chilling with ice are common techniques to avoid putrefaction used after the skin has been removed from the animals and before it is sent to other industrial plants for further processing. At this stage there is a high risk of damaging the skin collagen fibres and this would lead to leathers of lower quality. Therefore drying, often by salting, is carried out to minimise this risk (Beghetto *et al.*, 2013).

Once the dried skin is received it requires further treatments to clean the collagen fibres by removing unwanted materials and to prepare/open the fibres for the tanning process. Dirt, dung, salt, and soluble non-collagenous proteins are removed through soaking in drums which also permits the hide collagen to rehydrate (Reich, 2005). Alkali, calcium hydroxide or calcium oxide are used, often in conjunction with sulphides, in the liming process to make the basal membrane less resistant and to obtain effective dehairing and epidermis removal. This is then followed by an enzymatic process called bating, which uses trypsin or other bacterial enzymes to clean the substrate. Finally, the chemicals introduced through the liming process must be removed from the substrate, thus a deliming treatment is carried out by using lactic acid (in the past also ammonium salts were used) (Reich, 2005). The resulting material is called a pelt.

Tanning process represents the most important step in leather processing. It is performed treating pelt to obtain an intermediate (‘wet white’ for vegetable tanned or ‘wet blue’ for chrome tanned leathers) which is further processed to become leather. Reich (2005) explains that, thanks to the tanning procedures, collapse of collagen fibres after the removal of water is prevented thus stabilizing the structure. Collagen fibrils are not able to adhere to each other, in fact, the presence of tannins in the voids between fibrils and fibres reduces the tendency of collagen fibres to stick together. Once tanning is completed the level of cross-linking increases resulting in the lowering of the swelling capacity and increasing the hydrolytic resistance and hydrothermal stability.

After tanning a number of other operations are still necessary before the actual leather is usable. Re-tanning using vegetable tannins or syntans provides the intermediate with further resistance (Beghetto *et al.*, 2013). In addition dyeing processes with anionic or cationic dyes imparts the requisite colour for the desired final material. Sammying and shaving are performed to make a smoother and more attractive the substrate. Fat liquoring (or chemical lubrication) is then carried out to achieve the following goals:

- softening the leather by allowing the fat to penetrate into the matrix;
- limiting the water take-up;
- improving tensile and tear strength (Reich, 2005).

After the application of the fatliquoring further stages of sammying can be necessary before drying and softening operations.

Finally, further finishing treatments are performed to improve the physical and aesthetic properties of leather. This creates a substrate with the desired quality and performance standard (Meyer *et al.*, 2008). The application of polymeric coatings is often carried out to obtain materials with the required characteristics, followed by embossing and buffing (Reich, 2005).

Not all the procedures described above are regularly performed on leathers, similarly, on some occasions more operations are necessary to produce specific substrates. The quality of raw skins and the effectiveness of each stage have a significant influence on the final leather, therefore it is important to perform every operation with great care.

As already discussed most of the current operations have evolved over a number of years but there have been a limited number of technical refinements over that time period. Bating is an example of the change in procedures and chemicals that has occurred in the last two centuries. In fact, bating was among the most unpleasant processes to be performed in leather manufacturing because it involved the use of dog dung or bird droppings (Thomson, 2011b). Another example of change in the practice regards vegetable tanning, which in the past was carried out in large pits where layers of hides were meticulously piled in presence of water and tanning agents. This historical process required up to two years (Dirksen, 1997) and it is clear that with that manufacturing timescale it would have been impossible to meet the increased demand for leather items in the nineteenth and twentieth centuries.

The identification of certain chemicals, manufacturing procedures or the physical features imparted by the different machinery on leather can be crucial in conservation. The clear understanding of these changes throughout history has been essential to help conservators to restore objects in collections (van Soest *et al.*, 1984). Completing this understanding by including innovative materials and leather substitutes will become essential in the future, when the new materials of today will transform into historic materials.

2.2.2 Synthetic Leather

The origin of coated fabrics, and subsequently of artificial leather, is difficult to assess with certainty (Ciesielski, 1999). Depending on the definition of coated fabric, one could argue that the practice of fabric wrapping with addition of oils and balsams was common in the Egyptian culture and was an early example of coated textiles. Some researchers consider the eighteenth century practice in use in England and Germany of spreading and drying oils over fabrics as another example (Fung, 2002b). Others think that early evidences of waterproof clothing and footwear articles should be attributed to Aztecs and Mayans. Ciesielski (1999) says that the first testimonies of these articles go back more than two thousand years even if the discovery of natural rubber was attributed to Cristoforo Colombo. During his travels in the early 1490s, Colombo reported that he came across the inhabitants of Haiti while they were playing with a ball made of a tree extract. This event opened the door for the introduction of rubber technology in to the European Market. However, the actual development of coated fabrics did not take off until the first part of the 1800.

The following sections will describe the development of synthetic leather and will then introduce the common technologies used for the production of synthetic leather, providing also a list of other technologies used for coated fabrics.

2.2.2.1 Modern Synthetic Leather

Artificial leather is today readily available and used for the production of a diverse range of goods, e.g. sofas and footwear, as well as for covering material used in transportation. It is normally available in rolls of 1.40 metres widths that can be easily cut to size and is able to be produced in a wide range of colours.

Towards the end of the eighteenth century gas works experienced an increase in the production of waste as a consequence of the introduction of street lighting. Charles Macintosh started to conduct research on this type of waste and he discovered that naphtha could effectively dissolve rubber. A few years later, in 1823, Macintosh patented the first waterproof raincoat produced by a sandwich of three layers: the outer layers were made of fabric and the inner one of rubber (Macintosh, 1823;

Grace’s Guide Ltd., 2016). These products had a strong smell and showed several problems during the ageing process, but these issues were partially overcome when Hancock patented the vulcanisation process in 1844. The clothing industry introduced almost immediately the new substrate to develop waterproof apparel and was quickly utilised in the emerging automotive and aircraft sectors.

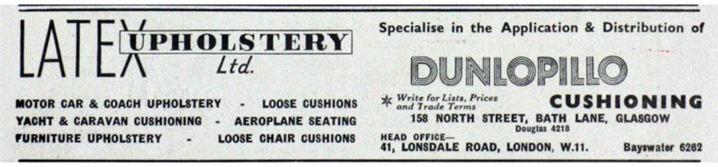

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Figure 2-4: Grace's Guide. 2016. Latex Upholstery - October 1937. [Online]. [Accessed 10 June 2016]. Available from: http://www.gracesguide.co.uk/

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Figure 2-5: Grace's Guide. 2016. Latex Upholstery – April 1957. [Online]. [Accessed 10 June 2016]. Available from: http://www.gracesguide.co.uk/

These early successes encouraged the development of new coating materials, for example nitrocellulose, produced on a wide scale since about 1850, was used as a coating material for cotton. Then in the early 1900 new synthetic rubbers arrived on the market and finally polyvinyl chloride (PVC) provided a core group of performance coatings (Fung, 2002a).

Until the late 1950s/early 1960s it was difficult to envisage a real alternative to natural leather, but since then polyurethane (PU) bonded products started to replace traditional substrate driven by an enthusiastic combination of industries and users. The increased cost of leather, the limited availability of raw skins in relation to their high demand and the reduction in the price of polymeric materials provided an enormous impetus to the development and sales of PU based fabrics, particularly in the sector of shoe uppers, upholstery, and automotive seats (Pseja, 1974). Even though early products were not always up to the requisite expectations, continuous research into the field led to significant improvements in the first years of the 1970s.

In the same years interest into the field of breathable films for fabrics increased (Westfall and Mayfield, 1974) with the aim of developing porous matrix characterised by highly interconnected pores. Today the applications of synthetic leather is very wide and the material has often replaced traditional leather for applications which require inexpensive, high abrasion-resistance and low-waste products.

Coated and laminated fabrics are the result of a multi-material processing that has been optimised over the past fifty years and it is still in development. When referring to synthetic leather, one is generally talking about a substrate which is the sum of a fibrous substrate of woven, knitted, or nonwoven fabric with one or more coating layers on it (Sen, 2007). A schematic section of laminated and coated fabrics is given in Figure 2-6. Each layer represented in the figure has distinct chemical and physical features.

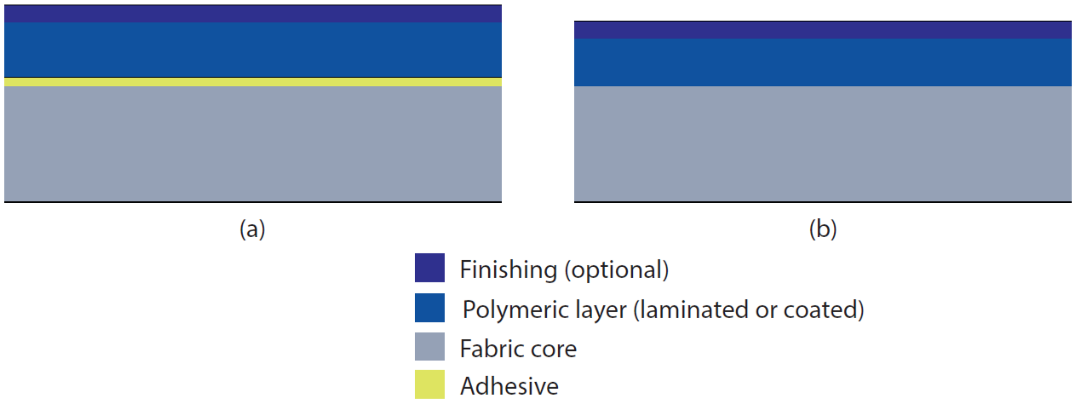

(a) (b)

Figure 2-6: Schematic section of synthetic leather. (a) laminated fabric, (b) coated fabric

A deeper description of typical fibrous layers and coating or laminating polymers will be given in Chapter 4.

2.2.2.2 Manufacturing Procedures

Coating and lamination are two processes that enable the production of synthetic leather products. Holme (2003) explained that these procedures are often used to enhance textile properties and extend the range of their applications by utilising flexible machinery and engineered polymers with broad performance characteristics.

One of the main processing challenges for coated and laminated fabrics is the adhesion (Holme, 1999) between the fabric and polymeric layer, or between one polymeric layer and another. If these layers do not effectively bond then delamination or coating fracturing will occur resulting in a loss of product integrity. For this reason the interface where adhesion takes place must always be clean and a pre-scouring stage is often carried out to minimise potential problems (Fung, 2002a).

An understanding of the different types of coating and lamination process is important when studying leather substitutes, their evolution and possible degradation problems.

2.2.2.2.1 Coating

Coating techniques combine fabric and the natural or synthetic polymer by spreading an aqueous dispersion or a solution (aqueous or solvent-based) on to the fibrous layer. The polymer can be directly applied to one or both the sides of a fabric (Holme, 2003). Once applied to the fibrous layer, the polymer is then heated to cure the polymeric matrix. A range of coating techniques for textiles have been developed and the most significant of these are discussed below.

Direct coating or floating knife techniques, are the simplest methods to create coated fabrics and consist of the polymer resin being spread over the fabric while the latter moves below the knife or blade. The thickness of the coating is adjusted by regulating a fixed doctor blade that removes the excess of polymer. During processing, resin viscosity and the drying process are important parameters which need to be constantly controlled due to their influence on the uniformity of the layers. The coating layer reduces the porosity of the fabric and can result in complete fabric impermeability. Also the coating must be flexible and durable to ensure high technical performance. Fung (2002b) reported that direct coating is generally used for woven fabrics and is commonly applied for tarpaulins, waterproof garments and car seats production.

Transfer coating is another technique that provides high quality textiles and is used for knitted and more open-structure fabrics. It is frequently characterised by patterns obtained through the use of embossed release paper. The result is a pre-formed embossed film that finally becomes the top layer of the fabric. This technique requires the preliminary formation of a polymer layer (in some cases embossed) which is laid and dried on a release paper. A second polymeric coating, or adhesive, is applied over the first layer and, then, they are pressed onto the fabric and heat cured (Durst, 1985). This process is often used to produce synthetic leathers.

Another process used to create leather substitutes is through a coagulation process, which consists of dissolving the polymer, commonly a PU, in an appropriate solvent and then applying the resulting solution to the fabric through a controlled precipitation procedure. This technique is relatively expensive and requires the careful control of the coagulation and drying/curing process stages (Fung, 2002a).

There are many other methods to apply coating on fabrics and sometimes also to leather. Foam and crushed foam coating allow the coating of knitted, spun yarns or spun fabrics. This technique is similar to the previous but is characterised by low add-on levels and limited penetration into the fabric. Foam coating leads to softer handle and more opaque substrates when compared to fabrics obtained through direct coating (Fung, 2002b). In hot-melt extrusion thermoplastic polymers are applied after heat rollers are fed with polymer granules. In this case the film needs to be supported by a fabric (Holme, 2003). Calender coating may be used to produce unsupported films and consists of a number of rollers which squeeze the malleable polymer into a film which is then pressed and bound to the fabric. Finally, rotary screen coating consists of a machine in which the compound to coat is forced through a cylindrical screen which applies the coating (Fung, 2002b). To the author's knowledge, no publication mentions any of the last three methods associated with the synthetic leather production.

2.2.2.2.2 Lamination

Lamination combines two or more layers of pre-formed material by mean of an adhesive applied to the surface to be laminated. The pre-formed film or a membrane is treated with adhesive and bound to the fabric by heat or pressure. In the early years of production PU foams were spread on the surface of fabrics but the process was too slow and the product showed technical deficiencies. Subsequently, pre-formed sheets of polyurethane foam were flame laminated with the foam superficially melted and the fabric was joined by squeezing it together with the foam. This treatment was significantly faster and became an industry standard (Holker, 1975). Also in this case, similarly to coating methods, various alternatives are available on the market.

The main method used to produce car seats both on fabric and leather substrate is flame lamination (Fung, 2002c). In the flame lamination process PU foam is passed over a gas flame at high temperature, the foam surface melts, depolymerises and it is physically and chemically combined with the textile. A series of rollers applies pressure to the foam-laminated material to achieve better adhesion and increase chemical bonding of the layers.

Hot-melt lamination is another method of lamination that makes use of thermoplastic adhesives. Powders are heated, melted and finally applied to the fabric and pre-formed film. Differences in the lamination process can also involve the nature of the adhesive and they can be classified into two categories, i.e. aqueous based and solvent-based. The former is conducted with knife-over-roller technique. However, the adhesive can also be applied to a release paper and then transfer coated on a fabric. Also rotary screen-printing can be used, and in this case water is evaporated by mean of IR heating. Finally, in solvent based adhesive lamination process the bonding occurs between a micro-porous membrane and a textile. PU is normally used for this application, which is applied over the fabric carrier and cures thanks to the interaction with moisture (Singha, 2012).

2.2.3 Latest Generation Materials

2.2.3.1 Textile Fibre/Leather Composites

Composite leather refers to a category of materials that does not have a standard definition. However, the term is frequently used to describe materials partially made of leather fibres which are re-formed, in rolls or boards, after processes of fiberisation have been performed on actual leather waste. Despite the lack of a clear definition of composite leather, the BSI included some guidelines regarding materials obtained from conversion of leather fibres into the standard dedicated to leather terminology (British Standards Institution, 2015).

> ***"leather fibre board***
> ***bonded leather fibre***
> ***recycled leather fibre (and similar terms)***
> *material having a minimum amount of 50 % in weight of dry leather fibres, where tanned hides or skins are disintegrated mechanically and/or chemically into fibrous particles, small pieces or powders and then, with or without the combination of chemical binding agent, are made into sheets*
> *Note 1 to entry: If there is any other component apart from leather fibre, binding material and leather auxiliaries, then this is declared as part of the description.*
> *Note 2 to entry: Where the material has been disintegrated and reformed in some way, the appropriate generic term is"...X leather fibre"- for example," bonded leather fibre," or "recycled leather fibre." On this basis, the terms "recycled leather" or "recycling leather" are used incorrectly."*
>
> Extract from BS EN 15987:2015

Accordingly, the most appropriate term for defining materials that have been re-constructed after leather pieces have been subject to fiberisation is composite leather fibre.

Reich (2005) reports that it is estimated that only 50 % of skin collagen is converted in leather and the remaining half needs to be reused or it becomes waste. In an attempt of reducing the collagen waste coming from tanneries, which can be difficult to manage because of its large amount and the presence of chromium (Famielec and Wieczorek-Ciurowa, 2011), several research groups and companies are developing methods to use skin trims and shavings (Tatàno *et al.*, 2012).

A large number of substrates having variable ratios of leather fibres and polymeric substances can be included in the composite leather fibre category and E-Leather® is related to this family of materials. A description of the characteristics of this type of composite and its manufacturing process is provided below.

2.2.3.2 E-Leather®

2.2.3.2.1 Characteristics

E-Leather Limited is a company that manufactures a series of products comprising a certain amount of leather fibres, coupled with synthetic fibres and a woven fabric, which are finally covered with a PU coating. The end-products are identified by the letters SL and a number. These substrates can be different from other composite leather fibre materials, such as leather fibre boards, that are often rigid and frequently not refined.

In the FAQ section of the company website the material is defined 'composition leather' (E-Leather, 2016). However, in this case the term does not have a universal definition. It could be thought that the term refers to the concept introduced above of composite leather fibre, but the exact percentage of leather is not definitely stated in the patent deposited by the inventor (Bevan, 2005) whilst the standard states that, to enter in that category, the leather fibres content should be more than 50 %. The only reference to the term was provided by the United Nations (United Nations Commodity Trade Statistics Database, 2016):

*"**4115** **Name:** Composition leather with a basis of leather or leather fibre*

> ***Description**: Composition leather with a basis of leather or leather fibre, in slabs, sheets or strip, whether or not in rolls; parings and other waste of leather or of composition leather, not suitable for the manufacture of leather articles; leather dust, powder and flour."*

Extract from United Nations Commodity Trade website

Even if the exact definition to give to this product might be minor in everyday applications, it is crucial to address the nomenclature issue in museum context. There are currently no evidences of objects made of E-Leather® in heritage collections but the substrate could soon become part of museums and private collections. In fact, the products sold by the company are increasingly present on the market, can be found in many public transport networks around the world, and production has been further boosted by grants and awards (Environmental Technologies Fund, 2016; Fast Track, 2015). Consequently, even if it is not certain that artists or designers will use this material to create artworks or design objects that will finally end up in museum collections, E-Leather products can be among the best candidates to be used for that purpose.

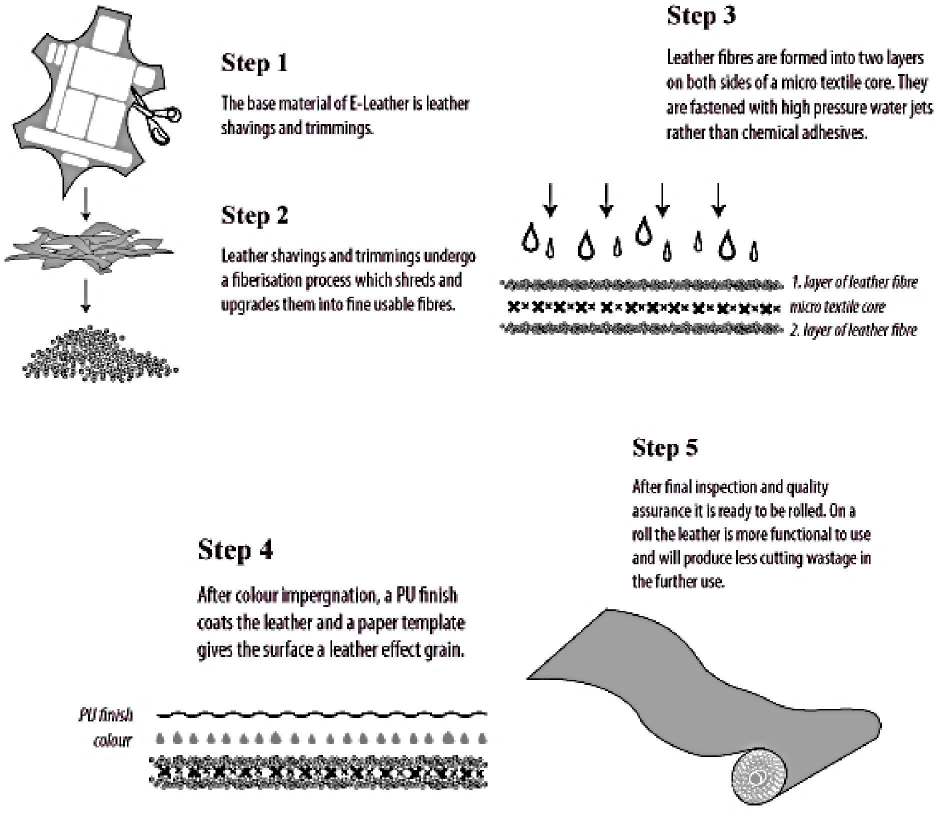
Technically, E-Leather® is almost half way between leather and synthetic leather, because the core is made of leather fibres but it also comprises a woven textile interlayer and a final PU coating. The following paragraph provides an insight into the manufacture of the substrates.

2.2.3.2.2 Manufacturing Process

Three main stages, which include a number of additional operations, are performed to create E-Leather® and are crucial for obtaining the desired product. The stages are:

- Formation of the web made of leather fibres;
- Bonding via hydroentanglement;
- Finishing.

Figure 2-7 illustrates the essential stages of E-Leather® production.



Step 1

The base material of E-Leather is leather shavings and trimmings.

Step 2

Leather shavings and trimmings undergo a fiberisation process which shreds and upgrades them into fine usable fibres.

Step 3

Leather fibres are formed into two layers on both sides of a micro textile core. They are fastened with high pressure water jets rather than chemical adhesives.

Step 4

After colour impergnation, a PU finish coats the leather and a paper template gives the surface a leather effect grain.

Step 5

After final inspection and quality assurance it is ready to be rolled. On a roll the leather is more functional to use and will produce less cutting wastage in the further use.

Figure 2-7: E-Leather production process (from Nurmi website (Nurmi, 2011)

Leather Sheet Formation

Shavings and trimmings of leather obtained from the waste of the tannery industry are selected after tanning, when the hide is still at the wet blue stage. An initial selection process is carried out to discard poor quality leather that, for example, has been attacked by mould or shows reduced mechanical properties. Leather bales are transported through a series of mills which act mechanically on the trimmings forming a pulp during what is called fiberisation process. This is the first crucial passage because it reduces the size of the fibres of both trimmings and shavings. The resultant leather fibres have small dimensions (length below 850 μm and diameter ranging between 5 and 70 μm) and loose aspect because they are not part of the coherent leather structure anymore.

At this stage the fibres would be ready to be hydroentangled to the woven fabric, but the process would be risky because they are so fine that could be easily displaced from the action of the water in the wet processing. Low melting point synthetic fibres are introduced to overcome this problem. These fibres melt after the application of heat and form a web with the leather fibres. Moreover, bicomponent splitting fibres (see Section 4.1.3.1) are added to increase the strength of the network in the final leather fibres sheet. This operation is carried out by transferring both natural and synthetic fibres to the air-laying machine, where they are mixed and laid on a tissue paper made of wood pulp fibres in the form of a non-woven sheet. The tissue paper with all the fibres on the top is placed on a moving carrier belt that passes through a vacuum box where the fibres are forced through the tissue paper, and then is compressed and heated at about 140 °C. This stage results in the low melting fibres melting and forming a low cohesive strength web composed of bi-component and splitting fibres, leather fibres, and tissue paper (Bevan, 2005).

Nip rollers are also used to lightly compress the surface and give the web the necessary strength to allow winding onto a reel which is then used in the next stage. The formed leather fibres sheets (defined as 'core') are left for a few days to rest before being subject to hydroentanglement.

Hydroentanglement

The goal of this operation is joining two or more cores and a woven fabric by using a series of hydroentanglement passages, that is 2 or 4 per side.

There are three stages, each of them comprising one or more passages, of consolidation:

- In the primary consolidation two cores are fed onto the carrier together with the fabric, the fabric being between the cores, placing the tissue paper on the upper side of the top core and on the bottom of the inferior one;
- Finish face consolidation takes place on the primary core and it is conducted at decreasing values of water jet pressure for reducing the penetration of the water and improving surface appearance;
- Additional web and final consolidation involve the addition of another layer, where necessary, and passing the surface under water jets to completely remove the watermarking features left by the water itself (Bevan, 2005).

The fabric reinforcement is joined with two or more air-laid webs. The jets are sprayed from the top and towards the face which has the screen (or tissue paper) on it which becomes the surface that can receive other layers through following hydroentanglement. The shielding tissue paper minimises the superficial entangling of leather fibres. This phenomenon would occur in the absence of shielding material obstructing both the deeper jet penetration and making it less effective in the tangling in the lower part of the web (Bevan, 2005). Leather and synthetic fibres are intermeshed with each other and pulled through the woven sheet due to the jets action. During this hydroentanglement the splittable fibres are split and also become entangled with the rest, enhancing the cohesion within the web.

During E-Leather® production high pressure is commonly employed to obtain the highest consolidation possible, and it is then gradually reduced to have lower penetration. The pressure is normally between 200 and 50 bar according to the number of passages and the side of the sheet to be treated. The speed of the operation has also an influence on the final product.

At this point the entangled web (defined 'HE') is almost ready to be finished (Hartung, 2014). Coloration with pigments and fatliquoring with an oil emulsion are performed, the latter being carried out to improve the handle after the hydroentanglement stage.

Finishing

The coating of a material with PU-based polymer is obtained through a stage procedure typically used for synthetic leathers, that is the transfer coating.

A paper reel with a defined pattern embossed on it, called release paper, is used to imprint the desired textured design into the top coating. The formation of the coating is performed in two stages to reduce the thickness of the polymeric material, thus increasing the quality of the finished surface. In fact, the gas formed in the PU coating could produce bubbles throughout the layer giving rise to faults during the material lifetime. By applying two different coating layers each of these layers would permit possible superficial bubbles to escape. However, the presence of bubbles in the final product is difficult to avoid. Another layer of PU, less dense and more adhesive, able to stick to the HE formed, is then applied on top of the previous two layers (Durst, 1985). Through this method the outer coating of the final composite is the one in contact with the release paper and the first to be formed, whereas the last layer will constitute the adhesive surface between HE and top coating.

During this processing stage the PU polymer was not cured and it did not achieve its final chemical and physical shape. Therefore, the final finishing passage consists of pressing together the two layers, the one with the coating and the one with the HE, while the curing process is taking place.

Abrading of the surface coating is performed with sand paper, then buffing and pulling take place to complete the manufacturing operations (Hartung, 2014). If necessary, a flame retardant is also applied to comply with the relevant regulations. A series of quality controls conclude the production cycle and prepare the material for the market of destination.

2.3 Properties of Interest in Leather-Related Materials

The properties of leather-related materials are extremely variable and can be adjusted according to the final application needs. Leather and coated or laminated fabrics are easy to find in everyday life, for example in clothing and upholstery, and in recent years also composite materials have started to appear. However, even if the requirements that clothing needs to satisfy are similar to those of upholstery, they do not always overlap.

Moreover, properties tend to change with time and wear and tear, therefore the study of those factors which influence the long-term ability of the materials to perform optimally is crucial. This is true for many industries, which are concerned with the quality control of their products, but it is less important for museum collections. In fact, artworks or design objects are not subject to the same kind of stresses of everyday objects and sometimes they have never been subject to any stress connected with their usage. In this case, failures in the constituent materials are frequently associated with time and conditions of storage, exhibition or transport.

The following sections will describe some crucial properties of leather-related materials that will be relevant to this thesis.

2.3.1 General Properties

2.3.1.1 Appearance

One of the first qualities to be evaluated is visual appearance. Assessment of appearance is rather immediate, generally it does not require sampling and does not involve expensive tools or instruments. Appearance can provide important information regarding other properties, such as structure, drape (Wang and Hurren, 2008), manufacturing problems or presence of impurities. Moreover, it is one of the key factors in customers' decision process during purchase and this makes it essential for merchantability.

Uniformity of the surface, colour difference and presence of holes or bubbles are some important properties for the final impression of any item. One the one hand, the presence of holes, bubbles, grooves or any superficial geometrical deformation on a flat surface produces a discontinuity that interacts with the eye and can be perceived as a defect. On the other hand, repeated and regular patterns, as well as repeated and regular imperfections, can pass unnoticed to the naked eye and be identified only through accurate microscope observations. These patterns can affect the macroscopic appearance of materials both in positive and negative ways.

Surface uniformity influences the macroscopic appearance of materials. Pilling and wrinkling are two examples of properties normally tested through appearance investigations and a number of standards are available to effectively replicate the tests in different laboratories (British Standards Institution, 2001; British Standards Institution, 2009). Pilling is generally related to yarns and therefore it is not central in this context. Wrinkle formation, however, is also a quality of interest for leather-related materials.

Wrinkles tend to form in leather, artificial leathers and composites after they have been worn for variable amounts of time or after a stress has been applied. The number of wrinkles and their depth changes depending on materials' properties and the factors the samples are subject to. Moreover, leathers and fabrics used for automotive and garment need to withstand specific types of stresses that can lead to the formation of wrinkles.

Roughness is often used to assess the presence of wrinkles (Wang and Hurren, 2008). The surface peaks and valleys can be measured by means of various techniques obtaining information on how flat the product is according to the material profile (Figure 2-8). Other qualities are related to roughness, such as friction (see Paragraph 2.3.1.2).


(a) (b)

Figure 2-8: Schematic representation of roughness analysis via image processing method (conducted along the red line) on two surfaces having different roughness. (a) higher roughness and (b) lower roughness.

Colour differences are perceived in different ways by customers. Colour variations of the substrate within a short distance are typical of leather after tanning and dyeing treatments because of the differential ability of collagen fibres to absorb. This sort of variation in leather colour is perceived as a distinctive and normally desirable characteristic, because it is irregular and strictly related to chemical and physical properties of the collagen in the raw material. Shade sorting is regularly used in industry to choose which leather pieces must be selected for covering wide areas of leather end-products (Landman, 1999) where one only hide is not enough. Synthetic leathers and composite substrates do not have similar colour variations because they are manmade materials constituted by unique defined colours and a repeated pre-designed pattern. This difference can make discrimination between leather and synthetic or composite materials easier to achieve.

Grain leather surface is characterised by holes, called follicles, left empty by the animals' hairs. Their distribution throughout the hide is typical of the animal (see Figure 2-9). With closer inspection these holes have an impact on the leather appearance because the surface is not flat and they refract light with different angles. Follicles are distinctive of the outer layer of hides (the grain), which is the one used to realise the highest-quality items.

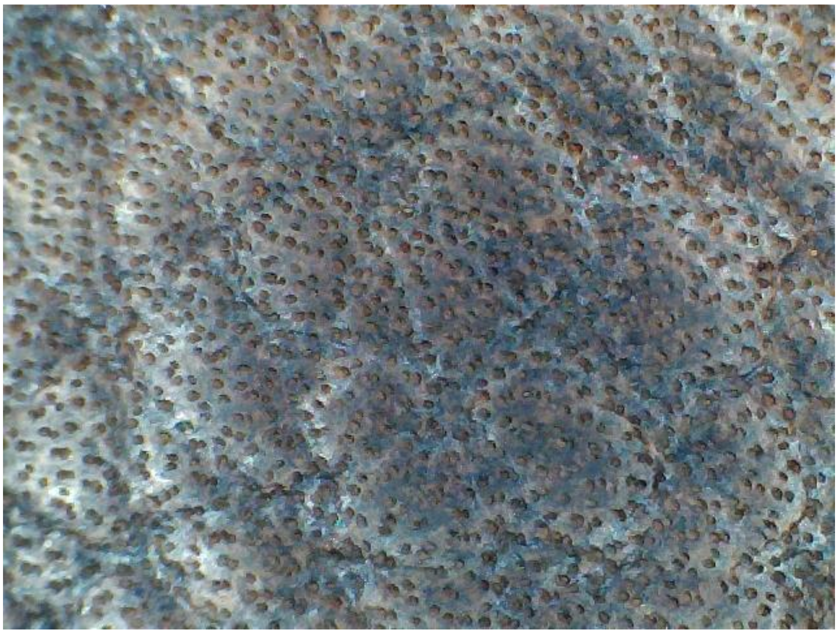


Figure 2-9: Textured pull-up leather micro-photograph, magnification x20

For certain applications it is a common practice to add a finishing coating onto the grain and this makes the identification of the follicles pattern difficult when not impossible. In some occasions the follicles are also responsible for the appearance of defects visible to the naked eye (Garro *et al.*, 2006). Synthetic leathers and composites are subject to embossing treatments that replicate the morphological and aesthetic characteristics of leather on the outer polymeric layer. This layer, along with containing the leather morphological information, can present imperfections typical of polymeric coatings, such as bubbles and streaks. Identifying the defects allows to improve the quality of the coating (Gutoff and Cohen, 2006) because, for example, whenever bubbles are present they can incorporate dust that with time can lead to degradation.

Binjje and Hu (2008) characterise the assessment of fabric appearance into subjective and objective and this depends on the way the assessment is carried out. The former indicates the use of visual analysis while the second implies the intervention of digital tools. Hair follicles and surface defects can be identified through the naked eye and microscopy depending on time and technology available. These methods can be used both in an industrial and museum context.

2.3.1.2 Surface Friction

Surface friction is generally related to roughness: the greater the friction, the higher the roughness value. However, friction can act at different levels of leather and fabric structure, starting from the inner fibre or yarn and finishing with the outer layer which is in contact with the environment.

Fibre friction in leather can be linked to the amount of fatliquoring agent introduced during the manufacturing procedure; as Limin *et al.* (2015) stated, oils are essential to lower the tendency of collagen fibres to assemble during the drying process. This application of fatliquoring is crucial for many types of commercial leather, because it makes it softer and therefore more appealing to customers. Van Soest *et al.* (1984) commented that similar benefits are also evident in leather conservation, where well preserved leather objects must contain a percentage of fat higher than 5 %.

Friction is a force that varies according to the materials involved, their chemical composition and physical structure. It is the phenomenon responsible for preventing or allowing the movement between two bodies and it is of two types: static friction, describing the initial force necessary to move one object, and dynamic friction, that is the force acting against the movement once the initial friction has been overcome (Saville, 1999).

The coefficient of friction is the parameter measured in textile applications and it is defined as the ratio of force necessary to induce sliding between the surfaces in contact and the force acting to keep them together. Both static and dynamic coefficient of friction can be calculated through the formula, Equation 2-1:

$$\mu = \frac{F}{mg} \qquad (2\text{-}1)$$

where μ is the friction coefficient and F is the force needed to start the movement.

Three main methods can be used to determine frictional forces (Saville, 1999). The first approach is based on a block of a fix weight, with the fabric laid flat under the block, linked via filament wire to a load cell. The load cell measures the force required to start and keep moving the block and enables the friction coefficient to be derived from Equation 2-1. The second method involves a block of known mass (m) and an inclined plane (angle value θ) where the fabric is laid (Saville, 1999). The plane inclination can be varied until when the block slides, meaning that the static frictional force (F) has been overcome according to the (2-2):

$$F = mg \sin\theta \tag{2-2}$$

The third approach to calculate friction uses the Kawabata Evaluation System (KES) (Saville, 1999; Wang and Hurren, 2008). In particular, the KES-FB4 instrument performs measurements aimed at assessing two surface characteristics: friction and geometrical roughness. On one side the sample is firmly clamped to the instrument, while the other side it is subject to a tension which is determined according to the sample type – 600 grams is used for heavy materials. The friction coefficient (MIU) and its mean deviation (MMD) are calculated by applying a load to the material (the standard is 50 gram-force, gf) and evaluating the amount of force required to allow the sample to move (Kato Tekko Co. Ltd., 2002).

2.3.1.3 Chemical Composition

The composition of leather-related materials is variable and it has an influence on physical properties and ageing resistance. Visual and instrumental techniques are crucial to assessing the composition of the substrate.

Preliminary observations with visual techniques are useful to assess the presence of recognisable staples which form the end-material structure. According to British Standards Institution (2015), leather doesn't contain any fabric and the coating thickness should be less than 0.15 mm. Visual analyses are therefore the first essential techniques to be used in order to discriminate between leather and synthetic leather. In fact the composition of leather is mainly made of collagen fibres with the addition of tanning agents, fatliquors and residual chemicals deriving from the manufacturing process. In contrast synthetic leather in general consists of a fabric core of natural or manmade fibres and a coated or laminated polymeric overlayer. The situation is different when considering composites where it can be difficult distinguishing between leather and some types of composite leather fibre, but specific techniques can help in this case. The polymers used to provide the outer, superficial layer on leather-related materials are relatively few, making the classification of the polymer easier but not possible by the naked eye. Once initial observations have been concluded, more specific analyses are used to further understand the chemical composition.

Elemental and molecular investigations allow the identification of specific chemical elements that are typical of certain treatments or of additives. Energy Dispersive X-ray microanalysis (EDX) is a technique often used to investigate leather elemental composition in new and aged materials. The output of the instrument is a spectrum where any element present in amounts greater than 1000 parts per million is revealed. For example, Siddique *et al.* assessed the presence of unwanted hyaluronic acid prior the liming process by EDX (Siddique *et al.*, 2015) whereas Malea *et al.* (2010) used EDX, coupled with scanning electron microscopy and together with molecular analysis, to ascertain the effectiveness of cleaning treatments. Moreover, EDX is used to carry out investigations on additives used in the formulation of coated materials as in any polymeric material. For example, Shashoua (2001) describes the distribution of plasticisers in the hoses made of PVC and nylon which were part of the Apollo Space suit used in the 1960s. Elemental mapping is also possible and it is particularly useful in examining additives distribution.

The range of polymers available on the market has exponentially increased in the last fifty years leading also to an increase in the products available to manufacture coated and laminated fabrics. This increase is visible both on the number of synthetic fibres used as fabric cores and on the variety of polymers applied as coating or lamination layers (Sen, 2007; Kinge *et al.*, 2013). Identification of molecular groups is crucial because many polymers have an organic structure composed of carbon, hydrogen and oxygen thus elemental analysis may not provide a definitive indicator of the composition. One of the most common techniques used to investigate the molecular structure of polymer is infrared spectroscopy and in particular Fourier Transform Infrared, FTIR (Shashoua, 2008; Sano and Suzuki, 2009).

The samples to be studied can be ground to a powder and analysed after mixing with potassium bromide powder, as a powder or as a compressed disc, or can be analysed without being subject to further preparation. The second method, namely Attenuated Total Reflectance FTIR (ATR-FTIR) is widely used in both industrial and museum contexts because of its ability to provide quick and reliable responses. Shao (2005) explained that FTIR is effectively used to discriminate between natural and synthetic leather and described the main peaks found in leather samples. Also Scott (2005) described which are the most important bands to be assigned to polymeric coatings in order to assess the functional groups present in the test samples. Ollè *et al.* (2011) investigated the effect of different ageing factors on leather upholstery and, thanks also to FTIR analysis, they were able to state that chrome-tanned leather is more resistant than wet-white leather to tropical high humidity/heat testing. Similar tests were also conducted on historical collections by Mitchell *et al.* (2013) to assess the ability of ATR-FTIR to characterise aged polymers.

The exact determination of the chemical composition is crucial in museum environments to allow correct preventive and interventive treatments being put in place. This represents a fundamental challenge in leather-related materials, because these substrates are similar to each other and they can confuse the operator leading to erroneous designation.

2.3.1.4 pH and Humidity Content Effects on Leather

Chemical composition has an effect on many other properties such as pH and moisture content. These two properties are crucial in leather-related materials for various reasons.

The pH of fabrics is greatly affected by the nature of the raw material and by the manufacturing processes it was subject to. Because of this, the pH value can be variable and it needs to be evaluated, and adjusted if is required, according to the final application (Fan, 2005). When considering leather, other aspects should be considered. Collagen is a protein and as such it has a pH range where the overall protein charge is neutral. In this isoelectric region the protein molecule is more stable and less likely to undergo higher levels of degradation (Covington, 2009). The importance of pH is therefore apparent when manufacturing procedures are developed and it is also crucial during assessments of the conservation state.

Fan (2005) reports the AATCC Test Method 81-2006 used to evaluate fabric pH, which consists of boiling the sample in water and measuring the pH after cooling. The method differs from the one for leather analysis, which do not require the sample to be boiled (British Standards Institution, 1992; American Association of Textile Chemists and Colorists, 2006). The second method was used in previous research to calculate the pH values, among other properties, of leather and synthetic imitations (Sudha *et al.*, 2009). In leather samples if the pH conditions are too acidic ($pH < 3$) it can lead to degradation of the collagen macromolecule. Larsen (2008) has stated that hydrolysis occurs in vegetable tanned leather when the material is exposed to acidic pollutants, mainly sulphur dioxide, and it causes the collagen chain to break. Low pH is also accompanied by changes in the amino acid side chain content meaning that the lower the pH the higher the acidic amino acid content.

Along with pH the humidity content can also be influenced by the chemical composition. Polar functional groups, like carboxyl and ester groups, interact more easily with water than the non-polar moieties, affecting in a similar way fibres and fabrics consisting of the corresponding molecules. Some fibres have greater affinity to water than others, for example synthetic fibres generally absorb lower amounts of moisture in comparison to natural fibres (Timar-Balazsy and Eastop, 1998). However, this behaviour is not only due to the material's hygroscopicity but also to the physical properties of the samples; organised, compact and less porous materials are less prone to absorb water compared to disordered, porous materials (Figure 2-10). Nonwovens, for example, have been extensively used for at least two decades as highly absorbent materials because of the ability to be designed for specific end-uses. Factors that control absorbency are capillarity and other surface phenomena such as surface tension and interfacial energy (Chatterjee, 1993), and they can be controlled and modified in nonwovens.

Figure 2-10: Schematic section of disorganised (a) and organised (b) structures

If the substrates have high moisture contents deleterious effects, as swelling, can occur affecting the material's integrity (Timar-Balazsy and Eastop, 1998). In contrast if the moisture content in the sample is low it can lead to loss of flexibility, high distortion and fragmentation.

Similar considerations can also apply to leather. The total amount of moisture in fresh hides is between 60 % and 70 % (Covington, 2009) while the final product is required to have a moisture content of between 14 % and 10 % (Thomson, 2011a). After deterioration, the moisture content is often lower than 10 % and this can cause the appearance of cracks or fractures.

For decades there was uncertainty regarding the exact role of water in the collagenous matrix and still today there is a degree of doubt. What is known is that leather contains variable amounts of moisture within the collagen structure which can influence the functionality of the protein within that location. Reich (2005) presents a possible division of the roles played by water in leather explaining its interaction with collagen. He lists six distinct types of water which give rise to three main levels of interaction acting both in collagen formation and stabilisation:

- water type I a and b form strong bonds between and within the collagen helices which act as cross-linker to stabilise the helix;
- water type II a, b and c form bonds variable from strong to moderate between and within fibrils to stabilise fibrils and allow movement;
- water type III, 'free water' or 'bulk water', forms weak bonds with the collagen fibres and is mainly active as a solvent for chemical reactions.

Independently of the exact role of water, it is widely recognised that moisture can induce a number of effects into collagenous materials, in particular when high moisture in the environment is coupled with acid pollutants (Thomson, 2005). Despite the negative effects listed above, hysteresis curves of leather and textiles show that it is possible to use moisture to reduce the stress produced by creases through humidification procedures. This aspect is of great importance when conservation treatments need to be considered.

2.3.1.5 Shrinkage Temperature

Assessment of shrinkage temperature in leather materials provides an insight into the effect of tanning procedures and into the potential damage during manufacturing or degradation.

The phenomenon of collagen shrinkage is attributed to the presence of regions lacking hydroxyproline, which is associated with supermolecular water and effects the collapse of the collagen scaffolding (Covington, 2009). While Reich's characterisation of the types of water is in agreement with other researcher's views on collagen shrinkage, some authors do not agree on the ability of water to stabilise collagen helices (Cooper, 1971).

In his PhD thesis, Lampard (Lampard, 2000) reviewed the literature concerning the relationship between hydrogen bonding and shrinkage temperature with the view to develop a more realistic, unified shrinkage theory. He noted how, initially, Gustavson understood the relation between shrinkage temperature and pyrrolidine content; then Lampard reported that other researchers investigated the influence of water in stabilising the collagen; finally he described how Bella *et al.* proposed a model, in accord with Privalov and Ramachandran's suggestions, regarding the structure and interaction of supramolecular water around the collagen triple helix (Bella *et al.*, 1995). As opposed to this, another theory exists which claims that water does not act as a collagen stabiliser, but rather it affects the disposition of the solvent surrounding the macromolecule to induce the stabilisation (Cooper, 1971).

Regardless of which of these theories is more accurate, shrinkage temperature is normally used in industry to assess the degree of tanning achieved with tanning processes, and in museums to determine the degradation state of parchments and vegetable tanned leathers. For this reason, a variety of studies on this subject have been published in the last decades (Chahine, 2000; Della Gatta *et al.*, 2005; Popescu *et al.*, 2008). These publications provide a platform to understand the possible behaviour of collagen during degradation studies.

2.3.1.6 Tensile Strength

The term fabric strength refers to the resistance of the fabric to forces of tension, tear, shear and bursting (Mehta, 1992). Tensile strength, elongation and Young's module constitute central parameters for the characterisation of each leather-related substrates.

Studies highlighted the differences in leather materials in relation to their use in the clothing market and reinforced the importance of considering the kinds of stresses involved in the end-product environment. Both tensile strength and other tests can be used to achieve this type of data. Lange *et al.* (1999) investigated the possibility of using sheep leather in the garment industry using the objective measurement FAST system and they concluded that orientation and location of the samples have much more influence on the properties than sex or animal breed. This observation is particularly important when high quality products need to be manufactured. Gore *et al.* (2004) evaluated the elongation of cervine leather and its ability to recover considering different areas of the animal skin. They observed that cervine leather has greater extension than ovine leather and woven, indicating its better suitability to be used in garments.

The application of a coating increases the tensile strength of leather and fabrics. In particular, fabric generally has a limited tensile strength if compared to other substrates and therefore it is often coated to make it resistant to greater strains. Leather is an anisotropic material and as such it shows different strength, elongation and module values depending on the tested area of the skin. The tensile strength test is commonly used in industrial contexts to assess the effectiveness of fabric or leather coatings in providing greater resistance to failure and in failure analysis to investigate the ability to withstand certain conditions (Aglan *et al.*, 2008).

Standard procedures are available for both coated textiles (British Standards Institution, 1998) and leathers (British Standards Institution, 2011). They differ in the type of sample used and in the conditioning parameters, therefore it is always required to specify the standard used to conduct the measurement. In leather investigations tensile strength, T, and elongation, E, are the main parameters of interest and they are calculated according to the formulae in Equation 2.3 and Equation 2-4:

$$\mathrm{T} = \frac{\mathrm{F}}{\mathrm{w.t}} \qquad (2\text{-}3)$$

where F refers to the force (N), whilst w and t are width and thickness (both in mm)

$$\mathrm{E} = \frac{\mathrm{L_1} - \mathrm{L_0}}{\mathrm{L_0}} \times 100 \qquad (2\text{-}4)$$

where L_1 indicates the jaws or sensors separation at the specific load, L_0 reflects the starting position of the jaws/sensors.

Despite the amount of information provided by tensile tests and the wide literature available, it is still difficult to conduct this measurement on historical materials because of the quantity of the material required and because the samples are destroyed during the test. Replicas of historical materials are normally created to study their behaviour and simulate actual ageing conditions (Duffus, 2013). However, using this approach there is no guarantee that the results are effectively able to reproduce the behaviour of authentic materials, probably manufactured using different staples and machineries, nor the various stages of the degradation. Consequently, the data can be, in some cases, an approximation rather far from the reality.

2.3.1.7 Flexibility and Compressibility

These properties are among those commonly associated with fabric and leather handle and are crucial for defining the suitability of textiles or leathers to certain applications (Roh *et al.*, 2013). Moreover, they are central in consumer perception of sensory comfort, often guiding the preference of an item over another.

Roh *et al.* (2013) investigated the relationship between mechanical properties, studied by means of the KES instrumentation, and customers' preference for leather-like fabrics. They selected a number of categories of objects, from garment to shoes and furniture, and found that flexibility, compressibility and smoothness were essential in determining the preference of a product over another.

Many types of stress must be considered when a material must be selected to produce a piece of garment. For example, trousers need to withstand the stress of friction in the crotch area and must be flexible but not loose around the knees. In addition to flexibility, upholstery fabrics or leathers have to be compressible and able to recover after the force has been removed. Choosing unsuitable materials for a specific application can result in obvious aesthetic or structural defects and can eventually determine limitations in further using that item (British Leather Confederation, 1989).

Flexibility and compressibility, along with other characteristics that affect handle, can be measured both subjectively and objectively (De Boos, 2005; De Boos and Tester, 2005). Subjective methods are affected by variables such as experience of the operator and personal taste, therefore objective investigations are normally more reliable in terms of reproducibility. Two powerful tools in this field are the KES-F (Kawabata Evaluation System for Fabrics), already mentioned in paragraph 2.3.1.2, and the FAST (Fabric Assessment System for Textiles).

Harwood *et al.* (1990) presented an overview of the early applications used by Kawabata to introduce KES-F as a tool for improving and testing fabrics. The article started describing the establishment of the Hand Evalution Standardisation Committee (HESC) in 1972 and its work in the area of objective systems to assess fabric handle; it continued with the description of the methods used to correlate the subjective human perception with the objective instrumental values; it concluded with the presentation of research work conducted in the area of failure analysis and quality control.

KES-FB3 compresses the fabric, or any other material to be tested, applying a fixed force and the response of the sample is calculated both during compression and de-compression. Research in the area has continued to extend the range of use of KES-F, now including nonwovens (Kawabata *et al.*, 1994) and leathers (Gore *et al.*, 2004). Moreover, a recent study has recognised the possibility to apply KES-F, in particular the compression apparatus, for assessing the conservation state of textiles comprised in museum collections (Sato *et al.*, 2011).

Despite the great accuracy of KES-B the usage and output of the instrument is not as immediate as other simpler instruments, like FAST, and this can often have a discouraging effect in environments where quick responses are essential. Nevertheless this aspect, that can be a limitation in industry, should not restrict the use of the device in academia and museum laboratories.

With respect to flexibility, there are instruments that produce crumple stresses on materials by twisting cylindrical samples while they are compressed. These machines are useful to get an indication of flexibility and resistance to specific movements, for example they can replicate the typical stresses occurring in garments in the elbows or knees area (Fung, 2002a). Moreover, the test is able to give indications on the quality of the adhesion between coatings/laminates with fabrics. Standard crumple-flex tests specify the type of instrument and how to prepare samples, but they do not state the number of flexes because that is dependent on the application (British Standards Institution, 1997). Padleckienè and Petrulis (2010) tested PU-coated wovens used in outdoor to assess air permeability and water penetration after increasing number of flexing. They demonstrated that, even if the samples could have been still considered waterproof after 58500 and 75000 flexes, there were already evidences of cracks after 9000 cycles. This finding indicates that 9000 flexes can be considered as the first level as to detecting and identifying signs of damage in coated fabrics.

Even if crumple-flexing on new materials can provide a good indication of the substrate behaviour in the long term, it is an invasive test that can induce significant damages in the sample.

2.3.1.8 Rubbing Resistance

Colour fastness can be measured in many ways depending on the material final application and the type of factors it will be subject to once in use. A common method to assess colour fastness consists in evaluating the colour change after a certain number of rubbing cycles.

Martindale and Taber abrasion measure the resistance to circular rubs (Wang and Hurren, 2008). The sample is tested for certain properties, e. g. air permeability, before and after abrasion treatment to assess that the performance does not dramatically change as a consequence of the treatment. The crockmeter is another abrasion test machine used from both garment and upholstery manufacturers to assess dye fastness (Hurren, 2008).

Örk *et al.* (2014) explored differences in fastness and other physical properties between leathers tanned by the same methods coming from different manufacturers and between different tanning methods produced by the same manufacturers. The results indicated how the tanning method can affect these properties, including fastness to crocking, with semi-vegetable tanning more resistant than chromium and vegetable tanned leathers. It is likely that similar considerations apply when leather and synthetic materials are compared.

Friction has a critical effect on rubbing behaviour, because higher friction generally means higher levels of stress are occurring at the interface of the two materials involved. Being destructive methods involving a significant amount of sample, the tests described in this paragraph cannot be used to study artworks or design objects.

2.3.2 Failure Analysis and State of Conservation

When examining materials for industrial purposes, the change in properties are evaluated to investigate to what extent the samples are able to withstand stress or a condition before failing, or before leading to the partial loss of the product functionality.

This definition is important because it points out the importance of the function the material has and the fact that, in case the function is not preserved, the object reduces or loses its utility. The upholstery market in particular must consider this aspect. In fact, if the garment market is characterised by many reasons for an items disposal (Laitala, 2014), in the upholstery sector there are generally fewer reasons to influence customers to dispose of upholstery materials.

There are five 'categories of failure' that describe the factors that can produce a certain problem on the item:

- Process, referred to the manufacturing procedures used to create the product;
- Environment, related to the environmental parameters surrounding the item;
- Materials, referred to the components used during the manufacturing and comprising additives;

- Human Factors, referred to faults introduced by human action;
- Equipment, related to defects introduced by problems of machineries (Mehta, 1992).

Determining what kind of event, included in one of these categories, has determined a specific defect can be a complex operation. Moreover, in some occasions more than one category can be liable for one defect and this introduces further challenges in assigning the problem to the right cause (Gutoff and Cohen, 2006).

Tensile strength, crumple-flex and rubbing tests along with many other tests are normally used to assess the performances of the material under investigation. These tests are classified as invasive techniques because they require sample collection; normally more than one sample is necessary to obtain representative and reproducible results, hence significant sampling is required.

Items or materials used for artworks or design objects are generally characterised by certain properties that tend to deteriorate with time and the cause of the deterioration is often difficult to define. The term 'state of conservation' refers to the condition that the material shows once it has been subject to the passage of time (Giannini *et al.*, 2000). The assessment of the state of conservation is carried out in many different ways, according to the damage observed and the available instrumentation. However, it is normal practice to use non-invasive or micro-invasive techniques to limit the damage on the surface (Aldrovandi and Picollo, 2003; Lehmann *et al.*, 2005).

Non-invasive techniques do not require sample collection and are generally preferred to invasive techniques. In addition to invasive and non-invasive, there are also non-destructive techniques, which permit to analyse the sample without destroying it, Figure 2-11 (Shashoua, 2008).

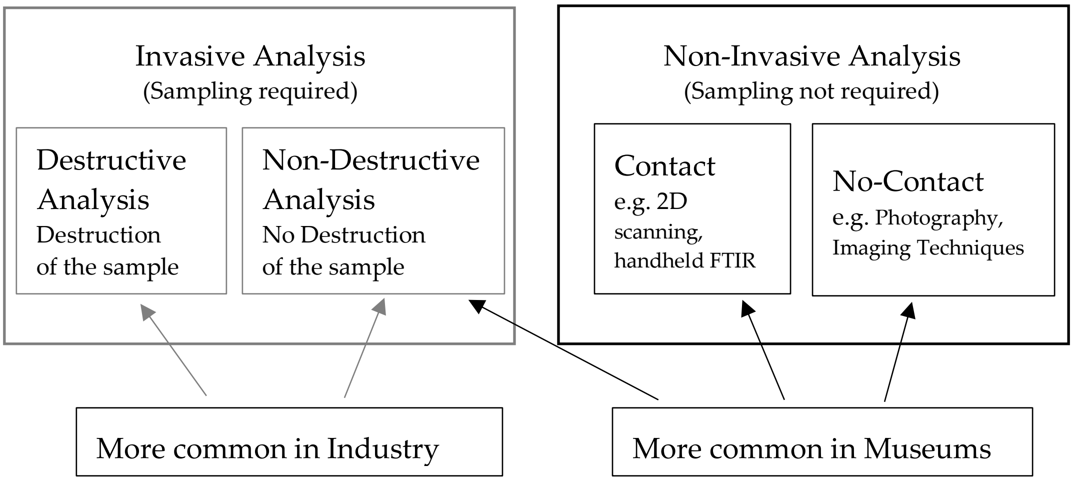


Figure 2-11: Distinction between invasive and non-invasive analysis used in industrial and museum context plus destructive and non-destructive analysis (adapted from Shashoua (2008))

There are analogies in both failure analysis and assessments of the conservation state. First of all, both investigate some aspects of the substrate materiality even if on different levels. Secondly they are focused on testing the material after it has been subject to some type of degradation. However, failure analysis is concerned with the preservation of the substrate functionality; state of conservation is more concentrated on the historical or artistic meaning of the substrate in its context. Finally, both the investigations look for ways to evaluate the substrate lifetime: failure analysis aims at providing results in line with the standards, whereas conservation state seeks to extend items lifespan, even at the cost of losing their functionality.

2.4 Degradation: Contexts, Types and Assessment Methods

Degradation is a phenomenon which can occur in a variety of environmental conditions and the extent of change is related to the specific material, which in this reference context of study comprises leather and coated textiles.

It has been reported that both vegetable-tanned leather and PU-based materials might undergo two main forms of chemical deterioration: acid hydrolysis and oxidative breakdown (Thomson, 2005; Lovett and Eastop, 2014). These studies refer to specific substrates and it is not certain that any other substrate having similar composition, e. g. chrome-tanned leather and non-foamed PU materials, will behave in the same way. For this reason it is important to find other methods and techniques for further and deeper investigating these materials.

2.4.1 Importance of Context

2.4.1.1 Material Degradation and Industry

In industry the evaluation of degradation is generally associated with the concepts of ageing and durability in use and can be part of the initial ‘quality control’ procedures (Shao, 2005). These procedures are useful both during the early stages of material production and development and after these phases are completed, then the material may be deemed fit for purpose and is ready to be sold. This is due to the fact that certain types of damage occur in the early stages of material production, whereas others are related to one or more phenomenon that occur when the material is in use (Gutoff and Cohen, 2006).

Manufacturers investigate the causes of phenomena leading to degradation to minimise the impact of faults in the following production stages. Research of this kind is performed in the research and development departments of companies and industries and it is vital to obtain quality materials (Yang *et al.*, 2010). Even if the best possible final material is produced, it will tend to deteriorate as a consequence of its intrinsic nature or for external factors. Therefore, the longer term resistance to deterioration should be investigated to predict the material lifetime by using accelerated ageing techniques or, in alternative, by comparing the product under analysis to two or more substrates having well-known lifetime. However, identifying the causes of faults and performing tests to assess the ageing behaviour of materials requires a significant level of interdisciplinary knowledge related to the area of interest and, in addition, can be extremely time-consuming (Scheirs, 2000).

The automotive sector has a commercial interests in the material's stability, because any vehicle will be subject to multiple types of environmental stresses which are variable in intensity and exposure. This market uses tests for simulating the long-term behaviour of materials, for example to investigate the stability of fabrics (Milligan, 1986) and leather (Meyer *et al.*, 2008). Along with stability, durability is also essential for cars and none of its parts should change its properties as a result of the action of the applied stresses, e.g. the car seats should always preserve and provide comfort. The same considerations are valid for products used in other transportation vehicles, which must meet the requirements dictated by regulations at national and international level. Aircrafts and their components, including leather and artificial leather seats which represent the main materials of this study, have their own regulations (European Aviation Safety Agency, 2016; Federal Aviation Administration, 2016).

Length of life is intimately connected with degradation, as explained by Laitala (2014) in her summary of articles that investigate how and why consumers decide to dispose clothing. As common sense would suggest, Laitala affirmed that perception of some sort of damage on the material represents one of the main reasons to lead consumers to dispose of apparel (Laitala, 2014). This statement can be coupled with an earlier publication on lifetime optimisation (van Nes and Cramer, 2006) where the longevity of industrial products was considered together with environmental needs and consumers preferences. Here, the authors pointed out that it is not the company that decides when the product should be disposed, but rather the user. Therefore, the consumer's perception of the degradation has a great impact on the lifetime of the material and on the idea that consumers have of a certain company. Moreover, product lifespan is also associated with sustainability because by prolonging the usability of products it is potentially possible to reduce product's disposal, hence minimising its environmental impact.

2.4.1.2 Material Degradation and Museums

Another type of degradation is linked to museum studies. The way in which deterioration is perceived in museum context is significantly different from its perception by industries and users. The so called conservation state examination is carried out to evaluate to what extent an object is damaged and, after this operation, it is decided if a restoration or conservation treatment is required or not. The concept of 'patina', which refers to those signs appearing on the surface of an object as a consequence of time and surrounding environment, is familiar in museums and it is linked to degradation (Giannini *et al.*, 2000). The way patina has been perceived has changed throughout the centuries, following the taste of aristocrats and the trends in the field of restoration. Even today there is not a universally accepted view on the perception of the patina and there are different opinions on the procedures to adopt in its presence (Hoeniger, 2009; Ashley-Smith, 2009) (Muñoz Viñas, 2009; Wharton and Molotch, 2009)

It is evident that degradation involves a considerable number of variables and viewpoints, both in industrial and museum context; in any case investigated, the description of the context is central for being able to do the most appropriate considerations and put in place suitable procedures.

2.4.2 Chemical, Physical and Mechanical Degradation

In talking about chemical, physical and mechanical degradation one can refer to both those events that caused the damage or to their effects. It is essential to be aware of this distinction and to know which is the one considered in the context or publication of interest.

There are a number of factors that can result in diverse types of damage and the amount of damage is frequently correlated with the application an object or material is made for. Binjie and Hu (2008) distinguished six classes of damage in textiles: chemical, mechanical, thermal, biological, due to defects and due to light radiation. The term class of damage refers to the reasons that determined the occurrence of the damage (factors) and not to the damage caused to the material. It is important to clarify this aspect because one factor can produce more than one type of damage – e.g. the presence of a contaminant can result in faults of the chemical structure and in different mechanical behaviour in that section of the material. A different sub-division of the factors of damage in textiles can be the following:

- Human action;
- Biological action;
- Physical and mechanical stress (not human induced);
- Chemical stress (not human induced);
- Disasters (natural and man-made).

This division is also valid in the case of museum objects. Conservators focus on damage in different ways depending on the approach that is applied: the focus lies on the factors that determine the damage when preventive conservation is considered, whilst the emphasis lies on the effects when the materials are in need of interventive conservation (see Paragraph 2.5). This distinction points out that the two areas of conservation can be distant from each other; also, it emphasises how difficult it can be to reach conclusions on the factors which produce a certain effect by starting from the effect and vice versa.

The previous statement is also applicable in quality control practice in industrial contexts, because generally the understanding of the reasons of a fault is not straightforward and the help of external experts or consultants can be necessary. The time a material is subject to a specific factor and its intensity determine the rate of degradation. Moreover, these factors can act singularly or in group, in a synergistic or antagonistic way, and can cause different kinds of damage; their collective action can produce damage which is different from the damage caused by individual factors acting singularly. On many occasions, once one of these deleterious effects becomes evident others are more likely to follow and, apart for chemical and physical damage, other kinds of deterioration can take place.

Feller (1994) distinguished between stability, referring to chemical damage, and to durability, referring to physical damage, of materials in museum. In his book on cultural heritage he explained how photochemical and thermal ageing affect objects conservation. Being one of the earliest studies of this kind, Feller’s publication can be considered as the starting point for investigations in accelerated ageing tests applied to cultural heritage. He pointed out the need for material-specific studies able to define what he called the “pathogenesis of their degradation” (Feller, 1994).

Chemical damage is associated with the molecular or atomic stability of the compound under consideration. To identify this type of damage a limited amount of material is required and, moreover, non-invasive techniques are often available to investigate the property of interest. As a consequence, in cultural heritage the damages related to the chemical nature of the samples are more commonly investigated than the damages of physical or mechanical nature (Feller, 1994; Richardson *et al.*, 2008). Tests of physical degradation generally require sampling and involve destructive techniques, making more difficult to perform them on museum objects. The possibility of sampling without restrictions allows industries to regularly assess physical properties of their products; however, in museum context chemical tests are easier to be carried out.

Physical damage has been taken in major consideration in this work and it has also been flanked by techniques to assess chemical damage.

2.4.3 Techniques to Detect and Investigate Degradation

Simulated ageing can be performed using natural environmental factors, thus exposing the samples to the action of light, temperature, humidity and so forth, or by accelerated ageing techniques. Ageing standards are available for quality control in industrial context (British Standards Institution, 1998; British Standards Institution, 2002) but it is less common to use similar procedures in museums and heritage preservation. However, sporadic research conducted in this field during the last two decades has demonstrated the potential of accelerated ageing to optimise museum practices and to test the ageing of newly developed conservation materials. As a consequence there has been an obvious increase in this type of studies. A draft for public comment specifically focused on the use of artificial ageing techniques in cultural heritage was published in August 2016 (British Standards Institution, 2016). This draft and the resulting standard point out the growing importance of these testing methods in the sector.

The type of technique used to detect the effects of degradation on materials is first of all dependent on the targeted information to be obtained and, of course, on the context of the study. Therefore, it is necessary to define the objectives of the research before identifying which techniques need to be used to assess the presence and the extent of degradation.

As mentioned above, the factors that produce chemical and physical-mechanical deterioration are the most common forms of damage investigated in industry and cultural heritage. Coupling analytical and diagnostic techniques it is possible to obtain a significant amount of data that would be complex to get with one of the two types of techniques alone. Chen *et al.* (2007) studied PU-coated synthetic leathers by using Fourier Transform-IR spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) to characterise samples coming from a Chinese manufacturer. In this article the approach allowed the determination of the material’s suitability for specific types of application, but with some changes to the protocol it might also permit the characterisation of degradation patterns. This translates in the evidence that this methodology can be also used to evaluate the conservation state, an approach that has been initially investigated by Lovett and Eastop, and Pellizi *et al.*, respectively (Lovett and Eastop, 2014; Pellizzi *et al.*, 2014).

Leather, polymeric materials and in particular composites have complex structures and are characterised by three-dimensional elements which require a broader investigative perspective to understand usual degradation behaviours. Only after a preliminary evaluation can the framework assessment be established and the identification of which kinds of interaction the substrate and its layers might show when subjected to different environmental factors recognised.

Complementary non-invasive and invasive techniques in the study of leather and its substitutes could provide novel information and might help developing new strategies to assess the presence of degradation markers. These techniques of investigation should be used before the beginning of the ageing procedure on the samples and after it; and on many occasions intermediate stages are also introduced between the initial and the final ageing time to test if there is any specific trends in the ageing behaviour.

2.4.4 Need for Degradation Studies

The ageing behaviour of coated and laminated fabrics is routinely tested in the automotive industry (Milligan, 1986). However, the degradation of items composed of synthetic leather is often overlooked for many reasons. First of all there is still a significant tendency, as with other polymeric materials, to think that polymer means plastic and, therefore, durable. This idea is misleading because not all the polymers are durable and, for example, some of them are even manufactured to be easily degradable; moreover, polymers subjected to specific ageing factors might suffer premature deterioration even if they were designed to withstand the passage of time (Aglan *et al.*, 2008; Chattopadhyay and Webster, 2009).

Garvin (1988) listed durability among the eight performance criteria of products or services quality. He related durability and physical deterioration, explaining that durable products start to deteriorate after a larger amount of time. This opens two scenarios:

- if the product is not repairable it becomes waste and it must be replaced;
- if it is repairable it is necessary to decide whether to repair it or not (Garvin, 1988).

Deterioration and durability have a clear impact on consumers' decision process and this is reflected on the market. Consequently, in an industrial context, quality control tests focussed on the ability of products to withstand to certain stresses are of primary importance.

Museums have a different approach to degradation. Once an artwork or a design object presents signs of degradation, conservation or restoration are the only viable options. In the past centuries it was not uncommon for artists to retouch portions of frescos or replace parts of statues. However, today the treatments considered as acceptable are less and less invasive (Ashley-Smith, 2009). Conservation helps to convey the message and the value of cultural objects. Losing an object today can erase a significant footprint of the cultural evolution for future generations. In addition, when viewing art in the context of an 'ecology of culture' (Holden, 2015), the loss of a specific artefact can influence wider areas of the culture.

The responsibility therefore lies with the current stakeholders and keepers to preserve art and assets both for people living today and for subsequent generations. To do so, preliminary degradation studies on materials that can possibly become part of museum collections in the future can help to prevent damages caused by unsuitable exhibition or storage conditions. Moreover, these studies can be useful to be prepared in identifying and facing unexpected types of damage.

2.5 Conservation Approaches

Product lifetime and resistance to degradation are essential aspects in both industrial products and museum items. However, the preservation of the item's functionality is central for industrial materials, but it can be less important in the case of pieces of museum collections and artworks. The material nature of items included in museums collections represents, in fact, only one facet of the conservation, that is the actual materiality of these items. As anticipated above, one should always take into account the manifold values associated with objects and artworks, with their material degradation potentially having an influence on other spheres, namely social and cultural ones (Marontate, 2013).

Until the end of the eighteenth century the collection of artworks and objects was the privilege of a few wealthy people who could afford their price. After the French revolution museums started to become public institutions and therefore their importance for the society's development began to be recognised (Hoeniger, 2009). Not only aristocrats could enjoy the vision of a famous painting or a precious sculpture, but even the "masses" could now participate. In the new climate of change, the role of restoration and that of restorers started to also assume a different meaning.

Up until that time, restoration treatments on artworks were undertaken by fellow artists, the only professionals considered to be able to perform the intervention. The examination of different approaches was launched when cases of unfortunate restoration treatments were performed on famous paintings (Hoeniger, 2009). A team of experts (comprising chemists) was introduced in France and then in Italy, to examine the best treatments to be performed on paintings of Raffaello in the 19th century. However, until the 20th century degradation studies of materials was not considered of primary importance, especially in the field of art, which has subsequently led to a series of "problems".

A number of monographic books and peer-reviewed articles are available on the conservation of textiles and leather in museum collections and researchers agree on the need for preventive approaches. Işik and Karavana (2012) reported that even if it is possible to reduce the leather degradation speed, the process cannot be stopped.

Shashoua (2006) presented a similar evaluation and conclusion for plastics and composite materials and stated that the development of preventive treatments is central to addressing the impossibility of stopping ongoing degradation. However other authors highlighted that the shift from active to passive conservation is producing negative effects on the ability of conservators to put in place essential maintenance treatments, e.g. cleaning (Ashley-Smith, 2009).

Conservation of cultural heritage involves a wide range of professionals. Conservators involved in the practical side of material care, curators, art historians, artists, conservation scientists and material scientists represent only some of the people involved, and each of them has their own personal, professional background and ethical concerns. It is the latter ethical position which often constitutes the root of disagreement among these practitioners, in the past and even today. For this reason collaborations among professionals with different backgrounds can be challenging, but should be fostered to achieve a more holistic vision of materials and phenomena.

Lundbye (2013) presented a publication on the so called PRIMI (Plastic Research and Innovation for Museums and Industry) project which moved in this direction. The PRIMI project was aimed at developing a common language between researchers in the art conservation field and companies interested in innovation. As the name suggests, the project was focused on plastic artworks and represented a pioneering approach of collaboration with partners like the National Gallery of Denmark, the Technical University of Denmark, the PVC Information Council, and Plastics Europe. This approach represented a clear attempt to tie the need for maintenance of museums and galleries collections with the industrial sector.

Focusing on cultural heritage alone, conservation can be divided into active, also defined interventive, remedial conservation or restoration, and passive, also non-interventive, preventive conservation or preservation. The main characteristics of these practices will be given in the following sections.

2.5.1 Active Conservation

The term active conservation is used in art and objects conservation to refer to those practices which involve a treatment or a series of treatments (chemical and/or physical ones) on the material that aim at restoring homogeneity to the asset.

The boundaries that determine when it is necessary to apply restoration treatments, or not, are always more difficult to define despite a general agreement on the fact that objects of aesthetical, social, historical significance deserve to be maintained (Marontate, 2013). In this respect, one of the biggest issues is the definition of significance, which is related to the concept of value and can have associated ethical issues (see Paragraph 2.1.2). First of all, apart for objects of recognised importance, it is not straightforward to decide when an artwork or an item becomes of such a significance to 'deserve' to be conserved. Likewise, the ageing process of artworks and design objects can start as soon as they are created and this means that it is not easy to decide when the right moment is to intervene. The subjective perception of what is artistically pleasant and which level of conservation, or patina, should be kept as the reference or norm is always debatable.

Other problems arise when considering the type of treatment that should be used on the item. Common practices in active conservation are:

- Cleaning;
- Consolidation;
- Coating;
- Humidification;
- Joining.

The fourth chapter of the POPART Project book, which stemmed from a European project on plastic degradation and conservation and involved partners of many museums, focused on the first three practices listed above (Shashoua, 2012). Flow charts describing the best cleaning treatments to perform on cellulose acetates, high density polyethylene, high impact polystyrene, polymethyl methacrylate and plasticised polyvinyl chloride are reported, along with the description of studies on PU-foams aimed at consolidating the foam matrix. The selection of these materials was partly related to the wide presence of objects containing similar products in museum collections, though other polymer categories are equally represented. Only a limited discussion was dedicated to PU-coated fabrics, a subject that was later investigated more in detail by Tim Bechthold (Bechtold, 2002; Bechtold *et al.*, 2006). He pointed out the irreversible negative effect of factors such as light and relative humidity on design furniture covered with PU-coated synthetic leathers. Hydrolytic processes take place mainly in the amorphous regions of the polymer leading to reduction of mechanical properties and appearance of aesthetic issues. Despite the description of a method to restore coherence to the flaking surface, Bechthold points out the necessity of setting up suitable preventive practices on similar products (Bechtold *et al.*, 2006).

Humidification is used on leather and textiles that exhibit marked wrinkles or do not show flexibility as a consequence of desiccation (Timar-Balazsy and Eastop, 1998; Woods, 2011) but its use must be carefully and constantly controlled to avoid fibres swelling and other deleterious chemical or physical reactions.

Joining is also an important active conservation treatment that is performed in those cases where textiles or leathers have become detached from a carrier substrate as a consequence of time, desiccation or other types of phenomena. Using the appropriate adhesive is crucial not only for obtaining good adhesion, but also for avoiding further and more aggressive degradation in the future. For this reason, conservators tend to choose among a number of natural (e. g. starch and gelatin) and synthetic products. The selection of the appropriate adhesive is different from case to case and it requires experience to decide the "correct" material.

Even if these and many other practices are available for restorers and conservators, the use of active practices often endangers the items and this is particularly valid in those occasions where an effective treatment has not been developed. Composite materials represent one of the main challenges in this area and new strategies to addressing deterioration problems in the future are needed.

2.5.2 Passive Conservation

One of the roles of cultural institutions, especially museum and galleries, is preserving their collections to allow a logical presentation and understanding of art, social and cultural expressions, historic, archaeological and scientific remains (National Museum Directors' Conference, 2003; ICOM, 2013). Therefore, preservation refers to all those methods which aim at controlling the storage and the planning of the display of these assets.

Examples of passive conservation practices are reported from many authors who represent leading museums like the Victoria and Albert (V&A), a well-known institution devoted to the collection of textiles and fashion articles. However, even in the case of the V&A, the materials found in clothing, accessories and design pieces and typical of the 21st century constitute a real challenge (Prichard and Smith, 2007). Together with the V&A museum, the British Museum is interested in preventive conservation treatments emphasizing the direction marked out by two of the most important museum in the world.

In the early 70s, the British Museum started a preventive conservation programme and subsequently, in 2005, a review was conducted to summarize the practices of the museum in the period 1970-2005 (Bradley, 2005). Early considerations on the importance of the environment surrounding museum collections were already recognised in 1922, but only in the 1950s did a publication clearly stated its influence. From that publication onwards more attention has been focused on parameters such as temperature, relative humidity, and pollutant present in museums.

Different parameters can influence the environment surrounding artworks and design objects:

- Temperature and Relative Humidity;

- Light System;
- Handling and Moving;
- Pest Control;
- Dust and Gases.

All these parameters could be the starting point of an investigation in the preventive conservation field; however temperature, relative humidity and light are considered as the most dangerous factors because in many cases it is extremely difficult to be able to control them. For this reason preventive conservation is generally performed by maintaining objects under strictly controlled physical conditions with constant levels of temperature and humidity (Liu *et al.*, 2010). Showcases are an affirmed symbol of the classical procedures applied to control air quality around artworks; however, Schieweck and Salthammer (2011) have pointed out problems which may be found in both modern-type enclosures and older versions, again underlining the necessity of collaboration between museum staff, technicians, and conservators. An important goal introduced in recent years was to realise exhibitions that were able to integrate preservation criteria into every part of the exhibition planning and design process (Raphael, 2005). If these targets could be achieved, objects will be safer during their exhibition and people will enjoy a better vision of heritage.

The importance of investigating preventive conservation technique stems from more than one need. The consequence of lack of data on the state of conservation of an object or the misinterpretation of these data can lead to wrong treatments of the item and in the worst circumstances, to its irreparable damage. Nonetheless, without the correct monitoring technologies it is likely that excessive degradation of objects could occur unnoticed and the item be too deteriorated to be effectively preserved. This would result in two kinds of issues:

- Damage to the social and artistic value;
- Economic consequences linked to conservation treatments necessary to undertake, and difficult (or impossible) exhibition of the item.

The relationship between consumer goods, cultural goods, conservation and sustainability should be subject to further studies aimed at developing novel global plans to support cultural heritage.

2.6 Research questions, aims and objectives

Despite the extensive studies on leather processing and tanning operations, a lack of publications was evident related to the comparative degradation of chrome tanned leathers, synthetic leathers and composite leather/textile materials. Indeed, only a few scientific articles have been published on the comparison of leather and synthetic leather characteristics, leaving questions about the discrimination between natural and artificial substrates in museum an ongoing challenge. As a consequence it was decided to concentrate on the following research questions:

1. Can leather, synthetic leather and composite materials be effectively differentiated by means of non-invasive techniques, avoiding to collect samples of the materials?;
2. Does the interaction among the various components of E-Leather® produce a noticeable effect on the properties which permits to distinguish it from leather and artificial leather?

   Understanding which techniques could be used to discriminate between the different substrates would be useful for museums. The application of inexpensive, or more expensive but common techniques was investigated in order to get a realistic perspective of the methods that museums could use in the future.

Innovative materials present the common issues encountered in many plastics in museum collections. As with plastics, the conservation of those items can be equally overlooked leading to marked damage. Essential questions are:

3. Which are the factors that have the worst effect on the preservation of the innovative materials involved in this study, that is traditional, synthetic leather and leather composites?;
4. Do the same factors have the same effect on any leather-related material or is their impact on the substrates substantially different?;
5. Is it possible to identify a list of degradation markers that may help in assessing the conservation state of innovative leather and related-materials? Are there specific markers, collected from non-invasive analysis, that correlate to invasive ones and have the benefit of not destroying the samples?

   The properties of any substrate have an impact on its degradation behaviour. Identifying the wrong scale of importance for the degradation parameters could result in the application of the wrong storage conditions leading to unexpected degradation phenomena. Evaluation of the morphological, chemical and physical properties and their variation with ageing is important to assess conservation state and put in place a new and more effective preservation plan.

Preventive conservation practices have been recognised as a legitimate, important branch of conservation science for some decades. However, the lack of funding available for museum studies and the increase in the amount of innovative materials entering in public and private collections have introduced a significant amount of unprecedented problems that museum staff need to urgently address. Some of the problems that characterise cultural heritage are related to their material aspect and therefore are similar to the issues faced from industrial products. Therefore a few questions can be drawn:

6. Is it possible to trace a common preservation plan for the different leather-related materials? Or does each of these substrates have specific characteristics that lead to different degradation patterns and, therefore, demand different preventive conservation plans?;
7. Can a new approach be developed that allows museums to gain data on the degradation of innovative materials despite the problem of the lack of funding?

The list of questions reported above has been crucial both for determining the strategic approach to adopt throughout this research and to decide which were the most suitable techniques to test the substrate under investigation.

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Chapter 3 Materials and Analytical Techniques

3.1 Introduction

The initial lack of technical information regarding characteristics and properties of the constitutive material of some artworks and design objects constitutes a common issue faced by institutions working with cultural assets. In this study the characterisation of innovative model materials constituted an effective way to reproduce actual situations that could occur in museums.

Three types of materials – leather, synthetic leather and a leather/textile composite – that can be often misleadingly interpreted when part of collections were chosen for this study. The initial aim of the project consisted in identifying the different substrates and assigning them to the appropriate category. The substrates were studied by means of non-invasive and non-destructive techniques, often used in museums to assess the state of conservation of objects in their collections, and by destructive ones, normally in force of commercial companies. Simulations of natural ageing were carried out by subjecting the materials to different simulated ageing techniques.

The ability of using non-invasive methods for discriminating and characterising each material from the others was considered and the merits and correlation of the results obtained by these techniques relative to the invasive techniques was established.

3.2 Materials and Methods

3.2.1 Materials

A range of leather substrates were provided by an aviation company. Three complete cattle hides characterised by different sizes, all dyed in navy blue with surface treatments to both fibrous and top layer, were used as the base materials (Figure 3-1).

Figure 3-1: Top layer (left) and fibrous layer (right) of the received leather for aviation

Synthetic leather, also used for the aviation market, was a commercial product known as Enduralite®. The material was dispatched as a reel containing twenty metres of a light grey product and its appearance was clearly different from that of the leather described above. The quality and nature of the leather and synthetic leather materials clearly reflects their end use and commercial development.

The composite materials were provided by E-Leather Ltd. Two types of products, dispatched in reels, were tested: SL2, which the company sells for bus seats, and SL3UL, sold for the aviation market (E-Leather, 2017a; E-Leather, 2017b). As reported on the company website, each material is characterised by their environmental footprint properties specifically studied for a particular application. In fact, every material has to comply with the performance and ethical regulations of its specific sector.

In Table 3-1 some of the two products characteristics are illustrated, as reported on their shipping label, together with the calculated weight.

Commercial Name	Gross (m)	Gross (m^2)	Gross (kg)	GSM (g/m^2)
SL2	30.00	42.00	20.50	488.10
SL3UL	29.84	41.75	21.74	520.72

Table 3-1: Characteristics of E-Leather SL2 and SL3 UL as reported in their shipping label

The four materials, natural and man-made, were labelled as follows:

- Natural leather, TL;
- Synthetic Leather, SY;
- E-Leather SL2, EL2;
- E-Leather SL3 UL, EL3.

3.2.1.1 Sampling and Conditioning

Each substrate to be tested was subject to specified sampling and conditioning operations; the same type and number of samples was collected from each substrate for all the accelerated ageing conditions selected. The samples labelling is reported in Table 3-2 together with their number and size.

Samples used for the early accelerated ageing were conditioned at 21°C and 65% RH. All the other samples were conditioned prior to testing at 23 °C ± 2 °C and 50 % RH ± 5 % RH for at least 48 hours. These conditions are stipulated as the standard parameters used for leather (British Standards Institution, 2012a) and as described as Atmosphere "B" for coated fabrics (British Standards Institution, 1992). Atmosphere B describes one of the five possible atmospheres considered as standards for conditioning coated fabrics, and it was considered appropriate to the study of leather materials because it simulated the conditions frequently present in museum environments (Waentig, 2008).

Analytical Techniques	Acronym	Size (*)	No. of samples
Non-invasive analyses	NI	8x15 cm 9x22 cm*	3
Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy, Moisture Content, pH Value	SEM-PD	8x18 cm 9x22 cm*	8
Kawabata Evaluation System	KA	20x20 cm 23x25 cm*	3
Tensile Test	TE	11x2 cm	10
Fastness to crocking	CM	5x23 cm 7x23 cm*	6

Table 3-2: List of the analytical tests conducted on the samples, their size and total number. * describes the size of the samples cut for the UV ageing.

Thomson (1986) explained that it is important to keep the relative humidity level below 65-70 % in order to prevent the formation of moulds, a phenomenon that could significantly endanger leather and other organic materials. Therefore, also for this study it was decided to maintain environmental conditions that would be considered optimal in a museum.

3.2.2 Methods and Techniques

Characterisation was crucial for this study because of the diverse chemical composition and physical properties of the materials involved. The initial characterisation, presented in Chapter 4, will provide a “knowledge platform” for future investigations and analyses of leather-related materials. In particular, it will be important in those cases where it is necessary to discriminate between natural, synthetic and composite leather.

The use of different techniques is required in order to collect as much information as possible and to gain a broad description of the sample properties; this is most valid in the identification of unknown materials because a number of variables must be taken into consideration.

As previously discussed, the techniques used for testing materials in industrial context may be different to those applied in a museum, with the prevalence of invasive and destructive methods over non-invasive or non-destructive methods in the former sector compared with the latter. Nevertheless even if the type of techniques used can change, many properties are of interest in both the case of manufacturers and museum curators. The use of techniques applied in the two contexts was thus essential in this research to compare the data with the relevant previous literature and to provide information relevant for the two partners.

Table 3-4, at the bottom of this chapter, summarises analytical techniques, category (morphological/topographical, chemical or physical), type of technique (non-invasive, destructive or non-destructive) and standards used to conduct tests on all samples.

3.2.2.1 Morphological and Topographical (Macro) Analysis

3.2.2.1.1 Photography

Although photography is widely used in museums as a documentation tool and to establish the nature and condition of samples or objects (Aldrovandi and Picollo, 2003), it is nevertheless rarely considered as an "analytical" instrument. However it can be viewed as a powerful tool to characterise materials and to focus research to specific features.

Photographic documentation of the samples was collected in a VeriVide CAC 60 box equipped with a D65 light source (artificial daylight), using a Canon EOS 550D camera device with Canon zoom lens EF-S 18-55mm. The standard lighting system provided homogeneous lighting of the sample under examination and avoided potential problems related to the use of the different sources of illumination that could occur in museum context. In fact, the VeriVide system is widely used to assess colour variations of a wide range of materials in research and for quality control in industry. The white point correction, an adjustment that is generally applied in daily use conditions, was turned off to avoid the automatic rectification of the colour which is integrated in the device.

A method for calculating the roughness of the samples was developed. The software ImageJ was used to conduct the investigation. Various attempts were made before deciding the final methodology for measuring the roughness. Initially, pictures were collected under different light-sample-camera setups at different ageing times in order to assess the most successful arrangement to conduct the investigation. Pictures of three samples on the coating and fibrous layer were taken in each photographic setup, both before accelerated ageing and after each ageing step.

Finally, setup a and c in Figure 3-2 were selected to conduct image processing. In Table 3-4 the parameters used for the capture procedure are described. 'Camera angle' refers to the angle formed when the camera lens was tilted to include the sample in the picture (0° = lens perpendicular to tripod, towards the sample). 'Sample angle' refers to the angle formed between sample and light source and representing the angle of incidence. 'Distance camera/sample' refers to the distance between camera lens and middle of the sample.

	Tripod height	Camera angle	Shutter Speed, Aperture, ISO	Distance camera/sample	Sample position	Sample angle	Height of sample
a	94 cm	20 °	1/60, 6.3, 800	51.5 cm	Tilted	45 °	100.5 cm
b	94 cm	25 °	1/60, 6.3, 800	51.5 cm	Flat	90 °	110.5 cm
c	52.5 cm	< 5 °	1/60, 6.3, 800	51.5 cm	Tilted	45 °	100.5 cm

Table 3-3: Conditions used for capturing the images of the samples

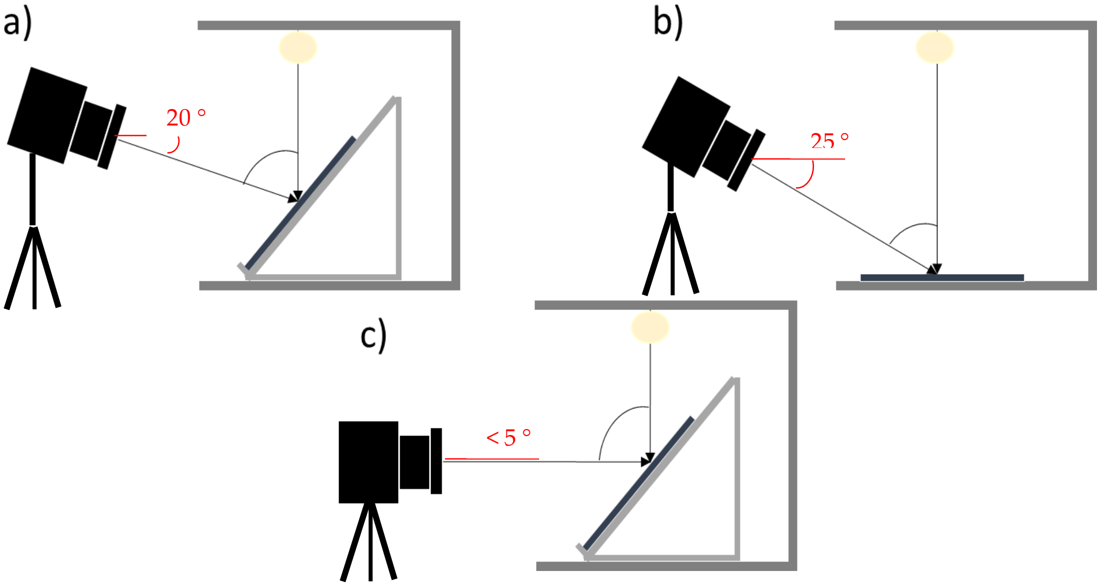


Figure 3-2: Schematic lateral view of the photographic setup

Images were then imported in ImageJ and two methods were tested to measure changes in lightness values associated with the surface roughness, in agreement with Thornbush (2014). Straight lines were adopted to carry out the investigation and total of nine measurements per each ageing step (three per sample) were collected. The profiles derived from the lines were then evaluated in order to obtain the standard deviation values of lightness, which were used to investigate roughness variations (see Appendix for the complete procedure with screenshots).

3.2.2.1.2 2D Scanning

A flatbed Epson Expression 1100XL scanner was used to collect images of the samples before accelerated ageing and after each of the ageing steps. The parameters used to collect the scans were kept constant throughout the measurements with the only exception of the Auto Exposure level.

A number of preliminary measurements were carried out by using different device parameters before deciding which conditions gave the best results in terms of image definition, accuracy of the visual information and size of the file. A preliminary verification of the scanner was carried out in order to assess the homogeneity of the light source and to verify the actual correlation between L* values, measurable on samples, and greyscale values, measurable on screen. A ColourChecker was used for this purpose. The L*a*b* values of the six bottom patches included in the ColourChecker chart, which range from white to black, were measured using a spectrophotometer. The same ColourChecker chart was then placed on the scanner bed and scanned alone in black and white mode. The scanned image was opened in Adobe Photoshop and the Histogram tab was used to measure the greyscale values. The procedure consisted in selecting the area of each patch with the 'Rectangular Marquee Tool', which provided the means of grey values. L* values were finally correlated with greyscale values correspondent to the same patches measured (see Figure 3-3).

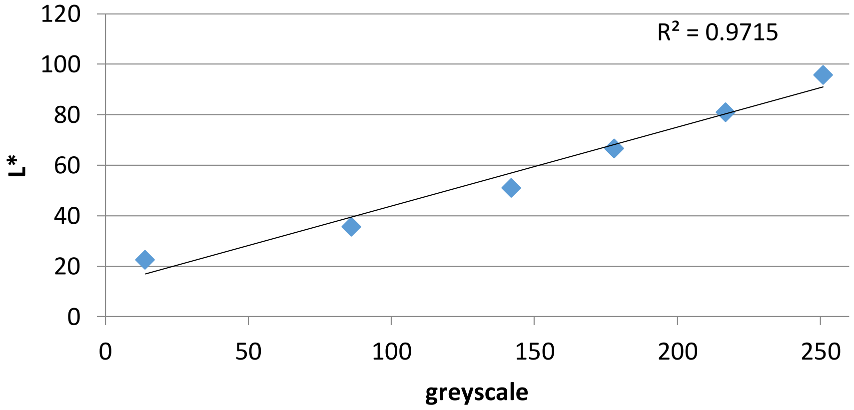


Figure 3-3: Correlation between L* values of ColorChecker chart and greyscale values of 2D scan

One sample for each accelerated ageing stage (for most of the samples 0, 56, 112 and 168 hours) was placed on the document table of the scanner together with a 24-colour ColorChecker chart. Only the bottom line of the chart was necessary for the calibration, therefore only this line was always left visible during the image capture. The ColorChecker chart was used in each observation as a reference.

Despite the remarkable accuracy that is possible to achieve with these devices, and even better with 3D scanners, the size of the files is rather high leading to difficulties in characterising and assessing data and images. Therefore, it was essential to identify the better parameters to guarantee accurateness whilst keeping to the minimum file size. The images collected were 8-bit in greyscale mode and using a resolution of 600 dots per inch, as identified in previous publications (Semnani *et al.*, 2009). Two different levels of exposure were used for the test to assess the ability of the scanner to detect differences in roughness in spite of the change in exposure parameters. The 'Continuous Auto Exposure' button, accessible from the 'Configuration' button and clicking on 'Color', was selected when the test was conducted with the automatic adjustment of the level of exposure; the same button was deselected when the adjustment was conducted manually, on screen. Care was paid to make sure that the scanner cover was closed above the document table and a homogeneous pressure was applied to the samples. ImageJ software was used after acquisition to measure the sample roughness and to evaluate changes in the roughness.

3.2.2.2 Morphological and Topographical (Micro) Analysis

Microscopy is widely used both in museums and industry because it allows inspecting samples microstructure by collecting only a small portion of the material (Mehta, 1992; Axelsson *et al.*, 2016). It represents one of the most used instruments for the assessment of dimensions, morphological observations and distribution of fibres.

Two types of microscopes were used during the identification stage of this project, while only one type (a scanning electron microscope) was used to assess the ageing behaviour.

3.2.2.2.1 Stereo-microscopy

Samples were collected from all the leather-related materials using a scalpel and then sectioned to be analysed according to the standard BS EN ISO 17131:2012 (British Standards Institution, 2012a). Two pieces of about 10 mm x 10 mm for each material were cut and sectioned obtaining perpendicular cross-sections. Observations of the top and fibrous layers of samples before accelerated ageing were performed by laying the samples directly on the microscope plate.

Objects were observed without further preparation and without resorting to the use of a microtome. The microscope was a Leica M205 C connected to a Leica DFC camera and to a bench computer equipped with LAS V41 software (Leica Application Suite) which was used for visualising, capturing and elaborating images.

The material identification was possible through the comparison with photos comprised in the Annex B of the standard BS EN ISO 17131:2012 (British Standards Institution, 2012a). Further comparison with Haines and Barlow (1975) confirmed the identification of the leather samples.

3.2.2.2.2 Scanning Electron Microscopy (SEM)

SEM analysis was essential to gain a detailed micro-scale picture of the both surface and cross-section for each substrate (Chen *et al.*, 2007; Sudha *et al.*, 2009). Initial stages of sample preparation were the same described for stereo-microscope observations (British Standards Institution, 2012a). Samples were immersed in liquid nitrogen for 5 minutes before being sectioned with a scalpel in all cases where the substrates were subject to cross-section investigations. This procedure allowed to increase the definition of the cross-sections. After samples were cut they were coated with a gold layer of about 30 nm depth using a Q150RS coater.

The SEM instrument was a JEOL JSM6610LV equipped with three detectors to collect X-rays, backscattered electrons and secondary electrons (see later for further specifications on the X-ray microanalysis spectrometer). The SEM micrograph parameters were constant throughout the observations with an accelerating voltage of the beam 4-5 kV, a spot size of 40 nm, and magnification levels between 50x and 1000x. For higher magnification analysis images were collected at 2500x magnification.

In an SEM instrument, an electron beam passes through a series of condensers that focus the beam towards the sample (Timar-Balazsy and Eastop, 1998). Several signals are produced once the interaction takes place and each of these signals provides a number of information on the material (Figure 3-4).

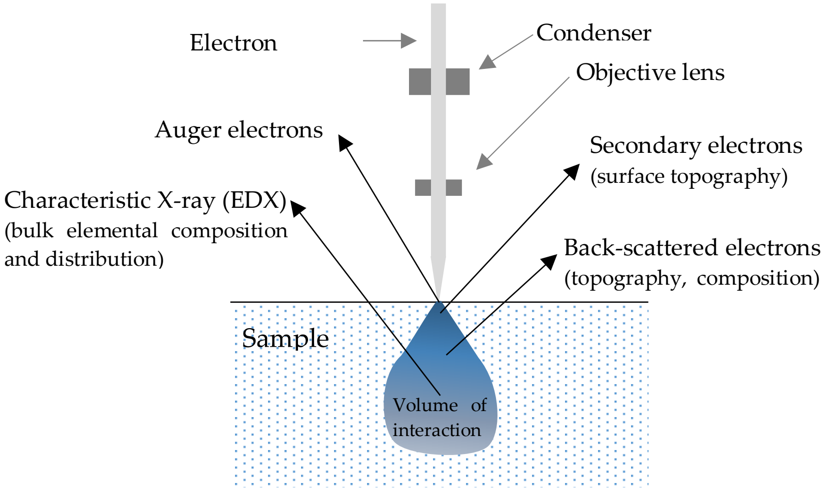


Figure 3-4: Main signals generated from the interaction electron probe-sample during the SEM analysis (adapted from Timar-Balazsy and Eastop (1998))

Secondary electrons result from the interaction of the primary electron beam with the atoms of the sample placed close to the surface (a few nanometres). They are routinely used to obtain high resolution images of the samples surface.

The material identification was conducted by comparing the analysed samples with the reference standard (British Standards Institution, 2012a) and with the relevant literature (Chen *et al.*, 2007; Sudha *et al.*, 2009). Details of the different specimens were also collected for comparison and further study.

3.2.2.3 Chemical Analysis

3.2.2.3.1 Energy Dispersive X-ray Microanalysis (EDX)

This spectroscopic technique was used to provide elemental identification and information on the elemental distribution (Timar-Balazsy and Eastop, 1998). The interaction of the incident electron beam with the sample atoms provides the X-rays characteristic of each element and the intensity that is related to the material composition. The technique is normally coupled with Scanning Electron Microscopy (SEM), therefore a number of information on the surface structure, topography and composition of the material can be obtained using a relatively small sample (Figure 3-4).

EDX analyses were carried out using an INCA X-Max 80 spectrometer (Oxford Instruments) linked to the stated SEM instrument. Cross-sections only were investigated via EDX because they can provide information on both top and fibrous layers (Figure 3-5); each leather-related material was analysed both before and after each accelerated ageing step (56, 112 and 168 hours). Elemental mapping was also conducted, where necessary, to assess the distribution of a particular element throughout the thickness of the sample or in specific areas of the samples.

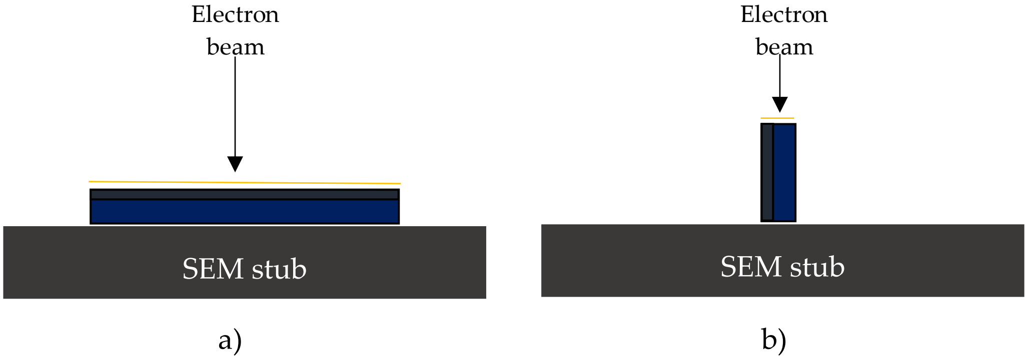


Figure 3-5: Schematic representation of EDX samples during spectra collection. In (a) spectra collection on the coating top layer, in (b) spectra collection on specimen cross-section. The yellow layer at the top of each sample represents the gold coating

EDX has some limitations, such as the accurate quantification of atomic percentage in relation with the material distribution. To address this concern it was decided to collect three spectra for each of the cross-sections investigated.

3.2.2.3.2 Attenuated Total Reflectance- Fourier Transform Infrared (ATR-FTIR) Spectroscopy

Infrared Spectroscopy may be used to assess both the chemical composition of a substrate and its chemical modification after degradation (Mitchell *et al.*, 2013). The importance of FTIR analysis in the field of cultural heritage is well-known and the use of the ATR mode is essential in application where sampling is not allowed (Richardson *et al.*, 2008; Mitchell *et al.*, 2013; Defeyt *et al.*, 2017). In this study ATR-FTIR was used for assessing chemical composition of the leather-related materials and to investigate changes in the molecular composition as a consequence of accelerated ageing procedures. A similar approach was used by Ollè *et al.* (2011) to identify differences in leather samples after simulated ageing.

A Perkin Elmer Spectrum BX instrument was used for the analysis comprising signals in the wavenumber range between 4000 cm^{-1} and 600 cm^{-1}, with 32 scans and resolution of 4.0 cm^{-1}; the software Spectrum v5.3.1 was used to collect the spectra while elaboration was carried out with both Spectrum v5.3.1 and SpectraGryph-id1.2 (free software).

Three spectra were collected on each side of the samples in absorbance mode. The vibrational frequencies of the object spectrum were identified and assigned to the particular molecular functionality.

3.2.2.3.3 Moisture Content

Measurements of moisture content of leather-related materials were carried out in new samples and in substrates that had been subject to 168 hours of accelerated ageing. Two methods were used as a reference to define a procedure suitable for this study: the first was described by Abdel-Maksoud (2011); the second follows the ISO standard which is equivalent to the SLTC official method for leather moisture content measurement (British Standards Institution, 2005). Abdel-Maksoud's method consists in weighing 0.2 g of sample, in his case parchment, and placing it in oven at 105 °C before repeating the weighing operation. The ISO standard requires 3 g of sample finely cut, a temperature in the oven of 102 °C ± 2 °C for 5 to 8 hours, and a cooling step of 30 minutes. Both methods calculate the percentage of volatile matter loss by means of Equation 3-1:

$$w = \frac{100(m_1 - m_2)}{m_1}\% \qquad (3\text{-}1)$$

where m_1 and m_2, respectively, represents the sample weight before and after drying. Due to the nature of this study, it was decided to use uncut samples weighing 1.5 g. This was compatible with the total amount of material necessary to carry out the complete project, because collecting samples weighing 3 g would have required specimens of bigger size. After standard conditioning, the samples were placed in oven at a temperature of 102 °C ± 2 °C for 6 hours. A cooling stage (30 minutes) followed before the weight measurement was repeated.

3.2.2.3.4 pH test

The pH analysis was carried out before the samples were subject to any ageing treatment and typically after 168 hours of ageing. Only in a few cases was the test conducted after 56 hours, and that was after the material was already highly compromised after the first ageing stage.

The pH probe was an Orion 8102SC calibrated using two standard solutions having values of pH 4 and 7. The procedure was performed according to the ISO standard for this type of measurement (British Standards Institution, 2008) after making some small changes. It consisted in cutting finely 2.5 g of the substrate and soaking it in 50 ml of distilled water for 6 hours. The leather-related material was stirred in solution and the pH was measured immediately after the solution was sieved.

3.2.2.4 Physical and Mechanical Analysis

3.2.2.4.1 Colorimetry

Colour coordinates are often measured to assess the homogeneity of a dye in new products (Landman, 1999) or to evaluate changes in colour due to time or other factors (Axelsson *et al.*, 2016). Spectrophotometers are devices able to calculate chromatic values and to provide an output value according to the selected colour space.

A Minolta CM 2600d, portable spectrophotometer that can be easily calibrated before every measurement, was used for this research. The test parameters were selected according to Lorusso *et al.* (2008) with a few changes, namely the target mask size and the delay time (0 second in the current study). The smaller target mask (diameter 3 mm) was secured to the measuring base before each measurement and the gloss was set to the S/I+E mode, defining the simultaneous collection of the specular component included (SCI) and excluded (SCE) measurements. In fact, some of the leather-related samples showed high gloss surfaces that were more difficult to determine their exact colorimetric values. The SCI mode includes both diffuse and specular light components in the measurement, therefore the analysis is not affected by the sample topography. The UV component derived from the light used during the measurement was included in the measurement (UV 100%); the Illuminant 1 condition was set to D65, which defines the standard for daylight (no Illuminant 2 was selected), and the observer angle was set to 10 ° with the reference colour space L*a*b* used.

The difference in colour values has been expressed by mean of ΔE* (Equation (3-2)), calculated from L*, a* and b*, which in turn are related to the tristimulus values X, Y, Z.

$$\Delta E^* = \sqrt{(\Delta L^2) + (\Delta a^2) + (\Delta b^2)} \qquad (3\text{-}2)$$

Ten measurements were recorded for each of the three NI (non-invasive) samples and repeated after 0, 56, 112 and 168 hours of accelerated ageing. The measurements were collected on the top and fibrous sublayer.

3.2.2.4.2 Kawabata Evaluation System (KES)

The Kawabata Evaluation System (KES) and Fabric Assurance by Simple Testing (FAST) are widely used to test the physical properties of sheet-formed materials and the measured parameters related to subjective human perception (Saville, 1999). The KES system comprises:

- tensile and shear tester, KES-FB1;
- bending tester, KES-FB2;
- compression tester, KES-FB3;
- surface tester, KES-FB4.

For this study the KES-FB2, KES-FB3 and KES-FB4 were identified as the most relevant and used. The devices were used to evaluate differences in the substrates properties and to investigate the effect of various accelerated ageing processes in agreement with previous studies (Sato *et al.*, 2011; Roh *et al.*, 2013; Tsukada *et al.*, 2013). Triplicate samples of leather-related material, sized 20 cm x 20 cm, were used throughout the ageing procedure and analyses. For leather, samples were cut parallel to the backbone according with the standard sampling position for physical tests. When this was not possible because of the hide size restrictions, samples were always collected in areas of the hide that, according to the literature, should present similar characteristics, i.e. left and right side of the backbone. Synthetic and composite leather specimens were cut parallel to the machine direction. Measurements were performed for each accelerated ageing before and after ageing (0, 56, 112, 168 hours).

The KES-FB2 device comprises a fix jaw and a moving jaw where the sample was secured and the moving jaw bent the sample in an arc following a constantly changing curvature (Figure 3-6). This curvature had a positive and a negative side and each point in the arc was recorded together with the bending momentum (Figure

3-7). The relationship between the bending momentum and curvature provides an approximation of the bending stiffness of the material. Parameters B (bending rigidity) and 2HB (hysteresis in bending) defined the bending properties of the sample.

The instrument settings were kept constant during all the testing to maintain comparable analysis conditions for all materials. Sensitivity was set at 5 x 1 and the "one cycle mode" was used, while the remaining settings where left in standard condition.

Figure 3-6: Sample during bending test

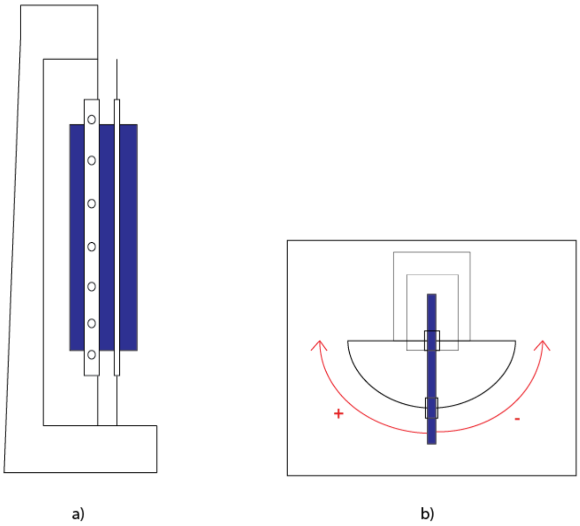


Figure 3-7: KES-FB2 schematic lateral (a) and top (b) view

The KES-FB3 instrument (Figure 3-8) is used to evaluate compressional deformations due to the pressure applied to the sample from the plunger. The force limit that the plunger applies was defined at the beginning of the test and when the limit was reached the plunger started to move back in the reverse direction (Figure 3-9). The output of the instrument provides a measurement of the plunger displacement calculated by an internal potentiometer. Along with compressional energy (WC), resilience (RC) and linearity of compression (LC), the materials' thickness could also be obtained (Kato Tekko Co. Ltd., 2002a).

Figure 3-8: Sample during compression test

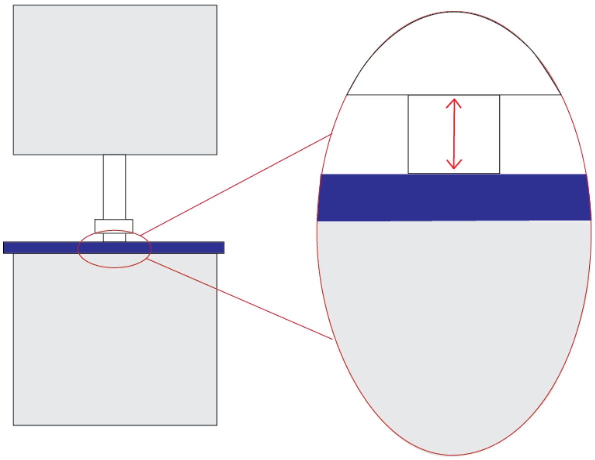
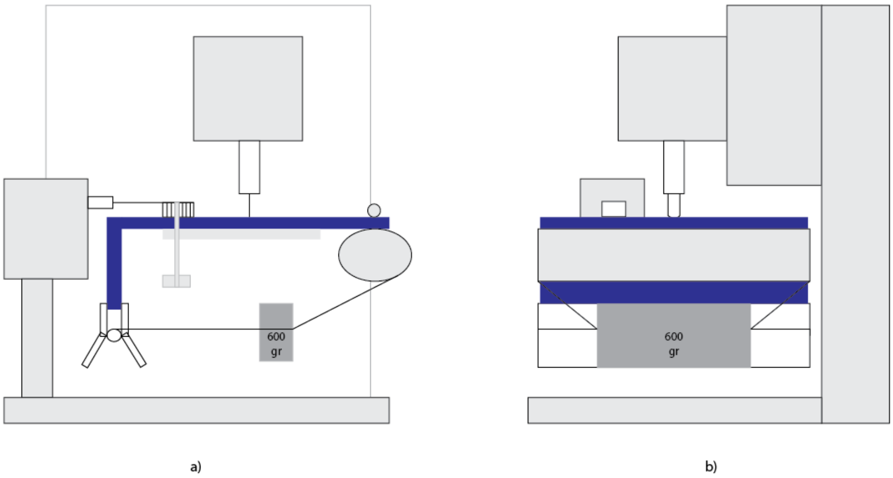


Figure 3-9: KES-FB3 schematic frontal view

The KES-FB4 instrument (Figure 3-10 and Figure 3-11) measured geometrical roughness (SMD), frictional coefficient (MIU) and the mean deviation of the frictional coefficient (MMD) by mean of a detector designed to simulate the human finger.

Figure 3-10: Sample during surface test



a)

b)

Figure 3-11: KES-FB4 schematic frontal (a) and lateral (b) view

Sensitivity was set at 2 x 5 both for SMD and MIU evaluations. The friction static load was set at 50 g, the geometric roughness static load was set at 10 g and initial tension was 600 g (Kato Tekko Co. Ltd., 2002b).

3.2.2.4.3 Fabric Assurance by Simple Testing (FAST)

SiroFAST is a system of four instruments that allows the measurement of mechanical and dimensional properties of fabrics (De Boos and Tester, 2005). It consists of:

- Compression tester for thickness measurement, FAST-1;
- Bending tester, FAST-2;
- Extension tester, FAST-3;
- Dimensional stability tester, FAST-4.

For this study the FAST-1, FAST-2 and FAST-3 devices were identified as the most relevant and their use was initially considered. However, these devices were exclusively used before and after the early accelerated ageing simulation (see § 5.3).

Measurements were performed before and after ageing on six replicates of E-Leather® samples sized 15 cm x 5 cm. E-Leather® specimens, from both the EL2 and EL3 substrates, were cut according with the standard sampling position for physical analysis of coated fabrics. Three specimens cut parallel to the machine direction and three perpendicular to the machine direction were obtained. Differences in the compression, bending, and extension properties were measured to investigate the effect of the Sahara test.

SiroFAST-1 (Figure 3-12, left) measures the thickness of a fabric surface layer by applying two loads (2 g/cm^2 and 100 g/cm^2). The instrument is normally used to assess thickness variations after treatments, for example after steaming (De Boos, 2005), while in this context it was used to provide quantitative information on the variation of the thickness occurred as a consequence of ageing treatment.

SiroFAST-2 (Figure 3-12, centre) works on the cantilever principle using a photocell to detect when the edge of the sample is bent over a certain angle. The device measures fabric bending length and provides data on the stiffness of the sample (De Boos and Tester, 2005).

The SiroFAST-3 (Figure 3-12, right) measures fabrics extensibility under three different loads that simulate deformations typical of garment manufacture (De Boos and Tester, 2005). The instrument has found large use in industry and an attempt was made in this study to assess the possibility of application as a tool to detect early degradation signs.

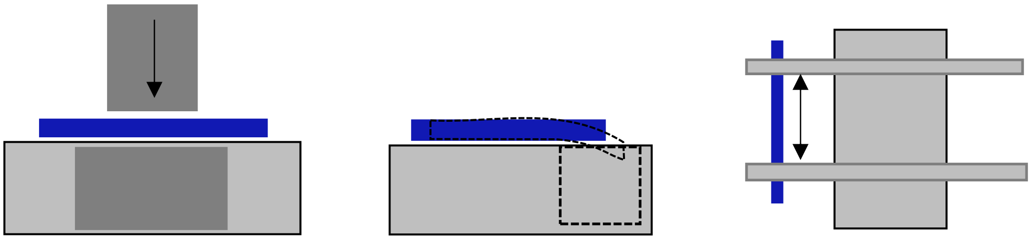


Figure 3-12: Schematic representation of Fast-1 (left), Fast-2 (centre), Fast-3 (right). The grey parts represent the instrument and the blue stripes represent the samples.

3.2.2.4.4 Tensile Strength and Elongation

Tensile properties can vary considerably for leather because they depend on parameters such as the fibres distribution and the skin thickness (Haines and Barlow, 1975; Mutlu *et al.*, 2014). Measurements were performed on untreated original samples and samples subjected to 168 hours of accelerated ageing or after 56 hours in the case of highly damaged samples. Ten test shapes were cut, for each substrate, according to the analysis standard for leather materials (Figure 3-1) in order to obtain: five specimens cut parallel to the machine direction (parallel to the backbone, in leather samples), and five perpendicular to the machine direction (perpendicular to the backbone, in leather).

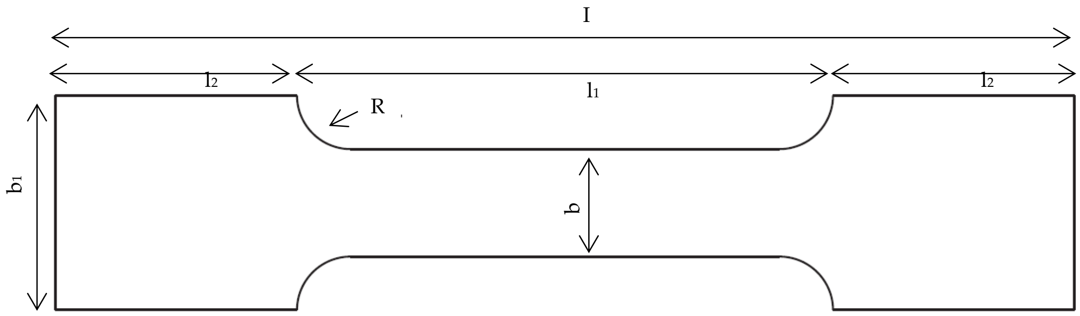


Figure 3-13: Standard test shape for leather, also used for leather-related materials

where: l= 110 mm, l_1= 50 mm, l_2= 30 mm, b= 10 mm, b_1=20 mm, R=5 mm. The test was performed after standard conditioning and thickness evaluation (British Standards Institution, 2002c). The measurements were performed with a James Heal Titan connected to a computer and equipped with the TestWise software. A 1000 N load cell (L9) and 5000 N jaws (T27) were used, the speed of the clamps was set up at a constant rate of 100 mm min^{-1} and the pre-tension load was 1 N.

3.2.2.4.5 Colour Fastness to Rubbing

Fastness to crocking was assessed with a James Heal Crockmaster instrument. An automatic foot of 16 mm diameter, fitted with a weigh that applies a load of 6N on the sample, moved back and forward for a defined amount of cycles. A standard 5 cm x 5 cm bleached cloth, in conformity with the relevant standard (British Standards Institution, 2009), was used in this study as crocking cloth and the assessment of the colour fastness was carried out using an assessment mask provided by James Heal (766-477). Six samples, three for each direction, were tested with the Crockmaster both before and after 168 hours of accelerated ageing procedures.

The standard procedure for leather (British Standards Institution, 2012b) fixed the number of reciprocations at 10, 10 to and 10 fro, whilst the procedure for coated fabrics (British Standards Institution, 1985) required 20 cycles, 20 to and 20 fro. In this study the samples crocking cloth was regularly checked after 10, 20, 100, 250 and 500 cycles.

3.2.2.4.6 Crumple-flex Test

The Crumple flex test was used to assess the ability of materials to withstand continuous push-ups and compressions. Due to the large amount of material necessary to perform the test, it was decided to carry out the investigation only in the first stage of the research. This provided an overall view of the appearance of leather-related substrates after they were subjected to crumpling.

Six samples, three for each direction, were cut for each material in accordance with the standard ISO 7854:1997 (Method C) (British Standards Institution, 1997). The test was also carried out on the same number and type of samples after they were subjected to the Sahara test (see § 3.2.2.5.1). A Garry Hanson Engineers crumple/flex tester (Figure 3-14) with four slots to host the specimens was used for testing the substrates.

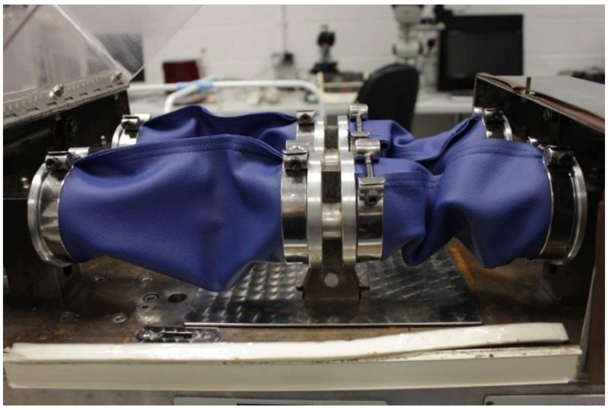


Figure 3-14: Samples secured to the crumple/flex clamps before testing

Visual inspection was performed on all the samples after 1000 and 3000 cycles. Inspection of the test materials was performed after removal from the machine following:

- 5000 cycles;

- 9000 cycles;
- 13000 cycles.

3.2.2.5 Accelerated Ageing

The type of devices and the parameters selected to carry out accelerated ageing simulations strictly depend on the kind of natural ageing that has to be simulated. Thermal ageing is often used to test the long term behaviour of industrial products. Along with heat, humidity and radiations are also factors that affect degradation.

Samples of all the leather-related materials were placed into the oven in horizontal position, laid over the metal shelves of the instrument; care was taken to avoid contact among samples, leaving at least 1 centimetre between each specimens. Only in one case, during the early accelerated ageing simulations described in Chapter 5, some samples were overlapped. Every procedure was stopped after regular intervals of 56 hours (± 1 hour) each to allow all the non-invasive analysis to be performed. The test was considered completed after three intervals, giving a total of 168 hours.

The following paragraphs describe instruments and conditions used in this research.

3.2.2.5.1 Heat Ageing

A number of procedures have been developed to assess to what the extent a substrate or an object can resist heat induced damage. BS EN 12280 (British Standards Institution, 1998) is a standard commonly used for accelerated ageing test of coated materials; it is divided in three parts with the first section focused on heat ageing. This standard requires a temperature of 70 °C ± 1 °C, with no specified RH, for 168 hours – or multiples of 168 hours. Milligan (1986) also described the so called "Sahara Test" performed on automotive fabrics where fabric samples were exposed to a temperature of 115 °C for six days and then the colour change assessed in conjunction with other specific physical properties.

In this research a Sanyo MOV 212 Drying Oven was used to conduct the ageing procedure in a controlled environment. The first test was carried out at 115 °C for 56 hours to evaluate if this interval was able provide valuable information on the early degradation of the samples. During the same test some of the samples were overlapped to investigate possible effects of this positioning, in contrast with the standard configuration that requires the samples to be laid on the oven shelves. After this initial trial, three different settings of the temperature were used to conduct investigations:

- 70 °C - moderately high temperature and labelled as "mild" degradation conditions;
- 115 °C - high temperature and labelled as "medium" degradation conditions;

- 150 °C - very high temperature and labelled as “severe” conditions.

The total ageing period, calculated aggregating the three 56 hour ± 1 hour intervals, was set at 168 hours which corresponds to the ageing interval described in the standard BS EN 12280-1:1997.

3.2.2.5.2 Heat and Relative Humidity Ageing

A Binder MKFT 115 weathering chamber was used to conduct investigations on the combined effect of temperature and relative humidity on leather-related materials. The machine works both in static and cycle mode.

Experiments were conducted on samples subject to the following conditions:

- 70 °C and 90% RH, in static mode and for three stages each composed of 56 hours (static mode);

The first experimental setting was carried out according to the standard EN 12280-3:2002 for environmental ageing of coated fabrics (BSI, EN 12280-3:2002); the only difference with the standard was that the relative humidity value was set at 90% instead of 95%.

3.2.2.5.3 Simulated Light Ageing

The ISO 4892-3:2013 standard (British Standards Institution, 2013) explains the nature of the materials and procedures required to run accelerated ageing using fluorescent UV lamps. An Atlas UV2000 equipped with eight UVB lamps emitting characteristic radiation was used to investigate leather-related materials behaviour when subject to accelerated light ageing.

The instrument was run in the ‘UV mode’ and the irradiance value was set at 0.77 $W.m^{-2}$; the black panel temperature was set at 23 °C and it reached 50 °C within the first hour from the beginning of the test. Humidity and dew point into the chamber were measured using an EasyLog datalogger device and the result of the measurement are reported in Figure 3-15. Also in this case the total ageing period, calculated aggregating the three 56 hour ± 1 hour intervals, was set at 168 hours.

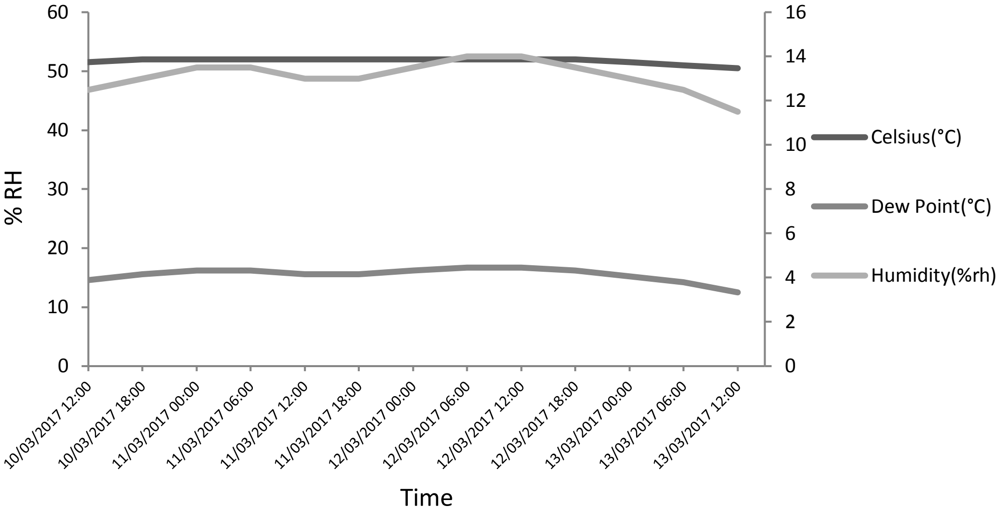


Figure 3-15: Graph showing the typical temperature and humidity fluctuations in the Atlas UV 2000 test chamber within a three days period

Category of the Analysis	Technique	Non-invasive (NI), Destructive (D), Non-Destructive (ND)	Standard
Morphological and Topographical (Macro)	Photography (VeriVide + Colour Checker)	NI	-
	2D scanning	NI	-
Morphological and Topographical (Micro)	Optical-microscopy	NI	BS EN ISO 17131:2012
	SEM-Microscopy	ND	BS EN ISO 17131:2012
Chemical	ATR-FTIR	NI	-
	Moisture Content	D	EN ISO 4684:2005 (volatile matter content)
	EDX	ND	-
	pH test	D	BS EN ISO 4045:2008
	Colorimetry	NI	-
Physical and Mechanical	Kawabata (KES) bending, compression and surface test	ND	-
	Tensile Strength/Elongation	D	EN ISO 3376:2002 and EN ISO 1421:1998
	Colour Fastness to Rubbing (wet)	D	BS EN ISO 11640:2012

Table 3-4: Analytical techniques, category, type and standard used (where applicable)

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Chapter 4 Materials Characterisation

Leather and related materials can be found in many different contexts. Museums often collect items made of these substrates that have a significant value for cultural, historical, artistic or scientific reasons (Ahmad, 2006; Vecco, 2010). Unfortunately, not always items are labelled or correctly labelled, which means including the composition and construction of the material. Moreover, despite in some cases a label describing the material exists, this cannot be regarded as totally reliable (van Oosten and Laganà, 2015). As a consequence, inappropriate preservation treatments that lead to premature degradation in the short or long term can be implemented.

Correct identification is therefore critical in addressing and implementing sensitive preservation without endangering any piece of collection, and is particularly important in contexts where materials that mimic the original natural products are developed (Keneghan, 1996). The morphological characteristics of collected items should be documented and chemical composition of any item entering a collection, or found without appropriate label, must be identified to the best of the heritage scientists' knowledge. In addition, information regarding their physical behaviour must be gathered in order to record properties that can be useful in future assessments of the items' condition with the passage of time.

After an initial overview of the characteristics and properties of leather-related materials, highlighting the similarities and differences between the substrates, the following sections will present the results of the characterisation of the four substrates under study.

4.1 Literature Review of Leather-Related Materials

4.1.1 Leather

A brief review of the historical evolution of the common leather manufacturing procedures was provided in Chapter 2, along with an overview of the properties considered of interest in this study. This initial section will focus on a literature review describing the chemical composition and physical structure of leather and then contrasting this database against the base materials used in this investigation.

4.1.1.1 Leather Composition and its Structure

The final chemical composition of leather is influenced not only by the nature of the raw skin but also by chemical additions during subsequent processing. About 64 % of the total mass is attributed to water, whilst about 33 % is contributed by proteins and only the remaining 3 % is made of fats, pigments and inorganic compounds

(Beghetto *et al.*, 2013). The major protein component is collagen, which is the fundamental component of any leather process from production to degradation (Florian, 2006).

4.1.1.1.1 Role of Collagen

Collagen is a family of natural polymers composed of 28 types of protein (Ricard-Blum, 2011). Each protein has a triple-helix structure but provides a specific function and tissue distribution (Gelse, 2003; Kadler *et al.*, 2007). Collagens are characterised by some similarities, such as the presence of the triple helix, but exhibit different chain properties and characteristics, like the type of repeating units (Ricard-Blum, 2011).

Collagen, being a protein, is characterised by covalent peptide bonding between the amino acids (Figure 4-1). In vertebrate skins, the dominant collagen is Type I and three amino acids are particularly important among the 20 different ones represented in the whole structure: glycine (about 33 %), proline and hydroxyproline (10 % each).

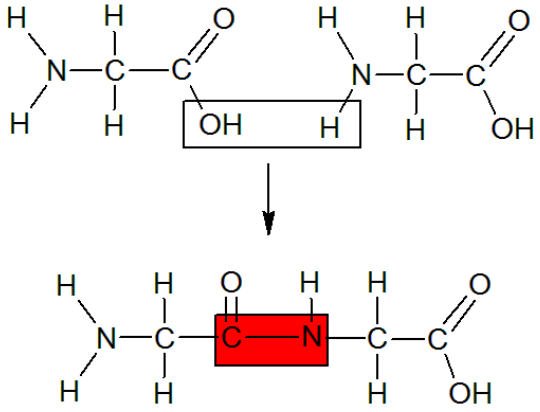


Figure 4-1: Peptide bond formation

Along with covalent bonds, other bonds stabilise and hold the polymer chains together within the molecules and between them. Glycine is always found in a position internal within the triple helix, and due to its small sidechain size (one hydrogen only) it allows the three α-chains to be stereochemically close so enabling hydrogen bonding to occur. Hydrogen bonds occur through N-H and C=O groups of adjacent chains. Another type of bond that occurs in the collagen molecule is the salt linkages (electrostatic), involving ionised carboxyl and amine side chains. Also covalent bonds, formed between the non-helical region called telopeptide (see below) and the helical region of an adjacent molecule are extremely important (Haines, 2011a).

Shoulder and Raines (2009) have published a comprehensive review of collagen, its structural hierarchy and the elements that interact to form the collagen molecule

(Figure 4-2). Initially the fibroblasts in connective tissue cells start the synthesis of single-strained α-chains (protocollagen strands or propeptides), that containing predominantly β-amino acids introduce a left-handed twist into the polymer chains. Subsequently, three propeptides go through a hydroxylation phase that leads to the formation of a procollagen triple helix characterised by a right-handed coil. This structure transforms into tropocollagen, after the N- and C-proteinases enter the protein and remove part of the non-triple helical region of the propeptides. A non-helical region called telopeptide is still part of tropocollagen and it is essential for the formation of microfibrils (or fibrils) via a self-assembling stage (Shoulders and Raines, 2009). In fact, telopeptide regions, which consist of about 20 amino acids, have the role to bond the collagen macromolecules together (Gelse, 2003).

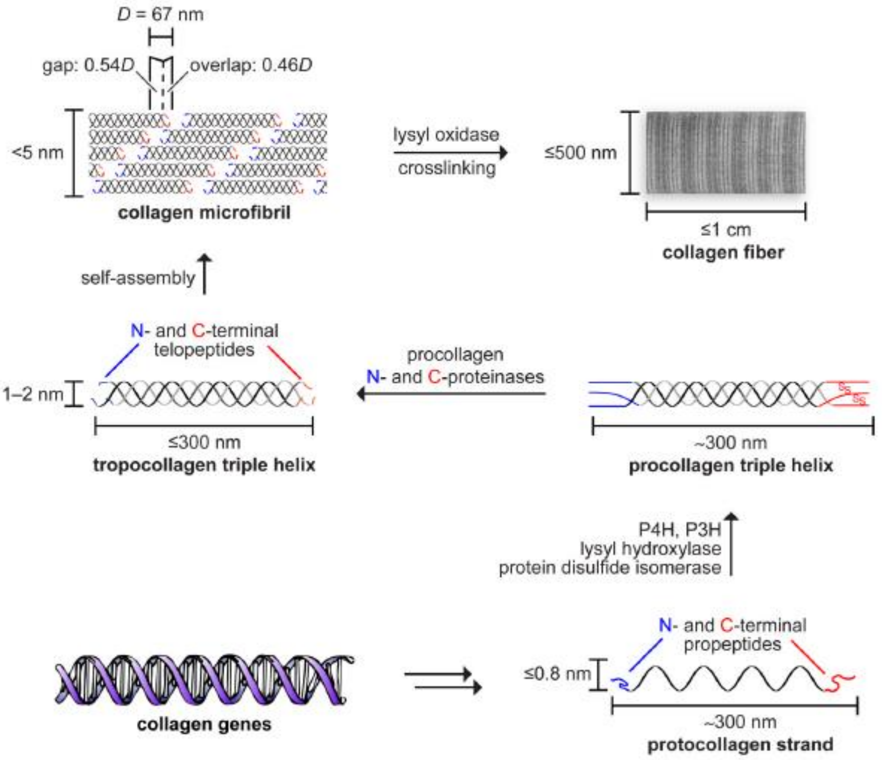


Figure 4-2: Hierarchical structure of collagen from its synthesis through to the collagen fibre formation (Shoulders and Raines, 2009)

When observed at high magnification under SEM, transmission electron microscopy (TEM) or atomic force microscopy (AFM) collagen fibrils exhibit a regular dark banding at every 67 nm interval (Covington, 2009). Since the collagen repeating structure is 300 nm long it was deduced that the collagen molecule must present a specific spatial repeating structure in order to exhibit this structural feature. In order to visualise this repeat unit a stain was applied and penetrated into the gaps between the end of one molecule and the beginning of the following one. Hence the formation of the *quarter stagger*, a term that describes the displacement of collagen molecules so that they overlap by one quarter of their length was observed (Haines, 2011a). The overlapped regions are 27 nm long and the crosslinking between the telopeptide, non-helical region, and the triple helix occurs here (Figure 4-2).

Regarding the disposition of collagen molecules along the z axis, two models have been proposed based on either a hexagonal close packing (HPC) and the pentafibril or microfibril model (Covington, 2009). Microfibrils or fibrils constitute the third step of the skin hierarchical ladder, just above the protocollagen and the triple helix, where fibrils tend to agglomerate in fibril bundles and form elementary fibres. Finally fibre bundles, that constitute the skin interwoven texture, are formed (Haines, 2011a).

4.1.1.1.2 Fibre Structure

The skin of cattle, calf, goat, sheep, pig and cervids (deer) are regularly used to obtain leather. Each of these animal families is characterised by distinctive characteristics of the skin layers, but all of them contain three regions: grain, corium and flesh (Haines, 2011a). Figure 4-3 shows the typical leather layered structure.

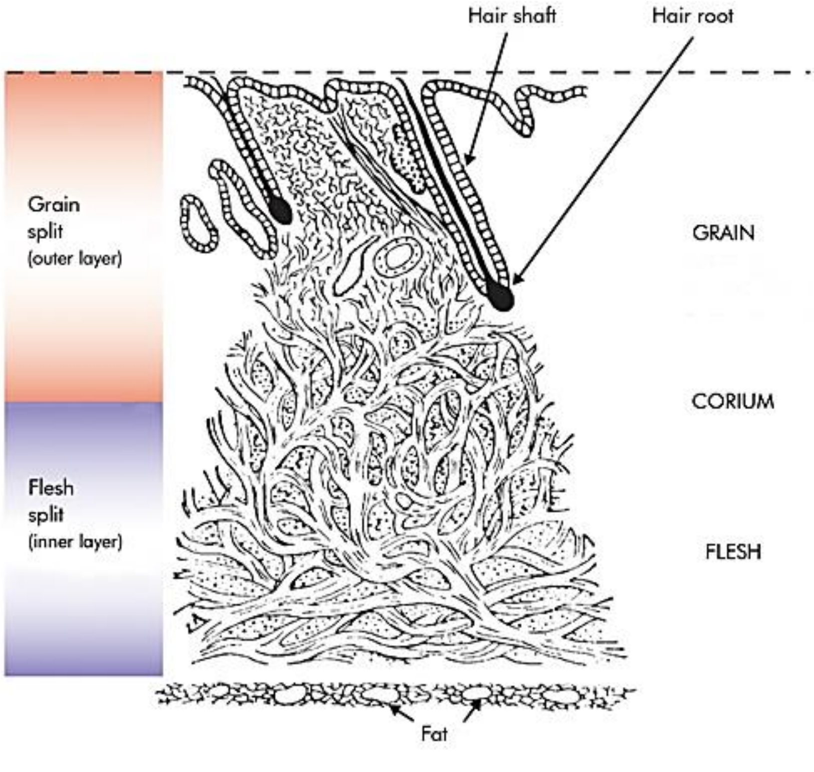


Figure 4-3: Structure of collagen fibres in hide skin (Satra Technology, 2016)

When the animal is alive the epidermis constitutes the outer layer of skin, and it is in contact with the corium. This layer must be removed to produce leather and therefore the grain becomes the outer layer. Hairs have their roots in the grain together with the sebaceous and sweat glands and blood vessels (Haines, 2011b). Fibres in this region are very fine, exhibit relatively little interfibre interactions and produce an outer grain surface with a pleasant appearance but minimal strength.

Below the grain there is a zone of transition that connects grain and corium and is characterised again by very fine fibres. Finally, the corium has fibre bundles of greater size (up to 0.1 mm in cattle hide) compared to those of the grain (up to 0.001 mm), interwoven and randomly orientated. The flesh layer has finer fibres and a horizontal orientation. It is the inner layer of the skin and is less used for high quality items because of its inferior characteristics (Haines and Barlow, 1975).

Variations of the layered structure can be observed according to animal type and other features such as living environment and diet. Along with having distinctive skin layer dimensions and thickness, the pattern of the grain surface is also characteristic of each animal and becomes more obvious after hair removal (Michael, 2014).

Collagen fibres change structure according to the position in the skin and may influence subsequent degradation and the necessary conservation treatments. Figure 4-4 illustrates the typical fibre orientations in an animal skin.

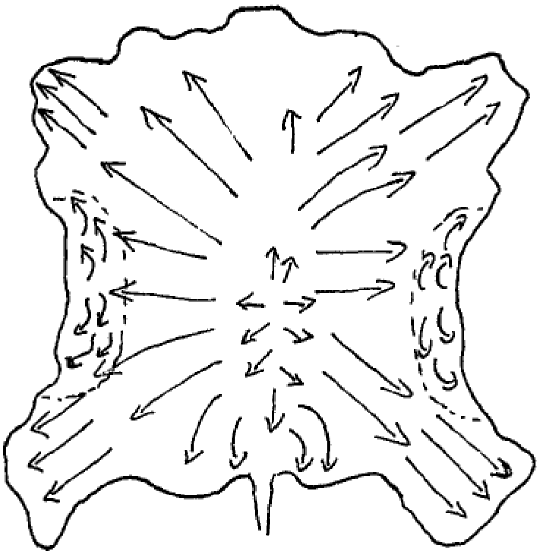


Figure 4-4: Orientation of fibres in animal skin (Haines and Barlow, 1975)

There is a predominant direction in the fibre bundles which arises during foetal development and tends to align along the backbone lines of tension influencing hairs pattern. Axilla and belly regions are rather weak and here the main changes in the structure occur, with fibres less frequently interwoven and running at a lower angle compared to other areas. This structure is in contrast to skin along the backbone of the animal where fibres are highly interwoven and the final leather has a lower tendency to roll up (Haines and Barlow, 1975). These structural elements significantly impact on the overall skin physical properties, in particular for strength and extensibility (Wang and Attenburrow, 1993; Mutlu *et al.*, 2014).

4.1.1.2 Tanning Mechanisms

When storage conditions are favourable untanned skin is stable, as demonstrated by the conspicuous amount of historical parchments in the global cultural archives (Della Gatta *et al.*, 2005). However when these substrates are exposed to wet and re-dry processing they lose their structural properties, stability and disintegrate (Hansen *et al.*, 1991; Larsen *et al.*, 2005; Woods, 2011). Tanning agents increase hydrothermal stability improving the substrate resistance to degradation. However the exact nature of this molecular stabilisation is still not completely understood. For decades it has been thought that tanning created bonds directly with collagen molecules; however Covington (2001) has suggested that this stabilising effect might result from the modification of the supramolecular structure of bound water. Depending on the tanning agent, therefore, different interactions can occur directly with the collagen or, as suggested above, with the water surrounding the collagen.

Many tanning methodologies have been developed over the course of the centuries, but only some of them will be presented in this thesis: vegetable tanning, syntans or synthetic tanning agents, mineral tanning, oil tanning (not covered here), and aldehyde tanning (not covered here).

Vegetable tanning has been practiced almost exclusively from the early years of leather production until 1884-1886, when chrome-tanning was introduced. Vegetable tannings are divided in two categories of products both of which have in common the presence of polyphenols. Hydrolysable compounds (gallotannins and ellagitannins) have the tendency to hydrolyse leaving the fermentation products in the collagenous matrix. They fade easily but can be effectively used with metal ions to achieve semi-metal tannage that increase the shrinkage temperature. Condensed compounds (flavonoids) used in tanning deposit polyphenols aggregates, give more intense colours and are not used with metal ions (Covington, 1997). Hydrolysable tannings interact with collagen fibres mainly via hydrogen bonding, while condensed tannings can also establish covalent bonds with lysine in the collagen fibres (Covington, 2009).

Aromatic syntans were introduced to tackle the shortage in vegetable tannings at the beginning of the Eighteenth century (Thomson, 2011). They are divided in three categories depending on their application: auxiliary, retanning and replacement syntans. Auxiliary syntans, that facilitate the vegetable tanning penetration, are sulphonated and polymerised materials starting from the reaction of naphthalene and formaldehyde. Retanning syntans, frequently used after chrome-tanning, are the sulphonated phenolic products. Replacement syntans are used as substitutes for vegetable tannings (Covington, 2011). The tanning power is strictly connected to phenolic and sulphonic group content, increasing together with phenolic content and with the reduction of sulphonic groups.

Other methods of tanning use reactive tannins, the combination of tanning agents or, alternatively there are methods that use oils with unsaturated double bonds to obtain chamois leather (Covington, 2011).

Finally, mineral tanning has been introduced in more recent times and with great success. Chromium, aluminium, titanium, and zirconium tanning agents have been investigated widely over last few decades (Lampard, 2000) and their study is still ongoing. Titanium and zirconium are more recent additions to the available range of tanning agents, but are not as popular as chromium and aluminium.

Aluminium salts have been used extensively by leather makers, normally together with vegetable tanning because of the limited ability of alum to interact with collagen. The interaction with the collagen molecule is electrostatic in nature, with the aluminium complexes not as stable complexes as comparable chromium complexes. As a consequence, aluminium can be easily removed from the tanned collagen structure. For these reasons its use as a tanning agent is not widespread (Covington, 2011).

4.1.1.3 Chrome-tanned Leathers

Chrome tanning with chromium [Cr(III)] salts is widely found in objects made after 1884. Today this constitutes the method most commonly used to produce leather (80-90% of the total is chrome tanned) because of the advantages of low cost, processing time and high hydrothermal stability.

The tanning agents are normally chrome sulphates with -OH or -O- bridges which connect polynuclear complexes, but the mechanism of interaction between collagen and chrome is still not yet fully understood (Nashy *et al.*, 2012). Chromium dichromates with thiosulphates or aldehydes have been used with the Cr^{IV} converted to Cr^{III} in situ in the pelt.

The process of tanning with chromium salts requires careful consideration of temperature and pH values throughout the reaction. pH value has a crucial role because both collagen and tanning salts have a specific range of stability: in the collagen it helps to acidify the molecule through protonation, which aids in chromium exhaustion and avoids precipitation (Covington, 2009).

After acidification during the pickling stage, the reaction between tanning agent and collagen molecule occurs at two amino acid sites. Aspartic and glutamic acid side chains (the two reactive sites) have acid dissociation constants of 3.8 and 4.2, which allows the salts of chromium to be formed in a processing range between pH 2 and

5. At the beginning of the reaction chromium (III) sulphate initiates the process and the pH is between 2.5 and 3.0, then the pH is increased up to 4.0. This procedure allows the chromium to penetrate into the matrix during the first stages of the tanning, at low pH, and then the rise in pH allows the higher reactivity in the collagen but reduces the chrome penetration. Finally the pH is raised to fix the chromium, making the collagen structure much more stable (Covington, 2011).

While chrome tanning has many advantages compared with vegetable tanning: higher hydrothermal stability, lower processing time, lower total tanning content in the collagen matrix, higher hydrophobicity, greater variability of colours and good lightfastness (Covington, 2009), it is however under an environmental "magnifying glass" because of its environmental impact and health concerns. Therefore there are ongoing developments in to alternative tanning systems.

4.1.2 Synthetic Leather

A review of synthetic leather manufacturing procedures and historical evolution was given in Chapter 2. In these paragraphs some basic chemical and physical characteristics will be presented.

4.1.2.1 Fibrous Substrate Composition

A tight interconnection between textile history and technological progress exists and can be clearly identified when synthetic leathers are considered. The composition of coated and laminated textiles have changed during the decades shadowing people's needs, market trends and fluctuations and advances in industrial machineries (Holker, 1975; Ciesielski, 1999; Roh *et al.*, 2013).

The most elementary component of the base fibrous layers are fibres that can be natural (e. g. cotton), modified natural (e. g. cellulose acetate) or synthetic (e. g. polymer based). Virtually any kind of fibre can be used for this fibrous base layer, because they are covered with the coating or layer in the following step of the process and essentially just provide a platform for the polymer. However, only a small range of them can be effectively utilised commercially due to need for good adhesion properties, flexibility, dyeability and so forth. Cellulose based (cotton and rayon), nylon, polyester, polypropylene and aramid fibres are the preferred fibre choices (Fung, 2002a; Sen, 2007).

The fibres that provide the base layer can be distributed following regular patterns that are woven and knitted fabrics, or deposited on a substrate more or less regularly before becoming a web (nonwovens). A wide variety of structures may be utilised and some of these examples are reported below.

Woven fabrics are formed by interlacing sets of two or more threads at the right angle. The warp yarns run in the same direction of production while the weft threads are inserted in the warp pattern (Figure 4-5a). Woven are not very extensible but can provide high dimensional stability and therefore are used whenever the final application requires shape stability.

Knitted fabrics are characterised by thread loops which interconnect one to another by using various arrangements that are chosen according to the final application (Figure 4-5b). Their structure has the effect of conferring elasticity in one or both directions depending on the manufacturing method used, therefore they are normally used when items need to be stretchable (Figure 4-5b).

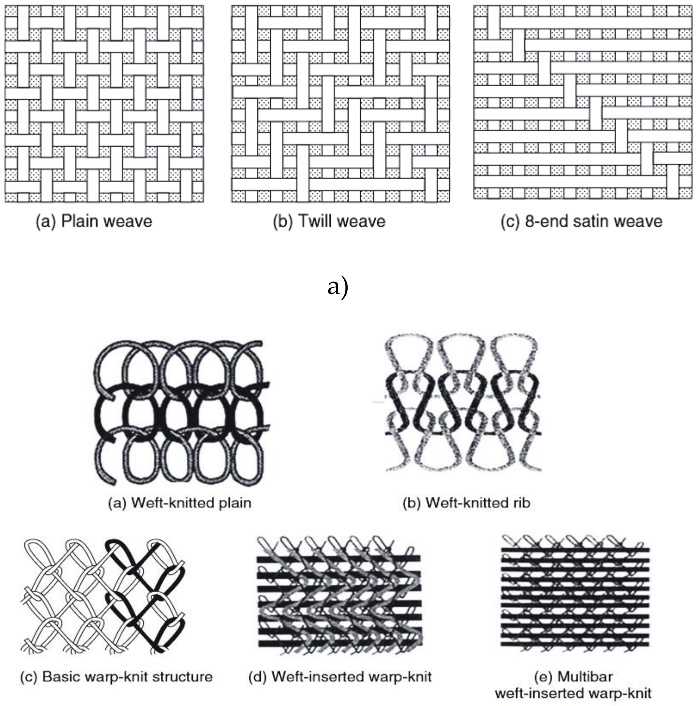


Figure 4-5: Patterns and structures of two-dimensional woven (a) and knitted (b) fabrics (from Hu (2008))

Unlike woven and knitted fabrics, nonwovens do not require yarns because they originate directly from fibres and fibrous webs. For this reason nonwovens were considered, in the early years of their production, less specialised materials that could be produced via drylaid processes for a lower price. This idea has gradually changed as different industries have started to use these substrates for different more sophisticated applications (Wilson, 2006). Cost-effectiveness is not the only advantage of these substrates, rather they possess distinct properties due to the chemical and physical features that make them a good alternative to woven and knitted fabrics (Wilson, 2006).

Nonwovens production is divided in to three main stages: web formation, bonding (or consolidation) and finishing. The variety of methods and machineries used in each stage of the production is increasing accordingly with the expanding number of applications. Therefore today a multitude of procedures can be used to obtain nonwoven substrates.

As in the case of woven and knitted fabrics, it is possible to use natural or synthetic fibres also for nonwoven manufacturing according to the final application needs. In the early 70s Beaulieu and Troxel (1973) identified cotton sheetings, drills and sateen as the most used fabric substrates for coating, followed by nylon and rayon, polyester/cotton blends, and finally 100% polyester woven and non-woven. They predicted a reduction in the use of cotton as a substrate in the following years, with a concomitant increase in 100 % spun polyester and non-woven. Their prediction was correct and nowadays nonwovens are the most used fabrics for both technical and daily applications (Fung, 2002b).

4.1.2.2 Polymers for Coated Fabrics

Typically the outer surface of synthetic leathers are made of polymeric materials. As described in Chapter 2, natural resins and oils were initially used to coat fabrics to obtain waterproof garments. Today the majority of artificial leathers are coated or laminated with synthetic polymers.

Sen (2007) provided an overview of the similarities and differences amongst the various polymers available for coating and lamination, and he also identified the major end-use applications. Polyvinyl chloride (PVC), polyurethanes (PU), and acrylic polymers are the most common coatings applied to obtain artificial leathers.

In the context of this thesis, PU was described by the supplier as the polymer characterising the coating of the substrates provided, thus a brief overview of the relevant PU coatings is discussed below.

Polyurethanes (PU)

Urethanes have acquired great importance in commercial applications from the 1970s and today this polymer family provides a wide range of materials from fibres, to soft or hard elastomers, to flexible and rigid forms.

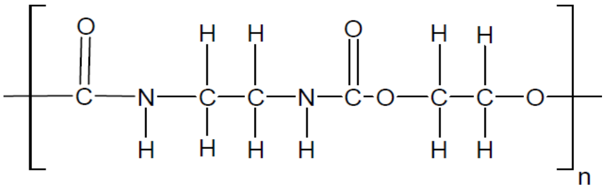


Figure 4-6: Structure of typical PU linkage

Di- or polyisocyanate and di- or polyols are the two chemical compounds that, reacting via polyaddition, promote the formation of the PU macromolecule. The synthesis of branched or cross-linked polymers is the result of initial reactants containing three or more functional groups (Sen, 2007).

Important examples of the precursor isocyanates are toluene di-isocyanate (TDI) and diphenyl methane di-isocyanate (DPMDI), cyclic compounds, hexamethylene di-isocyanate (HDMI) and other aliphatic variants. Aliphatic precursors have a lower tendency to yellow, and therefore they are often used for coating applications. Also polyols can be divided in two categories: polyesters, such as caprolactone polyester, and polyethers, such as polyethylene glycol. Along with isocyanates and polyols, chain extenders are often required in order to obtain polymers with the optimal balance between length of the molecule and number of reactive sites, thus regulating the reactivity and rigidity of the targeted material (van Oosten *et al.*, 2011).

PU is formed via two reaction routes: either a one- or two-shot process. The former consists of mixing together polyols, diisocyanates, chain extenders and catalyst to obtain a fast polymerization (exothermic). The latter requires the formation of a prepolymer by reaction of diisocyanates and polyols and then the prepolymer is reacted with a chain extender to form the polymer (Sen, 2008).

Coatings that are exposed to particular conditions need to satisfy the standards and regulations defined by national and international organisations. In the case of products to be used in transportation, it is normally necessary to certify that products are able to withstand the action of a flame for a stated period of time. This branch of the market is in continuous evolution, especially because flame retardants often contain aggressive chemicals or can develop harmful substances during decomposition (Weil and Levchik, 2009; Liang *et al.*, 2013).

To understand the coating composition it is necessary to remember that a number of compounds contribute to the polymer mixture, and therefore their “footprints” will be visible during the manufacture, performance and analyses.

4.1.3 E-Leather

E-Leather® fabrics are made using a variety of different components, from the fibrous substrate to the coating layer. The manufacturing process has already been described in Chapter 2 and, to summarise, it was divided into the three stages: formation of the web composed of leather fibres, bonding via hydroentanglement and finishing. In the next two paragraphs the components of the E-Leather® substrates will be observed in more detail.

4.1.3.1 E-Leather Composition

Leather scraps coming from tanneries that conduct the chrome-tanning treatment constitute the essential feedstock of the whole production. These fibres would typically go towards landfill without possibility of being reused, but E-Leather developed a recycling technology. This involves a preliminary separation removing mouldy or badly damaged fragments (Hartung, 2014) and then the two types of waste are processed in order to obtain fibres of wet blue leather:

- Shavings, the waste product of the shaving process which normally follows the tanning procedures;
- Trimmings, originating from the leather portions which are not usable because of discontinuity on the surface, or for defects that would be visible after finishing.

After the fiberisation process the size of the leather fibres is too small to be processed via hydroentanglement, therefore the addition of bicomponent fibres is required. Bicomponent fibres compatible with leather-like handle have a size of 4-6 mm and density 1.7 dtex (Bevan, 2005), and they are made of an outer skin composed of low melting point polymer and an inner core having higher melting point. In E-Leather® production these fibres are made of an inner polypropylene (PP) core and a polyethylene (PE) outer characterised by a low melting temperature. The amount of PP/PE fibres must not be higher than 4% of the leather fibre weight so that the final product handle is similar to that of traditional leather. Once heated, this structure encourages the formation of a web of fibres fused together (Bevan, 2005).

Moreover, a second type of synthetic fibres (splittable fibres) are jointly used as reinforcement to build the supporting web. Splittable fibres have an average length of 5 mm and are added to the fibrous mix during the web formation stage. They provide strength to the web by interweaving with the rest of the fibres following the action of the hydroentanglement process. Use of splittable fibres for the production of leather imitates is well known (Anand *et al.*, 2006); in E-Leather® they are made of polyester and must be around the 20 % of the leather weight (Bevan, 2005).

Fabric reinforcement is introduced through mechanical bonding to the leather sheet via hydroentanglement. E-Leather® uses polyester and aramid woven fabrics as a reinforcement. This reinforcement is generally placed closer to the outer surface of the finished material, however the position can vary depending on the product and its final application (Bevan, 2005). Normally more than one leather/synthetic fibres webs are bonded together to obtain the hydroentangled sheet (HE).

It is important to note that as for synthetic leather, it is often necessary to incorporate a flame retardant to satisfy the final end-use requirements. Where needed, E-Leather applies these compounds to the fibrous layer.

4.1.3.2 Finishing

In E-Leather® manufacturing the final layer that is in contact with the environment is made of a PU material similar to those described for artificial leather and leather.

The two precursors of PU are mixed together in order to obtain a homogeneous polymer with the correct viscosity. The details of the PU components were not provided from the company. The mixture preparation stage is vital in producing a coating with good appearance and properties. If the coating viscosity is not optimised then problems during the coating preparation or even in the adhesive process can occur. As already said, the method used to apply the coating is the transfer coating, therefore evidences of this treatment should be found when looking at the materials.

4.2 Morphological Analysis

The morphology of leather and related materials can provide useful information to solve the problem of identification. Visual appearance and microscopic analysis of both the top coating and reverse face may be able to detect the presence of characteristics typical of one or more substrates.

For this reason the results of the preliminary investigations of TL, SY and the E-Leather® substrates will be reported in this section. These results may be used in the future to effectively identify the different leather-related materials, in particular in the case of composite leather substrates.

4.2.1 Investigation of Surface

Appearance is one of the first characteristics that is manifest in any material, and even to a greater extent in museum context where there is far greater scrutiny of the object. Consideration of the appearance also represents the first step to identifying unknown materials that constitute items.

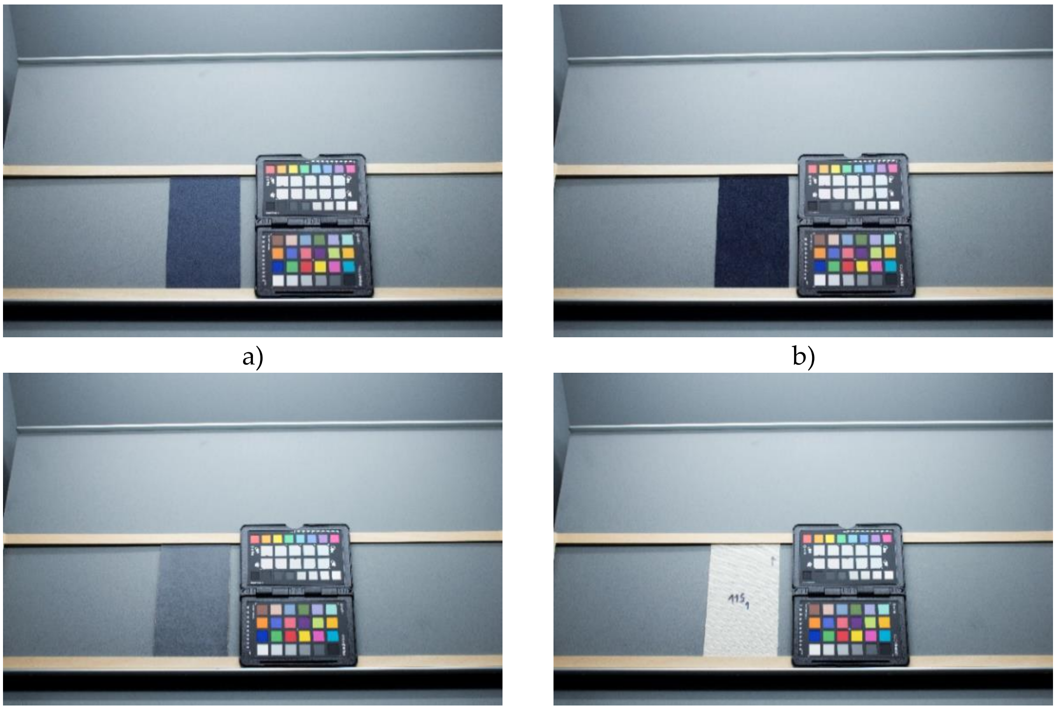
As previously described, the top surface of leather is variable depending on both the type of animal skin and the treatments it was subject to before being used for a specific purpose. Since the final application of the leather is also influenced by the manufacturing treatments, in a museum context it would be always useful to be aware of the application the material has been designed for. In this study, all leather-related materials were manufactured to produce seat covers for the transportation market which requires the use of substrates characterised by good abrasion resistance and uniformity. Manmade fabrics are manufactured with the aim of obtaining and controlling certain characteristics, thus it is easier to produce textiles with consistent properties; this is not always possible with natural leather. As Figure 4-7 shows, the leather colour on the corium side is not consistent indicating that the dye penetration is not homogeneous. One of the most common reasons for variable dye distribution is the presence of discontinuities in the fibres, for example due to density variations or tanning distribution (Covington, 2009).


a) b)

Figure 4-7: a) shows a whole leather hide after tanning and finishing treatments (flesh side). b) shows leather imperfections

The structural appearance of the base product in its almost original shape, Figure 4-7, makes it unmistakable that the product is of animal origin. A large colour difference was evident on the flesh side, but this difference was not visible on the finished side (Figure 4-8a and b). On the flesh side of the skin the variation of the leather coloration was clear, possibly because of the limited availability of binding sites left free after the tanning, resulting in a lack of binding sites for the dyes (Covington, 2009). The phenomenon is less visible on the grain side because of the presence of a polymeric coating.

Synthetic leather (SY), E-Leather® SL2 (EL2) and E-Leather® SL3 UL (EL3) were supplied and are commercialised in reels of variable length in contrast to natural leather (TL), and this constitutes the first important difference between artificial and natural products. Moreover, the former substrates have consistent properties throughout the length of the reel whilst TL does not. Artificial products find application in those commercial areas where many items with the same characteristics are manufactured, such as in the automotive and aviation industries and mass production items. Natural products are frequently used to accommodate smaller scale productions because of the difficulty in obtaining entire leather panels with homogeneous properties; however, one leather hide can be used to create a number of diverse articles with highly variable characteristics, which is perceived as desirable in craft industries. These differences in the materials must be considered whenever an unknown item which is part of a collection is investigated.



a) b)

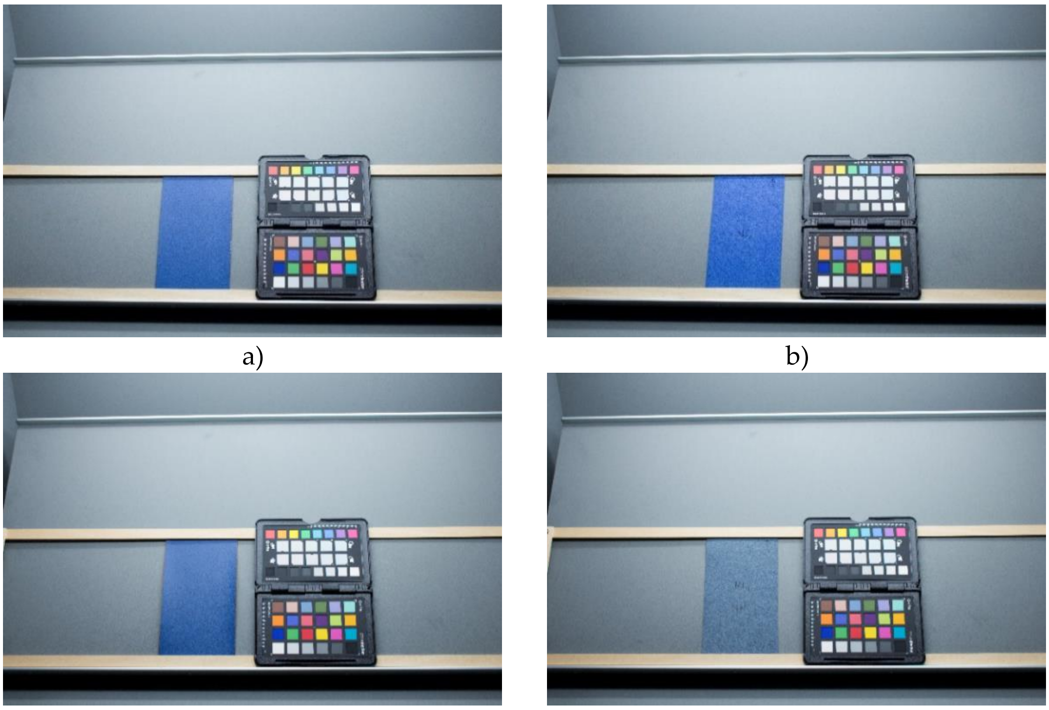
c) d)

Figure 4-8: TL and SY samples examined under standard lighting in a VeriVide light box. Grain and flesh layers of TL (a, b) and front and reverse layers of SY (c, d)

Figure 4-8 and Figure 4-9 show images of front and back of all the materials under examination. Natural and synthetic leather are shown in Figure 4-8 whilst E-Leather substrates are reported in Figure 4-9.

Figure 4-8d corresponds to the fibrous layer of a SY sample which showed a fabric underneath the polymeric coating, in Figure 4-8c. This was the only sample that visibly differed from the others because of its white/cream colour and for the pattern typical of a textile material (see later).

EL2 and EL3 were not visibly different from TL, a similarity that could potentially lead to wrong identification particularly in museum contexts, where these substrates have not arrived yet. In fact, this thesis which involves E-Leather® characterisation aims at providing basic information to help museum professionals during the material identification.



a) b)

c) d)

Figure 4-9: EL2 and EL3 samples examined under standard lighting in a VeriVide light box. Front and reverse layers of EL2 (a, b) and of EL3 (c, d)

4.2.1.1 Microscopy Techniques

Microscopy can effectively been used to reduce the risk of identification error. Figure 4-10 reports all the samples examined under grazing light: from the top to the bottom leather (TL), synthetic leather (SY), E-Leather SL2 (EL2) and E-Leather SL3 UL (EL3) are presented.

Leather and the two E-leather materials were dyed in shades of blue, while synthetic leather had a light grey coating. The perception of a change in the texture is influenced by the illuminant direction, as Chantler (1995) described. For this reason Figure 4-10 shows microphotographs of leather-related samples under illumination from both sides.

As explained by Ho *et al.* (2007), visual roughness perception can often fail to effectively assess the actual roughness of objects. However Whitaker *et al.* (2008) pointed out that the majority of research reported in literature focused on highly controlled patterns characterised by limited similarities with everyday materials. Leather and synthetic leather were used here to initially investigate the possibility of using visual appearance as a tool to perceive roughness. In order to do this, initial qualitative observations were carried out by focusing on different areas of the samples and drawing an imaginary straight line within those areas to project the sample profile. Morphological observations will be investigated by means of quantitative techniques in Chapter 5.

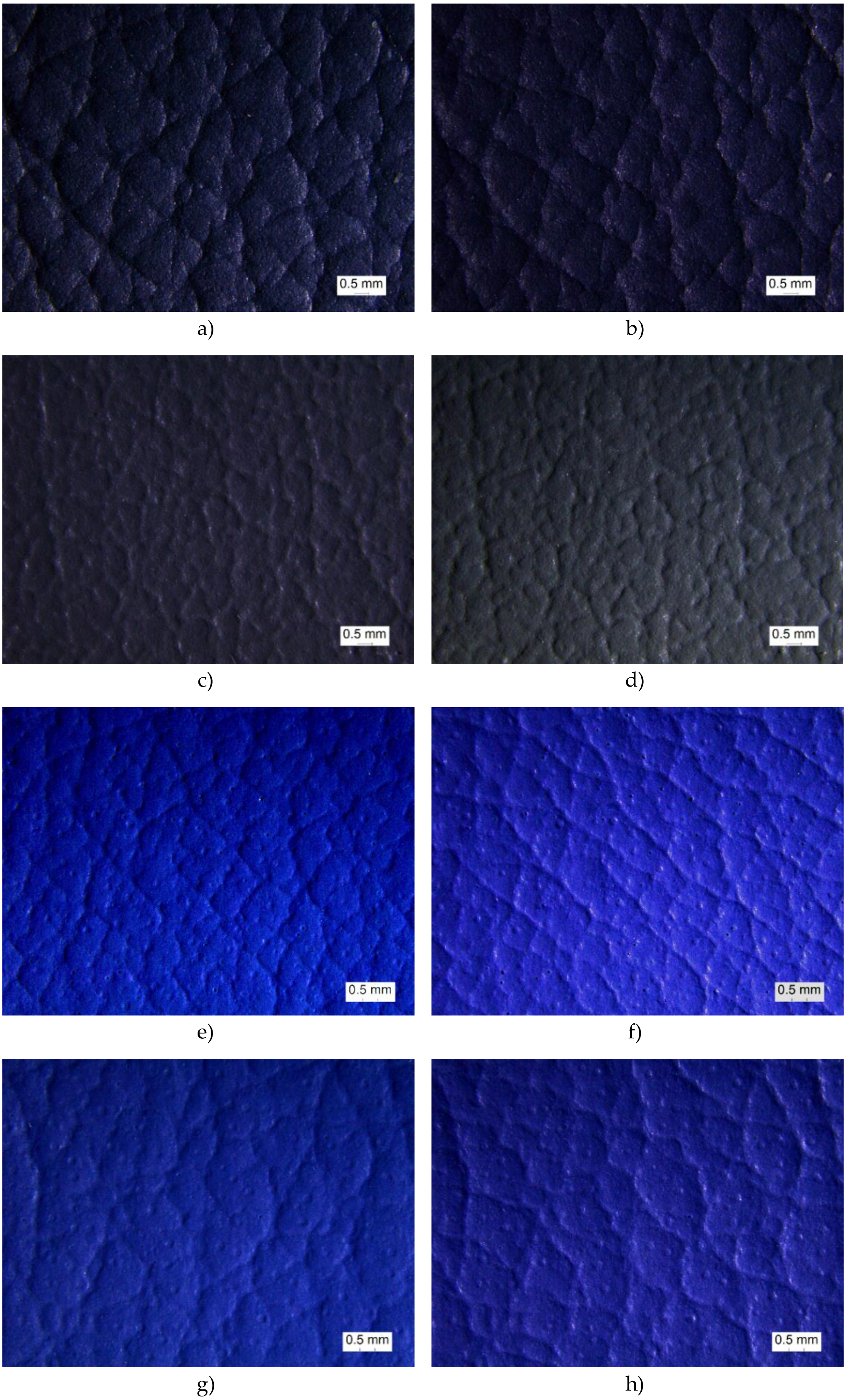


Figure 4-10: Stereo-microscopic examination of leather-related samples. From the top to the bottom: TL (a, b), SY (c, d), EL2 (e, f) and EL3 (g, h). Samples exposed to left-grazing light lighting (left column) and right-grazing light lighting (right column)

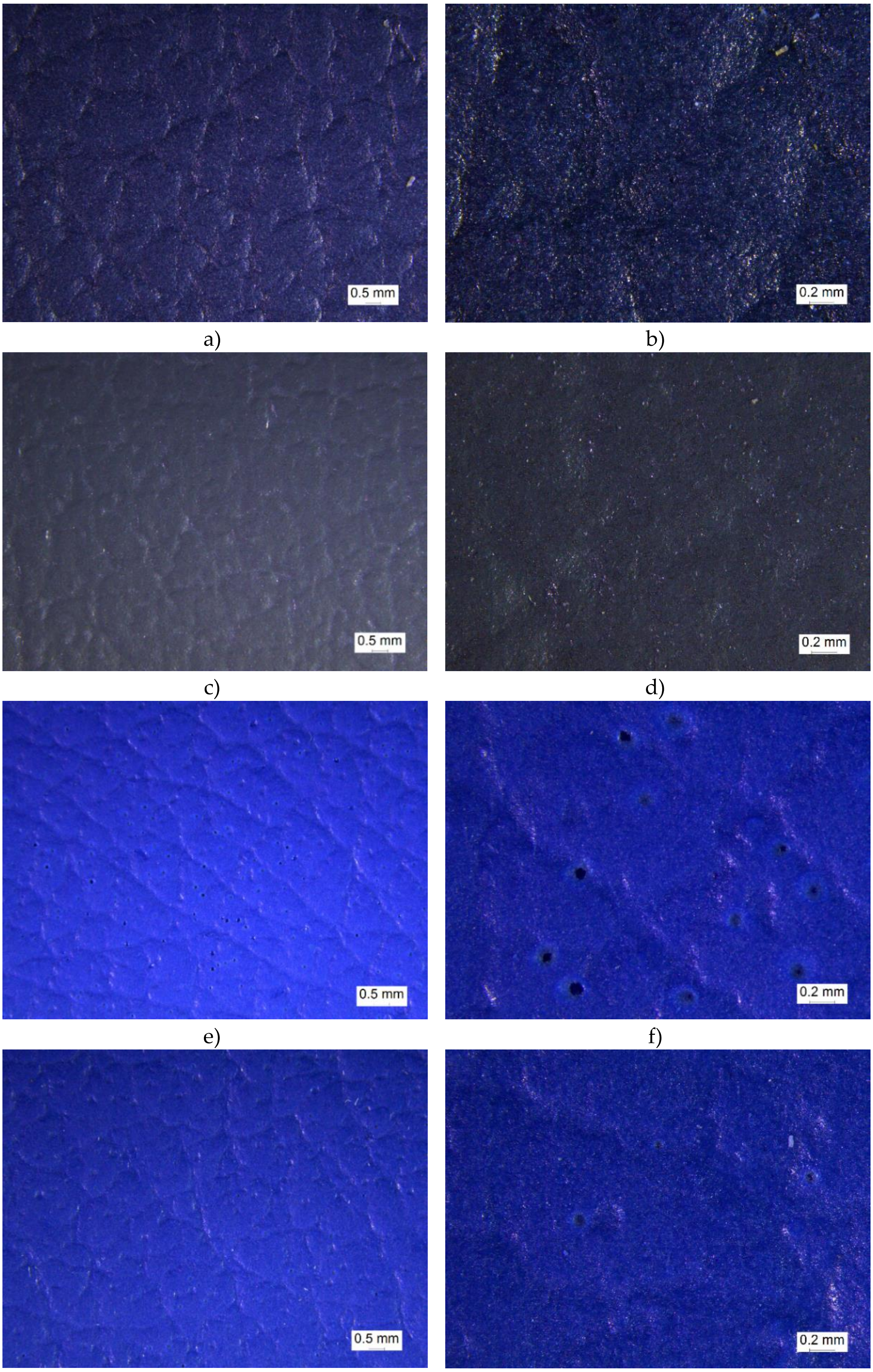
Figure 4-10 presents the slight differences in geometries of pattern on overall even surfaces. The respectively higher and lower roughness of TL and SY compared to EL2 and EL3 were observed with this method. In fact, the perceived profile of the TL material presented a lower number of wide peaks having higher crests compared to the other samples. Conversely the SY samples presented more frequent, tighter peaks with a minimal distance between their peak and valleys. Finally, both the EL2 and EL3 samples showed equally spaced peaks with intermediate profile values between the TL and SY materials. However, while EL3 appeared to present a smoother surface with mildly high peaks, EL2 presented more intense peaks that indicated a rougher surface. These observations were likely to be related to differences in the thickness of the coating, because the thicker is the coating the deeper can be the embossed pattern. They could also be related to differences in the design used to emboss the desired pattern on the surface. Partial confirmation of these observations can be found in the micrographs captured at a higher magnification (75x) in Figure 4-11.

Looking at both Figure 4-10 and Figure 4-11, it was not possible to find in the TL samples evidence of hair follicles, the typical holes left from the animal's hair after the dehairing process. This observation would be surprising if historical leather was examined (Mannina and Lombardo, 2013) or if the samples came from luxury goods, that are normally manufactured using 'full leather'. In this study, however, the leather application and its standards require the presence of a coating in order to provide high abrasion resistance. Polymeric coatings are often applied on the grain side and then they are embossed before being sold.

Colour can further complicate the identification of certain processing and base material problems, such as cracks or pinholes. This was evident in Figure 4-11, where the dark colour of the leather made less obvious the presence of bubbles on the surface despite the high magnification. Figure 4-11 also highlights the presence of tiny particles, of amorphous shape and composition, distributed throughout the coating surface of TL and SY samples (see later). These particles were not present in either EL2 or EL3.

At x10 and x75 magnifications (Figure 4-11) both EL2 and EL3 showed the evidence of circular shapes that were not observed in either TL or SY materials. Specifically, two types of circular shapes were identified:

- Smaller size, penetrating to a certain extent through the coating;
- Bigger size, more superficial.



a) b)

c) d)

e) f)

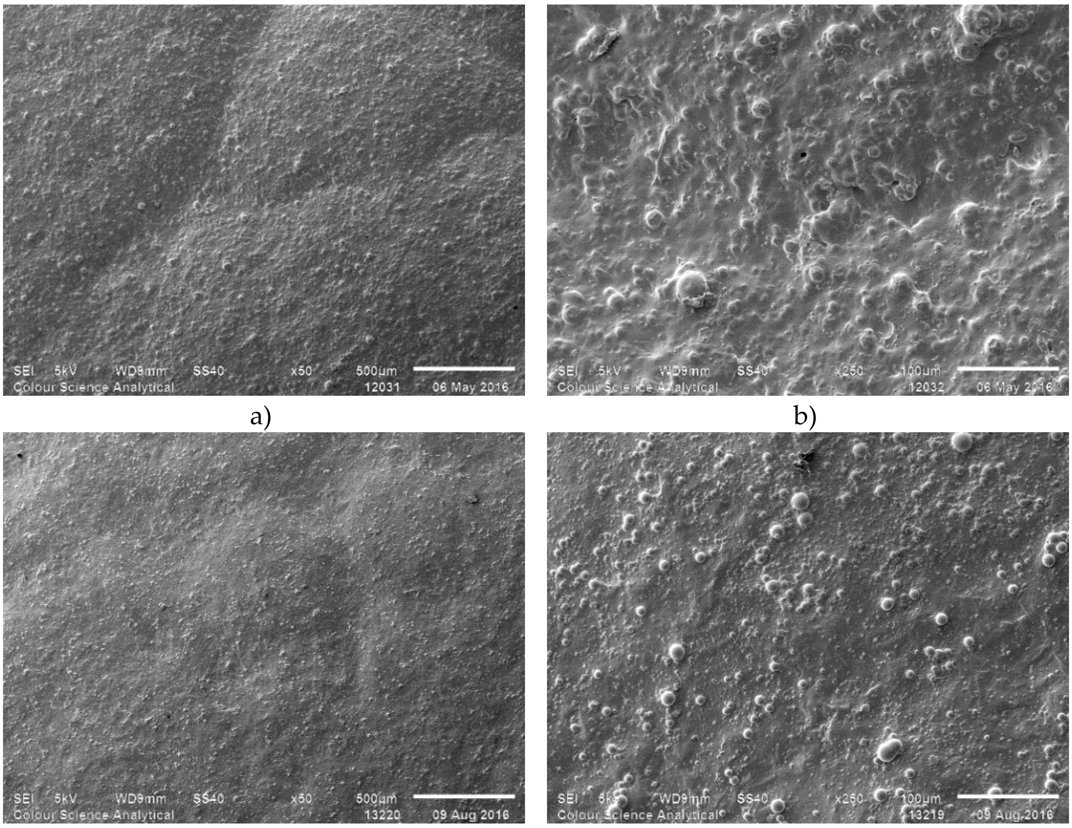
g) h)

Figure 4-11: Stereo microscopic images of leather-related samples. From the top to the bottom: TL (a, b), SY (c, d), EL2 (e, f) and EL3 (g, h). Samples at magnification x10 (left column) and samples at magnification x75 (right column)

The first of the two types was tagged as a defect and it was classified as bubble, according to the literature (Gutoff and Cohen, 2006). The second was likely to be an effect of the embossing process, probably to reproduce the follicles of leather grain, and therefore they constituted a desired element of the pattern. Confirmation of the different nature of these spherical shapes and of their desirability on the coating became apparent when other areas were analysed. It was found that bubbles were not homogeneously distributed, whilst the embossing elements were. Bubbles are formed when air is trapped in the viscous liquid prepared to coat fabrics (or leather) and they can be introduced during different stages of the coating formation. They can form during the mixing procedure as a consequence of incorrect mixing velocity, at the feed line and during drying because of excessively high temperatures (Zemlin, 1973; Gutoff and Cohen, 2006). Understanding the cause of the bubbles in E-Leather® was not part of this project. However it was essential to acknowledge their presence because this type of defects can lead to inclusion of dirt or pollutants during storage or exhibition speeding up degradation processes.

Both E-Leather® materials exhibited the presence of surface coating bubbles. In the EL2 coating they had a mean diameter of 88 μm (± 13 μm, SD of five measurements) while the bubbles in EL3 coating had an average diameter of 76 μm (± 20 μm, SD of five measurements). It should be noted that often the borders of the bubbles were characterised by a greater intensity of the coating colour and, in other cases, the presence of a hole was only detected underneath a thin layer of polymeric coating (Figure 4-11f and Figure 4-11h). These defects were classified as blisters. Both bubbles and blisters can be related to the viscosity of the solution used to create the final polymeric coating over E-Leather® fibrous substrate (Durst, 1985).

SEM images were recorded to further investigate the coatings and the nature of the tiny particles identified on TL and SY samples (Figure 4-12). As expected, these images provided insights difficult to glean from stereo-microscopic observations. x50 magnification scans showed that leather samples were characterised by extended dark areas that represented the valleys of the leather pattern (Figure 4-12a). Darker areas were also visible in SY materials (Figure 4-12b), but their grey level was much lower than in TL; this confirmed that TL, at magnification x50, had greater roughness than SY. This magnification did not allow the identification of the particles on the two coatings, but it did confirm their near-spherical shape and that the particles on TL had different sizes to those on SY.



a) b)

c) d)

Figure 4-12: SEM images of beads on TL (a) and SY (c) coating Mag. x50; beads particular on TL (b) and SY (d) Mag. X250.

Higher magnification imaging also characterised other aspects of the manufacturing procedures and it was evident that the finishing treatments carried out on TL and SY were rather different. In fact the TL coating had a relatively irregular surface and the spheres showed less defined borders. These two characteristics could indicate the use of the spray coating technique and a slow, less consistent drying procedure. Moreover, Figure 4-12b and d indicated that particles had a spherical shape which, according to the final step of the treatment the two materials went through, can be more or less defined. The mean size of the beads found on TL was 12.58 µm (± 5.51 µm, SD of twenty beads), whilst those on SY had a mean diameter of 5.91 µm (± 3.26 µm, SD of twenty beads). Beads on TL seemed to be incorporated into the coating indicating that they were included in the sprayed polymer or, more likely, laid on the coating while it was still drying. Beads on SY were not even partially covered by the polymeric coating, therefore they were laid on the surface once it was already dry. The amount of beads on SY appeared higher than that observed on TL, an effect possibly due to the fact that part of the beads on TL sunk into the polymer before it dried.

These observations allowed to identify important aspects of the coatings. Thanks to some of these aspects, e.g. the roughness and the presence of beads, the materials could be potentially distinguished.

4.2.2 Investigation of Reverse Face

Preliminary examination indicated SY had a different fibrous layer compared to the other substrates whilst TL, EL2 and EL3 were rather similar. However, the fibrous layer of each leather-related material was subject to a number of microscope observations to increase the understanding of the whole material.

TL was characterised by even agglomerates of fibres distributed in variable ways according to the position across the skin, as reported by Michel (2014). These difference in the fibre agglomerates influence the final leather appearance and physical properties and were used as indicators of the fact that the product is not man-made. Differences are much more evident when the hide is examined as a whole, which does not occur very often because, of course, leather is normally found in collections as constituent material rather than as an entire hide. Leather in fashion clothes, design objects, decoration elements or armouries can be complicated to identify, but knowing typical leather characteristics helps identification even in those cases where deterioration has occurred. The leather under investigation for this study was examined in order to gain data to be compared with the literature and the other leather-related products.

The neck and shoulders areas, along with the butt region, showed the higher consistency in terms of fibres agglomerates (Figure 4-13b). Here the skin has normally a compact structure that results in an even distribution of the fibre bundles. Typically compactness decreased progressively in the belly and axillae regions, resulting in looser fibres and a gradually more uneven appearance (Covington, 2009; Harris, 2014). Some areas of the skin showed traces of the animal veins (Figure 4-13a), a peculiarity that when found in museum items facilitates the leather identification but adversely affects the quality of the original final product.

SY samples had a completely different structure, as initially noted during preliminary investigations of the coating and fibrous layer (Figure 4-8c and d). It consisted of a fabric sheet and, in particular, a knitted fabric that is clearly distinguishable in Figure 4-13c and d. A number of yarns formed Z-twist threads which, in their turn, constituted the loops of the fabric.

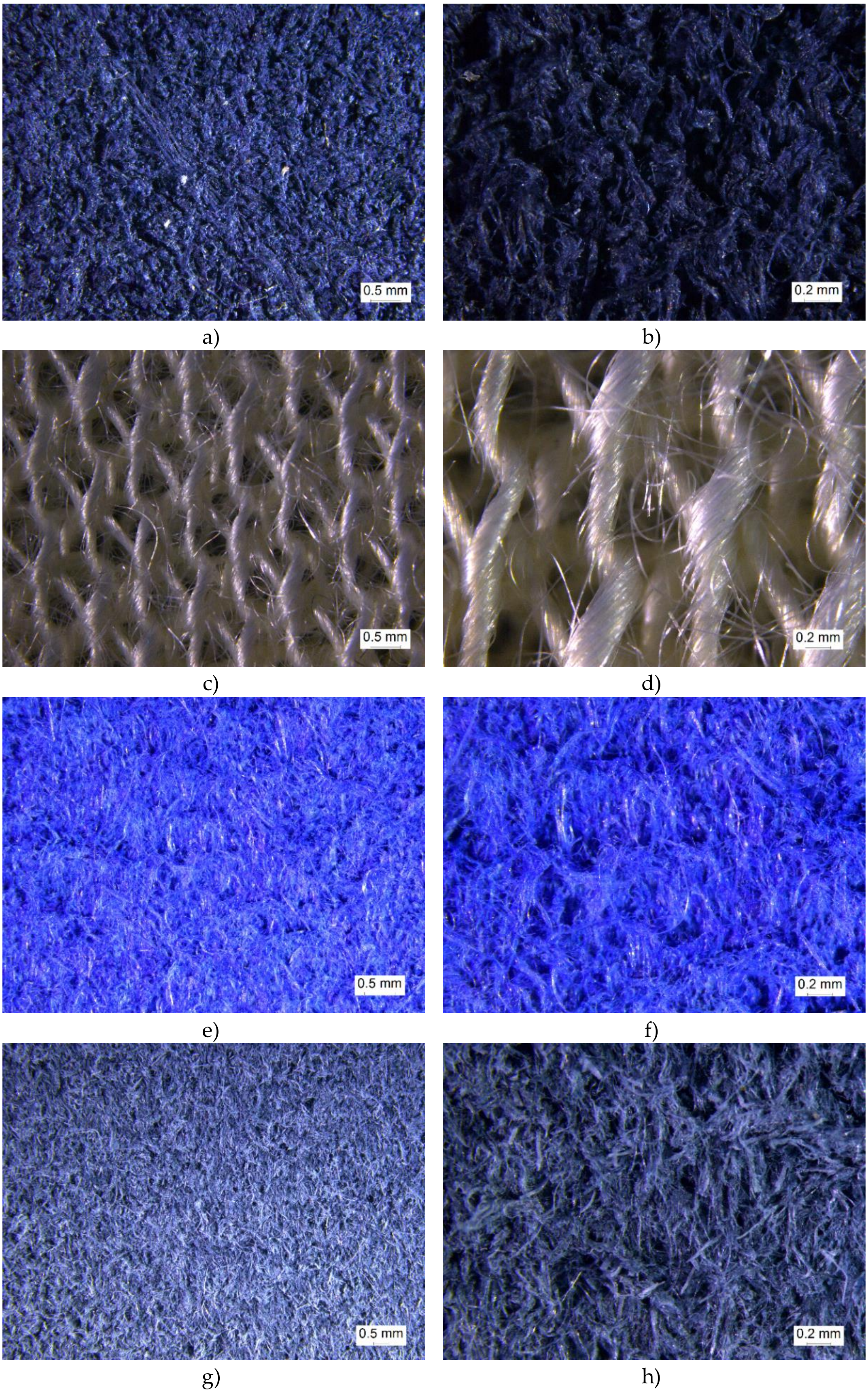


Figure 4-13: Stereo-microscopic imaging of leather-related samples (fibrous layers). From the top to the bottom: TL (a, b), SY (c, d), EL2 (e, f) and EL3 (g, h). Samples at magnification x10 (left column) and samples at higher magnification x40 (right column)

The yarns appeared glossy and even, two characteristics that, in agreement with the morphological characteristics of fibres reported in literature (King, 1985; Khan *et al.*, 2017), are often related to synthetic fibres such as rayon, nylon or polyesters. This type of industrially manufactured knitted fabric had a high degree of consistency across the roll and as a result the synthetic leather fibrous layer had an even appearance independent of the area of the roll observed.

The level of compactness of the SY fibrous layer was not as high as the TL materials and this is due to the fact that:

- collagen fibres are strictly bonded to each other by means of chemical bonds whereas knitted fabric fibres are rarely kept together by chemical bonds;
- in leather, fibres are interwoven one by one or bundle by bundle whilst in fabrics the fibre yarns constitute the threads which, in their turn, are woven or knitted.

This difference in the fibrous interconnection and distribution made the fibrous layer of SY less dense and, this may affect the perception of the fabric (Lee and Sato, 2001).

The EL2 (Figure 4-13e and f) and EL3 (Figure 4-13g and h) materials showed a number of similar aspects to TL because of the presence of leather fibres. The perceived compactness of E-Leather® substrates was similar to the one of TL as a result of the web-bonding and hydroentanglement processes. Despite the collagen fiberisation process during the early manufacturing stages, several bundles seemed still intact and spread across the fibrous layer. Unlike collagen fibre bundles in TL, the distribution in EL2 and EL3 was not necessarily even, because it was randomly determined from the air laying procedure (Wilson, 2006). Collagen fibres appear much rougher than synthetic fibres/filaments and disrupt the light so that the surface looks matt. However, the presence of a relatively high percentage of synthetic fibres in the E-Leather product made the fibrous layer more glossy than the TL materials (Figure 4-13f). The main difference between EL2, EL3 and TL was found in the consistency of the materials' visual properties across the roll, without any sign of veins or change in fibre orientation.

As already noted, the composition and structure of leather and its imitations has been studied in the past. However, being a newly developed material E-Leather® has never been subject to detailed investigative or comparative studies, thus the component fibres incorporated in its fibrous layer were studied. Staples were listed and their function explained in paragraph 4.1.3.1. Here microscope images of a leather trimming before fiberisation and of some melting fibres before air laying are shown in Figure 4-14 and Figure 4-15, respectively.

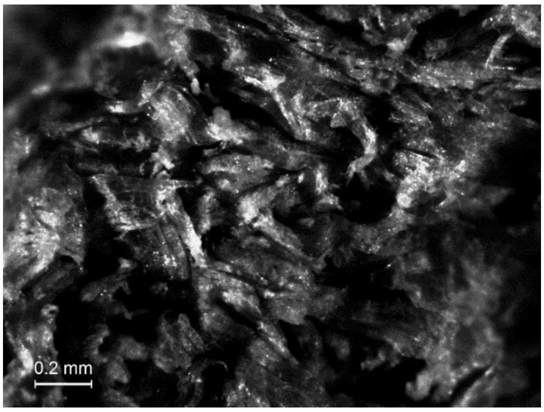


Figure 4-14: Stereo-microscopic imaging of wet-blue leather before E-Leather web formation (Mag x80)

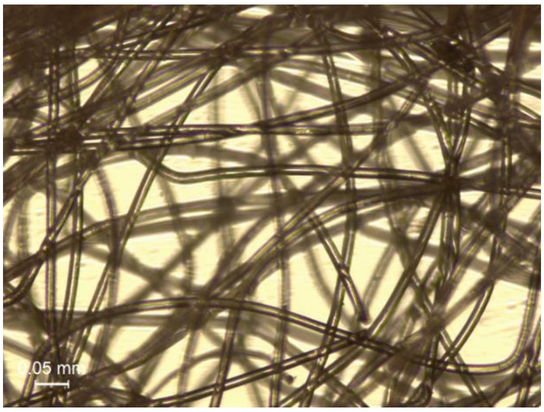


Figure 4-15: Stereo-microscopic imaging of E-Leather melting fibres before web formation process (Mag x160)

The sample of wet-blue stage leather above shows the typical leather structure characterised by interwoven collagen fibre bundles (Figure 4.14). The bundles are open and less compact if compared to those found in finished leather and this represents a benefit for the production of E-Leather web. This open configuration resulting from the chrome tanning stabilisation process leads to the formation of chrome-collagen complexes able to keep collagen molecules apart. Only a low percentage of the bundles will be preserved following the fiberisation process, whilst the remaining bundles will be separated along the collagen weakest bonds. Fibre opening is an essential step that precedes air laid web formation because the typical isotropicity of the process strictly depends on this structural change (Brydon and Pourmohammadi, 2006). Chrome-collagen complexes also allow collagen helices not to collapse once the molecule is subject to heat or combinations of heat and humidity (Ollè *et al.*, 2011). This aspect is particularly important in the case of E-Leather materials because high temperature is required to create the web, therefore the fibres need to be stable around the selected temperature.

Figure 4-15 shows the thermoplastic "melting" fibres that are used to make E-Leather web more resistant to mechanical stresses. These fibres are normally melted during the procedure that leads to the formation of the leather fibres sheet. Therefore it is unlikely they will be observed in the finished material apart in those cases where there are problems at the web formation stage. These fibres in fact go through melting as soon as the temperature passes a specific temperature, which in the case of EL2 and EL3 materials, is 120 °C (Bevan, 2005). In the case of unsuccessful melting, because of faults in the heating system or for issues related to the chemical composition of the fibres, low melting fibres are still present in their original shape in the finished product resulting in structural problems. The initial diameter of these fibres in EL2 and EL3 is 135 μm ± 9.66 μm but only until when the melting temperature transition is reached.

Together with these raw materials, bicomponent splitting fibres also have a significant role in the creation of a robust end-product. Their structure is much more complex than the melting fibres. In fact, initially the section of splitting fibres is divided in segments similar to wedges and after hydroentanglement this structure changes with the mechanical action of incident water jets leading to the separation of the splitting fibres in filaments and to an increase in the web entanglement (Anand *et al.*, 2006). The level of separation of the filaments is not always the same because it depends on a number of factors such as the power of the jet, the density of the web and the proximity to the outer surface.

Summarising, the investigation of the reverse face provided interesting data regarding the different fibrous components that characterise the materials. By having access to this face it would be possible to effectively identify the type of leather. The SY material could be easily recognised thanks to its macroscopic appearance, though the use of SEM or stereo-microscopy would be required to distinguish between the TL and E-Leather® substrates.

4.3 Structural Analysis

The mechanical properties of leather are strictly dependent on its structure, therefore the analysis of cross-section of the leather and manmade materials under study was carried out in order to gain a better understanding of the level of organisation within the substrate.

4.3.1 Investigation of Materials Cross-section

Cross-sections of leather-related materials have often been used to distinguish between natural and synthetic leathers (Sudha *et al.*, 2009). However, the use of the cross-sectional analysis to differentiate between composite and non-composite materials is not documented in literature.

In this study the samples were not subject to resin inclusion treatments prior to examination for three main reasons. First of all, few cultural heritage institutions possesses its own microtome and therefore its use in this research would have reduced the applicability of the method to those few museums that own one. In contrast, a greater number of institutions have access to microscopes and they could use this research tool to benchmark their samples with those investigated here. Secondly, microscopy may be used to evaluate thickness of coated substrates. Normally tests like thickness evaluations conducted with standard methods require a certain load to be applied to the sample (British Standards Institution, 2015) because factors like fibres compactness and density have an impact on this property. However standard procedures are utilised to accommodate the needs of specific materials and, in this case, the research comprised different substrates that would require different standards. It would have been counterproductive to test sample thicknesses applying a standard that only applies to one material, because that would provide reliable answers for that substrate alone. Therefore, it was decided to avoid the use of the standards and to evaluate the thickness using visual methods, without the application of a load. Thirdly, in this work measuring the thickness of the samples has a guidance use that is valid and needed exclusively within the boundaries of this research method. In fact, as explained in the two previous points, this research aims at being applied in various contexts where tools or instruments are not always available and whose primary focus is not the technical characterisation of the material from an industrial point of view. Thus the description of thickness is essential to provide an indication of the general characteristics of the material but it must not be compared to the measurement carried out using standard methods (even if in some cases results could overlap). Thickness of each layer was calculated based on microscopy image analysis at a magnification x40 for the fibrous layer and x80 for the coating.

The structure of the TL material (Figure 4-16 and Figure 4-17) can be divided in two main parts, the coating and the fibrous layer, with the second component itself divided in two sub-layers (grain and corium). The mean thickness of the coating was 31 μm (± 11 μm, SD of 10 points), whilst the grain measured 323 μm (± 74 μm, SD) and corium 793 μm (± 73 μm, SD).

Cross-sectional observations are crucial for the animal skin identification in those cases where finishing coatings have covered the natural pores of the top surface. In those situations fibre direction, layering and level of compactness provide indications regarding the animal the skin was derived from (Harris, 2014). As it is evident in the images presented above below (from Figure 4-16 to Figure 4-19), and previously also in Figure 4-11, the coating applied as a protective layer was too thick and opaque to allow direct observations of the grain top surface. Therefore other characteristics were necessary in this case to assess the animal type. The clear distinction between fibre direction and compactness in grain and corium layers, together with the absence of hollow interlayers and of long hair follicles typical of certain animal skins, confirmed that the material under study was a cattle leather.

The finishing layer adhered consistently to the leather grain and discontinuities such as bubbles or hollows were not visible. Moreover, the thickness of the finishing layer was not clearly constituted by two or more sub-layers, a characteristic that would suggest a reverse coating finishing (Meyer *et al.*, 2008) or flame lamination. These observations supported the hypothesis of a spray coating treatment.

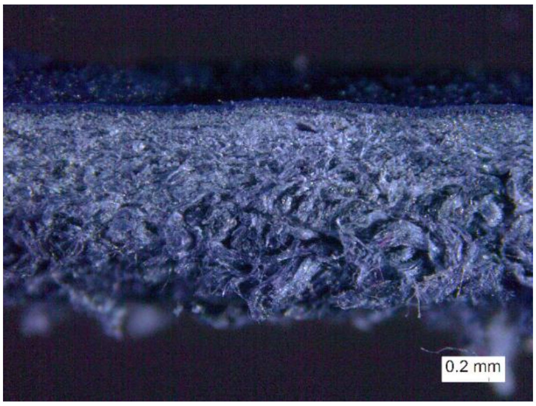


Figure 4-16: Stereo-microscopic imaging of TL cross-section at magnification 40x

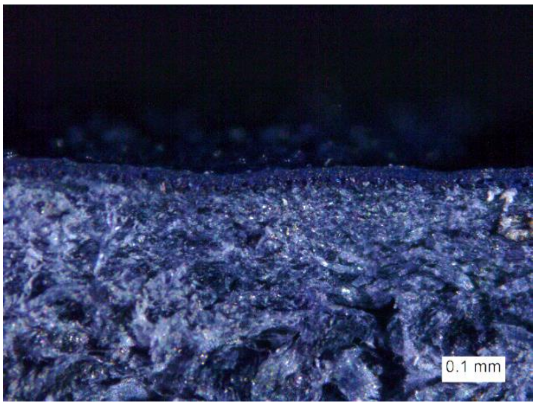


Figure 4-17: Stereo-microscopic imaging of TL cross-section at magnification 80x

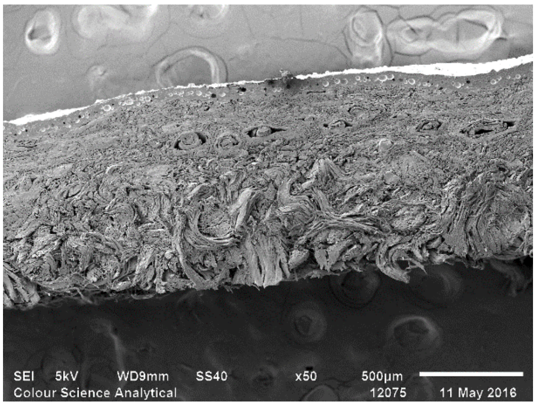


Figure 4-18: SEM cross-section of TL at magnification 50x

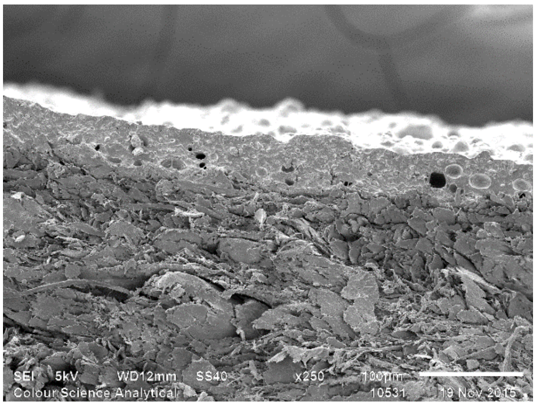


Figure 4-19: SEM cross-section of TL at magnification 250x

The same considerations reported for stereo-microscope observations were also valid for the SEM images in Figure 4-18 and Figure 4-19. In addition, these scans permitted the visualisation in a more definitive way of the direction of leather fibres. The grain was made of fibres that run almost parallel to the skin surface, whilst the corium presented gradually more perpendicular bundles. Likewise, micrographs indicated the presence of arteries and blood vessels (circular shapes) within the dense grain structure. These characteristics, when found in sample taken from items of uncertain animal or manmade origin, enable the researcher to identify the presence of natural leather.

The SY material examined (from Figure 4-20 to Figure 4-23) had a structure divided in two parts, but in this case the coating layer was subdivided in to two sub-layers. The evaluation of mean thickness was particularly difficult for this material because of the presence of loose fibres that constituted the fibrous substrate. TL was characterised by a compact structure that allowed clean cuts and straightforward measurements, but this was not the case for SY. The fibrous layer, as already pointed out in Figure 4-11, was made of a knitted fabric and was in direct contact with the coating. The coating, in turn, was composed of a darker, thin outer layer at the surface interface, in contact with the environment, and a slightly thicker and clearer layer that was in contact with the fabric. The thicknesses measured after knife cutting and conditioning were 225 µm (± 15 µm, SD of 10 points) for the whole coating and 3066 µm (± 160 µm, SD) for the fibrous. The two coating sub-layers, top and bottom, measured 19 µm (± 3 µm, SD) and 205 µm (± 15 µm, SD), respectively.

Figure 4-20: Stereo-microscopic imaging of SY cross-section at magnification 20x

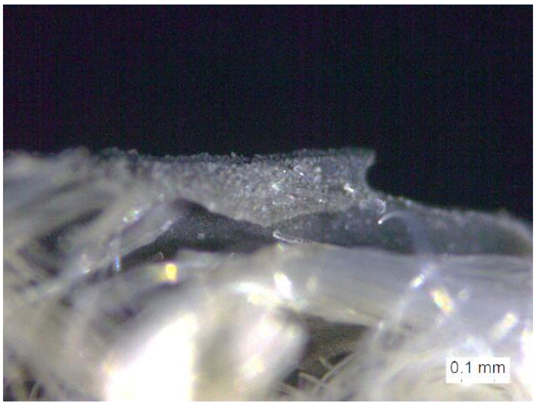


Figure 4-21: Stereo-microscopic imaging of SY cross-section at magnification 80x

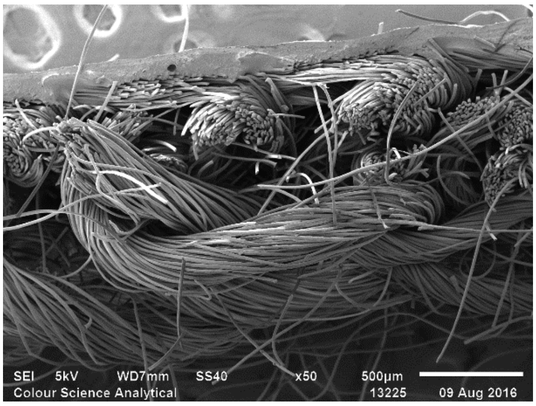


Figure 4-22: SEM cross-section of SY at magnification 50x

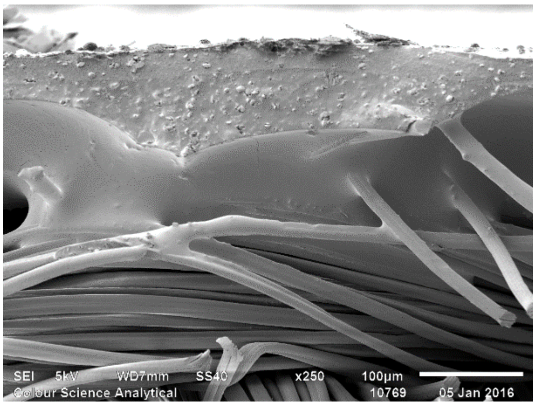


Figure 4-23: SEM cross-section of SY at magnification 250x

Examination of the stereo-microscope images (Figure 4-20 and Figure 4-21) indicated that the coating was not regularly joined to the fabric and that a limited number of contact points were responsible for the adhesion between the two components. The bottom sub-layer of the coating appeared spongier than the top layer, probably to guarantee the adhesion of the two layers it connected. The different morphological structure of the two sub-layers, emphasised in Figure 4-21 and Figure 4-23, suggested a difference in the chemical composition. All these considerations are in line with the hypothesis of a transfer coating treatment, often carried out on knitted fabrics because it does not stress the substrate as much as the direct coating method would do (Sen, 2007).

The EL2 material presented two similarities with the TL and SY samples. Firstly the presence of interwoven leather fibres in the fibrous layer made the fibrous substrate similar to the TL material and secondly the neat division between fibrous and coated layers resembled the previous materials and SY in particular. Despite these similarities a number of distinct differences characterised the EL2 material.

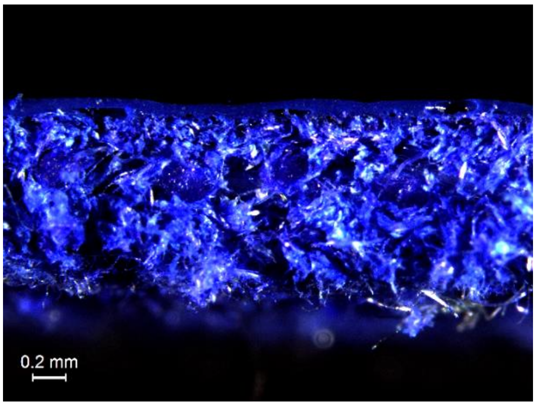


Figure 4-24: Stereo-microscopic imaging of EL2 cross-section at magnification 40x

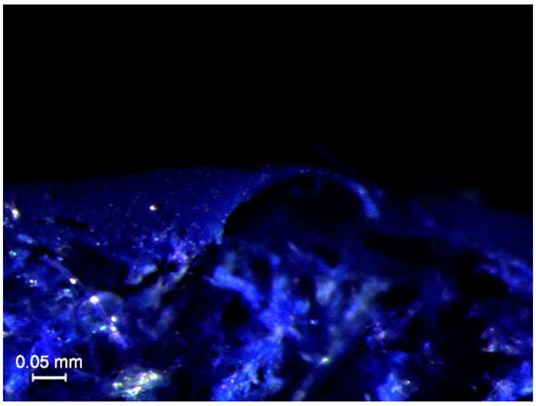


Figure 4-25: Stereo-microscopic imaging of EL2 cross-section at magnification 80x

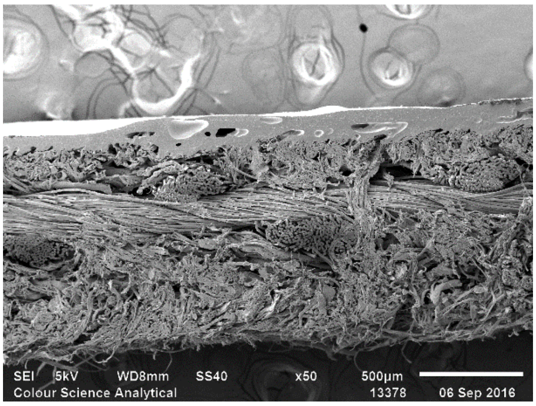


Figure 4-26: SEM cross-section of EL2 at magnification 50x

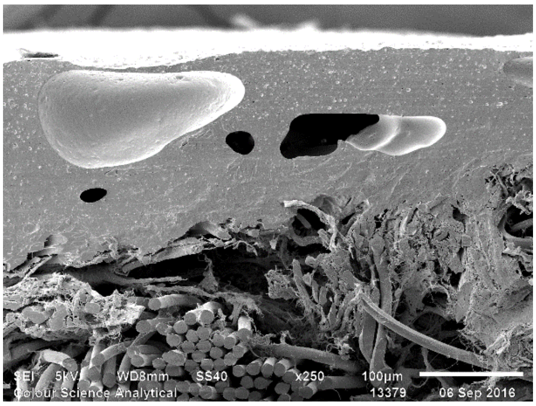


Figure 4-27: SEM cross-section of EL2 at magnification 250x

A fabric core was interposed between two layers of leather plus the synthetic fibres (HE webs) and it was clearly differentiated in Figure 4-24 and Figure 4-26 thanks to the presence of regularly spaced synthetic fibres agglomerates in two directions perpendicular to each other. The structure of a woven fabric was hence recognised, a characteristic that could be used in future for identification purposes. The thickness of the coating layer was 102 µm (± 3 µm, SD of 10 points), whilst the fibrous layer was 786 µm (± 10 µm, SD) and the two layers of HE webs, top and bottom, measured 285 µm (± 9 µm, SD) and 501 µm (± 7 µm, SD), respectively.

The coating layer in the EL2 material (Figure 4-25) was not as intimately joined to the fibrous layer as it was TL coating and was not as distinct (Figure 4-27) as with the SY coating. The process used to make E-Leather coat, transfer coating (Hartung, 2014), could be responsible for the adhesion problems. Dust (1985) described the faults that can be observed after the transfer coating process and some of them define the features found in E-Leather® such as the presence of blisters and the uneven adhesion between fibrous and coating layer. These two characteristics are typical of different phases of the transfer coating process, i.e. the formation of the coating outer layer and the formation of the tie coat (Durst, 1985).

Figure 4-28 is an SEM micrograph image digitally edited to illustrate the various staples present in EL2 and the level of separation of the splittable fibre filaments (pink). As pointed out in the previous paragraph (4.2.2) both melting and splittable fibres are made of polymeric materials specially engineered for the required application.

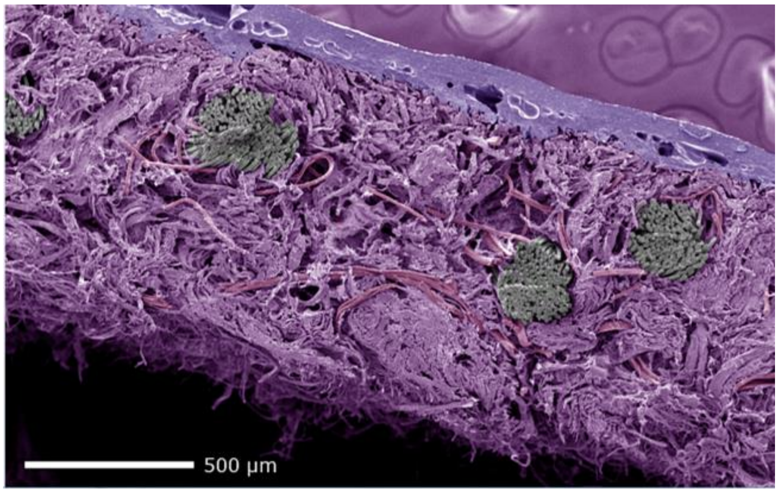


Figure 4-28: SEM micrograph of EL2 cross-section showing leather and synthetic fibres (purple and pink, respectively), woven core (green) and coated layer (purple blue)

The E-Leather® woven core was surrounded by leather bundles, single leather filaments and synthetic fibres (Figure 4-29). This interaction between the various elements was due to the action of hydroentanglement jets that impact with fibres on the outer part and push them into the web.

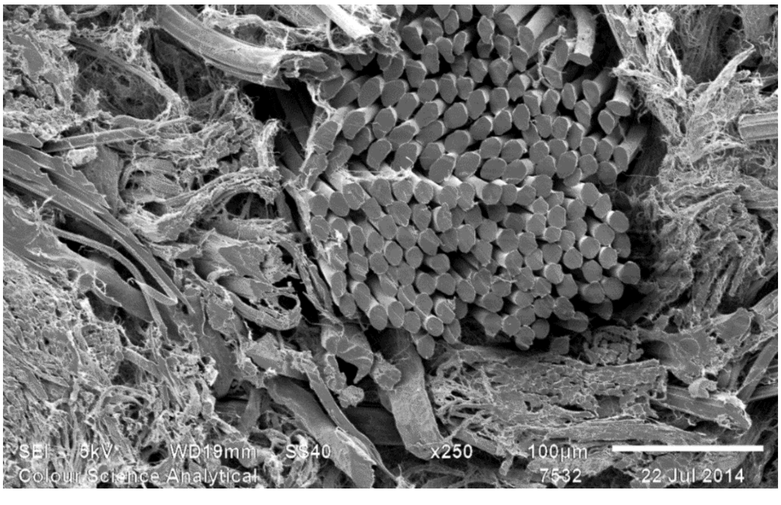


Figure 4-29: SEM micrograph of EL2 cross-section with incompletely separated bicomponent splittable fibres (left side)

Many of the aspects pointed out during the observation of EL2 cross-section were also valid for the EL3 material. The general structure and distribution of the layers, both fibrous and coating, was evident and repeated in both cases.

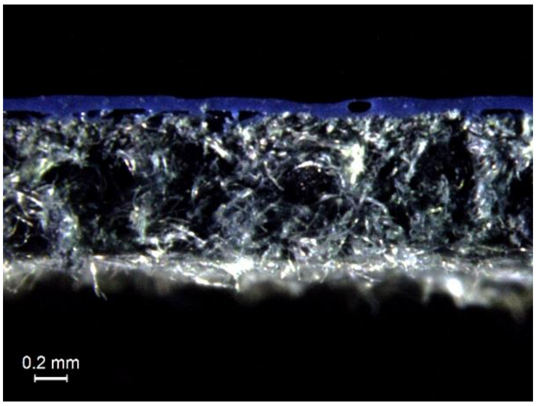


Figure 4-30: Stereo-microscopic imaging of EL3 cross-section at magnification 40x

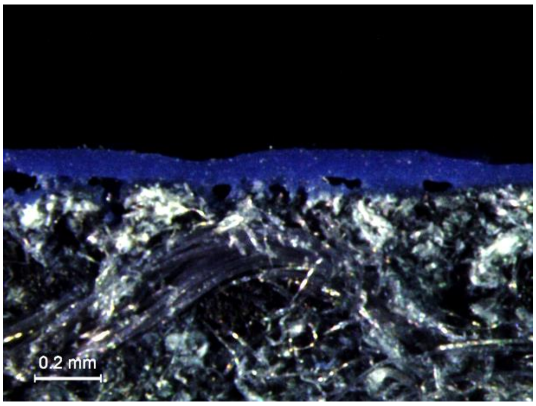


Figure 4-31: Stereo-microscopic imaging of EL3 cross-section at magnification 80x

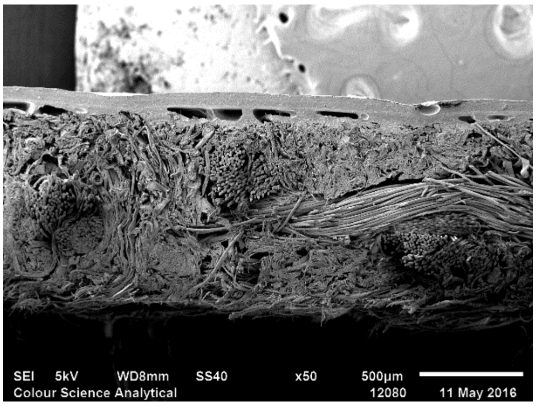


Figure 4-32: SEM cross-section of EL3 at magnification 50x

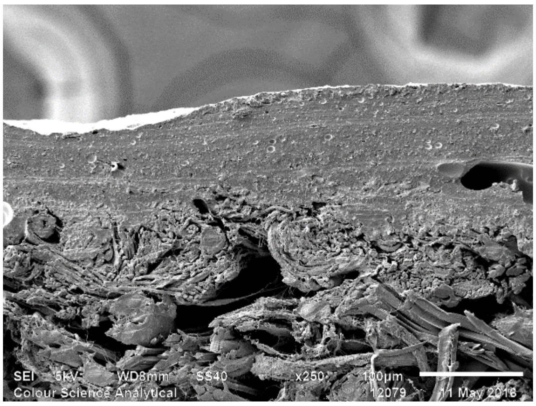


Figure 4-33: SEM cross-section of EL3 at magnification 250x

Two HE webs with an interposed fabric core constituted the fibrous layer, whilst the coating was made of an apparently continuous coating. However, EL3 also had its coating applied through transfer coating and therefore it is expected that a number of sub-layers are actually forming the top surface. Measurements conducted on the different layers showed that EL3 coating was 90 μm (± 3 μm, SD of 10 points) and its fibrous layer was 790 μm (± 92 μm, SD). The top part of the fibrous layer measured 352 μm (± 96 μm, SD) whilst the bottom part 438 μm (± 64 μm, SD). Apart for the coating layer, the other parts of the material showed a high level of variation which was attributed to the uneven thickness of the fibrous layer and a much more consistent thickness of the coating.

In the EL3 sample the tie coat, which connects the fibrous substrate with the outer cover, did not show uniform bonding throughout the entire cross-section (from Figure 4-30 to Figure 4-32). In fact, the level of structural gaps between the two layers in EL3 was much higher than the number of cavities found in EL2. The presence of dust or contaminants on the surface could potentially lead to failures during the adhesion of the tie coat to the fibrous layer (Durst, 1985; Gutoff and Cohen, 2006). Residual particles or solvents derived from procedures carried out before the coating application are likely to be responsible for this phenomenon.

Several conclusions stemmed from the visual comparisons of all the sample cross-sections. The coating versus fibrous layer ratio provided an indication of the amount of polymer used to obtain the finished material. Equation 4-1 was used to calculate the percentage of coating against the fibrous layer.

$$\text{Ratio} = \frac{\text{coating thickness}}{\text{fibrous layer thickness}} \times 100 \tag{4-1 }$$

The TL sample was found to be the substrate with the lower percentage of coating (2.8 %), followed by the SY (7.3 %), EL3 (11.3 %) and finally EL2 samples (13 %). This was possibly due to the greater processing confidence in the natural leather properties that allows producers to apply the coating mainly to protect the surface or add unconventional features (Yi *et al.*, 2010). A different situation was evident for the SY knitted fabric, which despite its elasticity and strength lacks properties typical of leather and its distinctive aesthetic appeal. Thus embossing patterns that replicate the finished leather surface has become a common procedure (Zürbig *et al.*, 2015). Finally with the EL2 and EL3 materials the nonwoven fibrous layers needs to be reinforced or coated in order to provide strength. In E-Leather® the coating has this dual role, aesthetic and functional, and this explained the reason why its percentage was higher than in the TL and SY materials.

As previously reported, the SY product had a looser, ill-defined structure that complicated the measurement of both fibrous layer and coating and could have introduced an error in the measurement. The fact of using the ratio should minimise this variation, even if care must always be taken when measuring this type of samples. Furthermore, comparing the thickness of EL3 with the EL2 material the former it was noticeably thinner than the latter. However this result must be carefully considered because of the standard deviation values.

In summary, stereo-microscopy and SEM were indispensable tools to assess microscopic aspects of the materials, such as the layer structure and direction of fibres. Both techniques allowed the identification of the material under investigation but only SEM clearly provided evidence of the different staple fibres. Measurements of each layer thicknesses were performed and the ratio of coating to fibrous layer calculated as a percentage value. Despite these measurements being potentially used as a guide for museum users, their future utility is still limited. While the ratio could be used to compare different materials (e.g. TL and EL2), it did not provide values sufficiently distinct to discriminate between similar materials such as EL2 and EL3.

4.4 Chemical Characterisation

Elemental and molecular composition are important to identify the main components and additives in coatings and fibrous layer. EDX and ATR-FTIR were conducted to characterise the each coating and fibrous substrate.

4.4.1 Elemental Analysis

The elemental composition of all leather-related materials was determined by means of EDX spectroscopy conducted in regions of the samples identified during SEM investigations. Spectra were acquired in two different coating configurations (see Chapter 3 for details), allowing the identification of elements on both the top layer and bulk of the coating.

Table 4-1 reports the mean percentage values (in weight) of each element detected from the spectroscopy device in each coating sample. The data were recorder after selecting areas of interest both in the coating and the fibrous layer. Mean values and standard deviation of each layer were calculated and are reported below. Considerations regarding the detection limits, in particular in the case of light elements that cannot be detected, will be also be discussed.

Four elements were found in the coatings of all samples: carbon, oxygen, aluminium and silicon. The first two elements were related to the organic fraction of both the polymeric coating of synthetic leathers and the finishing surface of natural leather. The standard deviation of the results demonstrated a limited composition variability within each sample, with the SY product showing the highest level of standard deviations: 1.95 % for C and 2.10 % for O against values lower than 1.90 % for all the other materials.

The aluminium content was attributed to the presence of inorganic pigments such as artificial ultramarine blue, a sodium alumino sulfosilicate ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$), already well-known before the development of its artificial surrogate (Guilmin, 1998). Its presence in E-Leather samples was also confirmed by a company spokesperson (O'Keefe, 2015). Also the observed silicon was partly attributed to the presence of ultramarine pigment especially in TL, EL2 and EL3 materials. One of the problems of pigments like ultramarine blue is its lightfastness, which has often limited its use outdoor (Considine, 2010). This aspect can become a problem in the case of materials used for the aviation market that, even if used indoor, are often exposed to the light passing through aircraft windows. Along with representing the ultramarine pigment, and particularly in the case of SY, silicon was also assigned to the presence of finishing agents to make coatings water-repellent (Fung, 2002b). This was confirmed after comparing the EDX results with the EDX mapping reported in Figure 4-34, where the distribution of the silicone throughout the top layer surface of SY coating was observed.

Titanium was another element associated with the coating coloration because it is often added in the form of titanium dioxide (TiO_2) as a white pigment (Harris, 1999). The oxide is also commonly used as a filler for polymeric films (Fung, 2002b), however researchers have commented that due to the reactivity of the titanium dioxide it can catalyse a number of degradative reactions (Harris, 1999). This reactivity can become important in the next step of the research, that is during the evaluation of samples ageing.

The bromine content corresponded to the flame retardant additives incorporated into the material in order to meet regulations for certain applications, such as the flame retardancy in the aviation market (European Aviation Safety Agency, 2003; Guillaume *et al.*, 2008). Once in the aircraft, the coating layer represents the part of the seat most exposed to the airplane environment and thus the most vulnerable in the event of a fire. Therefore, manufacturers introduce flame retardants into the coating to prevent the surface combustion and to protect the underlying fibrous layer, as in the case of TL and SY materials. In the TL product the bromine content had a lower and negative value (-4.19 % ± 0.64 %) compared with the levels found in the SY material (14.77 % ± 4.11 %). The reason for the spurious negative result for the bromine signal was not totally understood and needs to be further investigated. However, this phenomenon was only noticed when the relative amounts of bromine and aluminium were close and, as a consequence, it is likely that the software was not able to discriminate between the overlapping elemental signals.

Both the TL and SY materials contained further elements that are different in abundance and function. TL contained chlorine that was likely to be associated with finishing treatments to increase flame retardant properties of the material. Chlorinated paraffins are a class of compound with many applications in the leather industry, for example as finishing or fat liquoring product (International Organisation for Standardization, 2015).

	C	**SD**	**O**	**SD**	**Na**	**SD**	**Al**	**SD**	**F**	**SD**	**Si**	**SD**	**Cl**	**SD**	**Br**	**SD**	**Ti**	**SD**	**Fe**	**SD**	**Sb**	**SD**
TL-0hr-coating	66.11	1.73	25.40	1.02	-	-	3.72	0.62	-	-	8.85	2.14	1.35	0.78	-4.19	0.64	-	-	-	-	-	-
SY-0hr-coating	53.08	1.95	16.04	2.10	-	-	3.17	1.83	5.16	2.86	1.30	0.75	-	-	14.77	4.11	2.57	0.95	-	-	6.46	0.47
EL2-0hr-coating	54.67	0.25	31.62	1.56	2.05	0.17	3.09	0.37	-	-	5.35	0.85	-	-	-	-	3.22	0.29	-	-	-	-
EL3-0hr-coating	57.81	0.96	31.34	0.39	1.53	0.15	3.42	0.21	-	-	3.74	0.21	-	-	-	-	1.84	0.14	1.14	0.15	-	-

Table 4-1: EDX results showing the percentage in weight of elements found in the coating of leather-related materials

	C	**SD**	**N**	**SD**	**O**	**SD**	**Al**	**SD**	**Cl**	**SD**	**Cr**	**SD**	**K**	**SD**	**Br**	**SD**	**Ca**	**SD**
TL-0hr-fibres	51.90	8.47	18.15	10.48	27.34	1.67	2.14	1.52	-	-	-	-	-	-	5.44	1.33	0.62	0.36
SY-0hr-fibres	80.07	2.69	-	-	19.93	2.69	-	-	-	-	-	-	-	-	-	-	-	-
EL2-0hr-fibres	55.82	7.83	16.33	9.43	32.41	1.51	-	-	0.70	0.21	5.63	0.51	-	-	-	-	-	-
EL3-0hr-fibres	48.36	1.05	12.24	0.60	21.84	0.50	-	-	0.22	0.01	1.88	0.29	0.23	0.13	15.35	1.63	-	-

Table 4-2: EDX results showing the percentage in weight of elements found in the fibrous layer of leather-related materials

In the SY product antimony was detected (6.46 % ± 0.47 %) and, thanks to EDX mapping (Figure 4-34), it was possible to confirm that its presence was dominant in the layer where also bromine was distributed. They are the only distinct elements present in the SY coating bottom layer together with aluminium. The use of antimony as synergist with flame retardants that contain halogen compounds has been widely documented (Liepins and Pearce, 1976; Weil and Levchik, 2009) and in recent years has been re-examined and revised because of increasing health concerns (Liang *et al.*, 2013).

EDX mapping conducted on SY coating also allowed the location of fluorine, silicon and titanium (see above for description) to be confirmed mainly in the top layer. Fluorine is generally used as a powdered fluoropolymer and it acts as a flame inhibitor (Weil and Levchik, 2009). Due its powdery state and being only distributed in the top layer, fluorine had a relatively high SD value (5.16 % ± 2.86%) indicating a concentration variation.

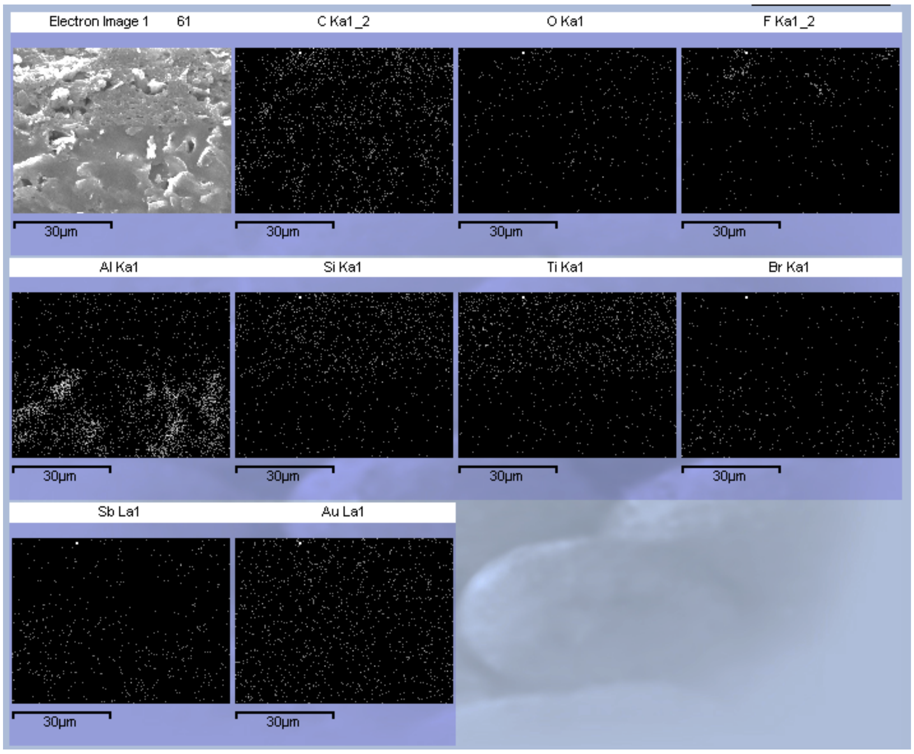


Figure 4-34: EDX mapping of SY coating at the interface between outer and inner layer. Mag. x2000. Area of interest in the top-left rectangle.

The EL2 and EL3 products showed the exact same composition, apart for the fact that iron was detected in EL3 (1.14 % ± 0.15 %). As in the case of aluminium and silicon, the iron peak was assigned to a pigment, in particular an iron oxide (Fe_3O_4) that can be used to confer a black colour.

It is interesting to note that no bromine was detected in the coating of EL3, the material sold by E-Leather for aircraft seats. This highlighted the different approaches that companies can adopt when dealing with flame retardants, because the TL and SY samples contained the additive in the coating, but EL3 did not.

As already observed in the scans showed in Figure 4-12, a number of spheres of different size were visible on the coating of the TL and SY products. EDX mapping was conducted on the top coating of the two materials in order to obtain a better understanding of the beads composition. The results of the mapping at different magnifications are shown, respectively, in Figure 4-35 (x75) and Figure 4-36 (x750). The analysis of the beads composition was essential to understand why the company decided to add them. Many reasons can lead companies to add beads, which are often characterised by different properties, and their composition can help to understand the purpose that wanted to be achieved. The elemental composition became clear after comparing the original image, on the top-left corner, with the ones showing the signals for each element. Despite fluorine, aluminium, silicon, chlorine, calcium, titanium and bromine all being detected, only two elements appeared to be associated with the beads whilst the other signals came from the top coating: carbon and oxygen.

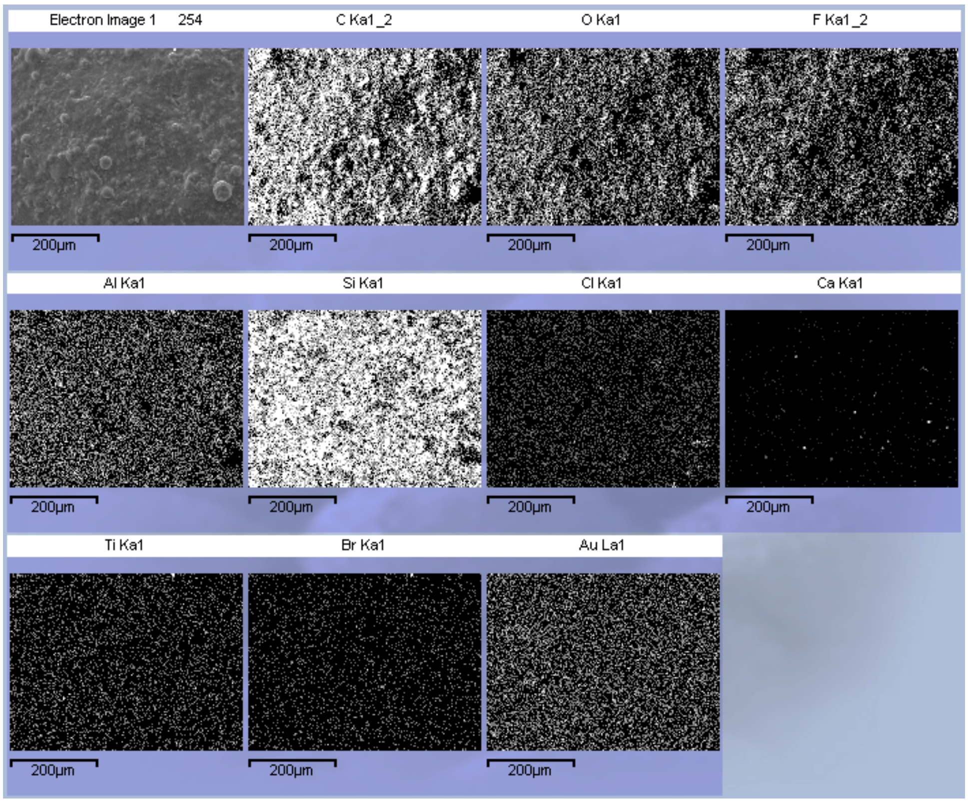


Figure 4-35: EDX mapping of TL coating Mag. x75. Area of interest in the top-left rectangle.

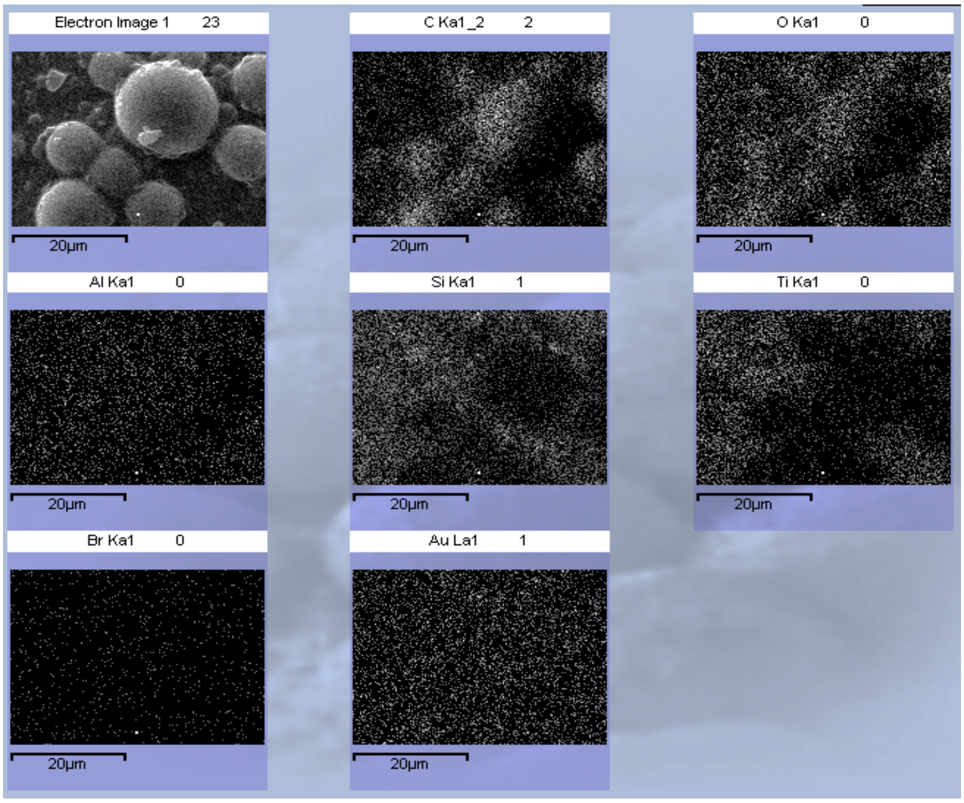


Figure 4-36: EDX mapping of SY coating Mag. x750. Area of interest in the top-left rectangle.

The presence of two elements alone in association with the spherical structures suggested the use of a polymer. Even if this observation helped to restrict the field, there was a variety of compounds that enter in the polymer category that could be used with different functions. The most logical possibility, compatible with the final application of the coated material, was that these beads acted as thermal regulators, increasing users comfort or reducing phenomena potentially detrimental for the material (Onder and Sarier, 2015). Phase change materials (PCM) are typical products used for thermal regulation purposes, and they comprise a broad range of natural and synthetic polymers carefully selected and developed to obtain specific characteristics (Rathod and Banerjee, 2013). Aside from being used in smart textiles and car seats (Mondal, 2008), the application of PCM in the leather industry has been documented (Izzo Renzi *et al.*, 2010), endorsing the hypothesis of the thermal regulation function. Further research will be necessary in order to confirm this hypothesis.

Before concluding this analysis of the coating, it is interesting to note the abundance of chemical elements found in the SY sample. This material during the morphological and structural analysis presented the least complex structure but in contrast the coating composition appeared to be heterogeneous in nature. This was ascribed to the high level of technological advancement required to textile products in sectors like aviation and other transport means. Such an observation become even more intriguing when the data of the fibrous layers were observed Table 4-2.

In terms of fibrous layer, the situation shown in Table 4-2 was rather different from the composition observed in Table 4-1. Here two elements, that is carbon and oxygen, were the only ones to be present in any of the leather-related materials. In particular the SY product, which exhibited the most complex coating layer composition, showed a simple two elements composition. Hydrogen cannot be detected by means of EDX spectroscopy (see limitations below), yet the use of ATR-FTIR discussed in paragraph 4.4.2 will confirm its presence thanks to the absorptions of specific molecular groups. The organic nature of the fibres will be discussed in the next paragraph.

Nitrogen, which is an essential part of the leather collagen because of its protein structure, was detected in the remaining materials in different amounts: 18.15 % ± 10.48 % in TL, 16.33 % ± 9.43 % in EL2 and 12.24 % ± 0.60 % in EL3. The detection of nitrogen, however, is not an easy analysis and it becomes clear looking at the SD values of TL and EL2. This lack of consistency became apparent when the test was carried out for longer periods of time when the number of scans collected was increased. As a consequence, it was decided to reduce the number of scans to a maximum of 30 in the following part of the study (during ageing procedures), in order to avoid the appearance of misleading nitrogen signals that would have compromised the test.

The EL2 and EL3 products showed EDX signals attributed to chromium, the tanning agent used to produce the intermediate "wet blue" that E-Leather recycles in order to obtain the fibres for its HE webs. The amounts of chromium in the two materials were different, 5.63 % ± 0.51 % and 1.88 % ± 0.29 %, respectively. This was probably due to the EL2 sample not containing any flame retardant, thus the weight percentage normally associated to bromine in EL3 was re-distributed among EL2 elements. Detection of chromium peaks was also expected in the TL sample as a consequence of what was initially stated from the provider. However this evidence was not confirmed and another element that could potentially identify the tanning was found. Aluminium was detected (2.14 % ± 1.52 %) and its peaks attributed to the use of an aluminium tanning agent. Even if this hypothesis is likely to be correct, there are other types of tannings available that would not be detectable by EDX (Falcão and Araújo, 2013). This unexpected finding pointed out the importance of effectively characterising modern materials and of checking any "reliable" information provided with items and materials, not only when they are part of a museum collection but also when they are provided by industrial partners and their complete manufacturing process is not part of a well-documented protocol. In fact, if the TL product was to be used in conditions of high temperature and in presence of moderate humidity the material would be expected to degrade faster than chrome-tanned leather (Covington, 2009).

As explained earlier both the TL and SY materials contained flame retardants in the coating layers, but it was only the former that also contained FR agents in the fibrous layer. Bromine in the TL fibrous layer (5.44 % ± 1.33 %) was not evenly distributed, indicating an equally uneven penetration of the flame retardant in the bulk of the collagenous matrix. Also associated with the flame retardant (bromine content 15.35 % ± 1.63 %) is the presence of limited amounts of potassium (0.23 % ± 0.13 %) in EL3; this observation was also confirmed by a company's spokesperson (O'Keefe, 2015). The presence of bromine in the EL3 fibrous layer but not in its coating confirmed that a different approach was used by E-Leather in designing their product for aircraft applications.

Two other elements were also found in the samples but in minimum quantities. Chlorine was detected in both the EL2 and EL3 samples and it might be due to three reasons: the first was the detection in leather fibres of residual calcium chloride used during tannery operations before arriving to E-Leather, the second was the presence of chlorine in the water used during the hydroentanglement procedure, and the third was the use of chlorinated paraffins as fatliquoring agents. The second element found in the TL sample was calcium and its presence could be due, again, to imperfect procedures during tannery operations (Covington, 2009).

EDX analysis is a powerful instrument able to detect even small amounts of heavy elements, but the identification of light elements can be challenging. Light elements which are characterised by low photon energy, as nitrogen, are in fact difficult to be detected via EDX (Goldstein *et al.*, 2012) because part of the signal is dispersed while reaching the detector or because their peak overlaps with other peaks (background noise or other elements). This issue can be sometimes overcome in those cases where the concentration of the desired element is high, like in the case of carbon and oxygen, but it is not always possible.

Despite these limitations, EDX allowed to identify elements associated with the flame retardants that could be involved in degradation processes. Thanks to this ability, the technique permitted to easily distinguish between EL2 and EL3.

4.4.2 Molecular Characterisation

ATR-FTIR was used to characterise the molecular structure of the leather-related materials. The depth of penetration of IR radiation is variable and depends on three factors: wavenumber; angle of incidence of IR light within the sample; and the refractive index of both sample and device prism. The light penetration can thus change depending on the type of crystal prism, but the resulting spectra is always referred to as the surface of the sample and not to its internal composition (Shashoua, 2012).

Three spectra were collected for each coating and fibrous layer of the leather-related materials and the average of the three spectra are shown below. Figure 4-37 shows the spectrum of each coating layer.

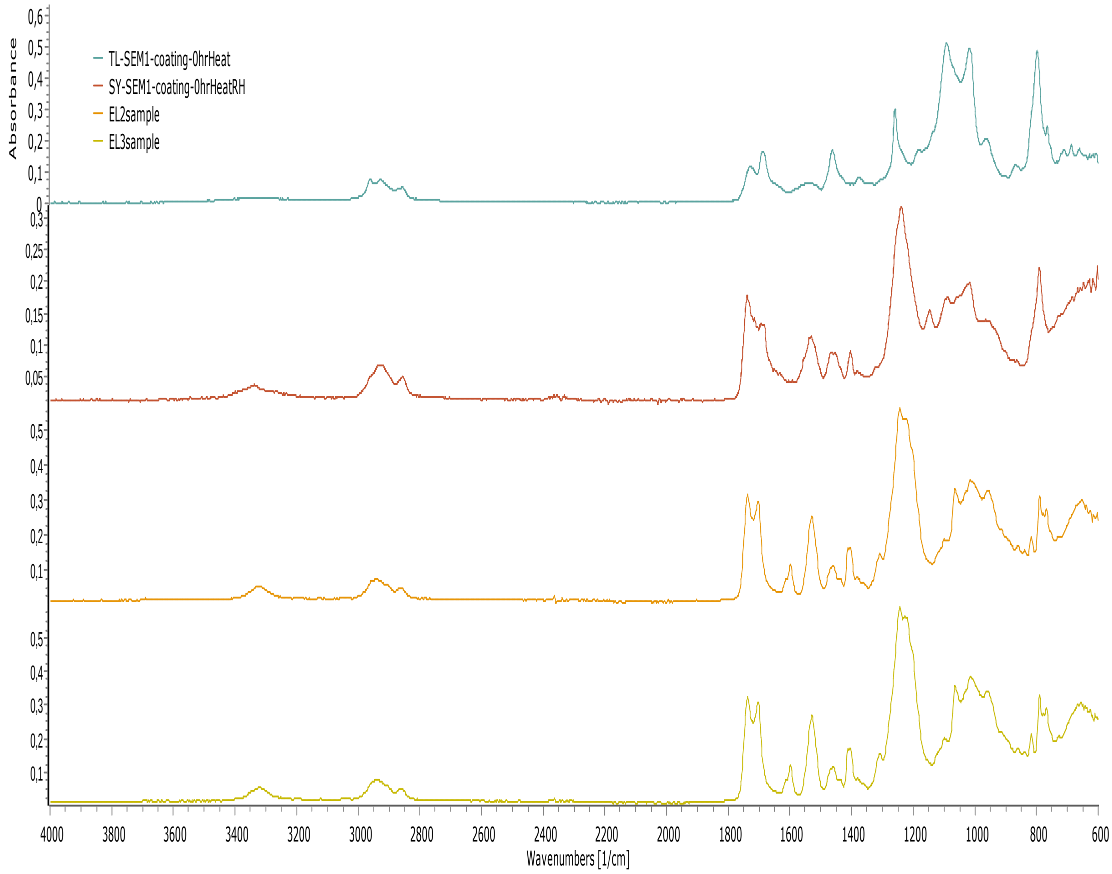


Figure 4-37: FTIR spectra showing absorbance peaks of TL (blue), SY (red), EL2 (orange) and EL3 (yellow) coatings

The close similarity between the spectra of the SY, EL2 and EL3 coatings was immediately clear, in particular the EL2 and EL3 coatings presented almost overlapping spectra. Two regions of interest were identified: the spectral region between 2800 and 3400 cm^{-1} and the region below 1800 cm^{-1}. In the TL sample the wide peak around 3300 cm^{-1} was relatively indistinct and the relative intensities of the peaks in the region 950-1260 cm^{-1} were different to those of the other three samples. Therefore the discussion of the ATR-FTIR results was conducted separately to facilitate the assignment of the absorptions for each coating.

The TL coating spectrum is illustrated in Figure 4-38 and the spectra main peaks are presented in Table 4-3. Two areas of the spectrum were of major interest to assess the molecular groups present on the coating. The first area was comprised between 800 and 1100 cm^{-1} and it contains the strongest peaks of the spectrum, possibly associated with a silicone compound. The strongest signal at 1092 cm^{-1} and 1017 cm^{-1} could indicate the stretching of the Si-O-Si bond, and the associated sharp signals at 798 cm^{-1} and at 1259 cm^{-1} could be assigned to the Si-C and the CH_3 bond typical of the group Si-CH_3 vibrations, respectively.

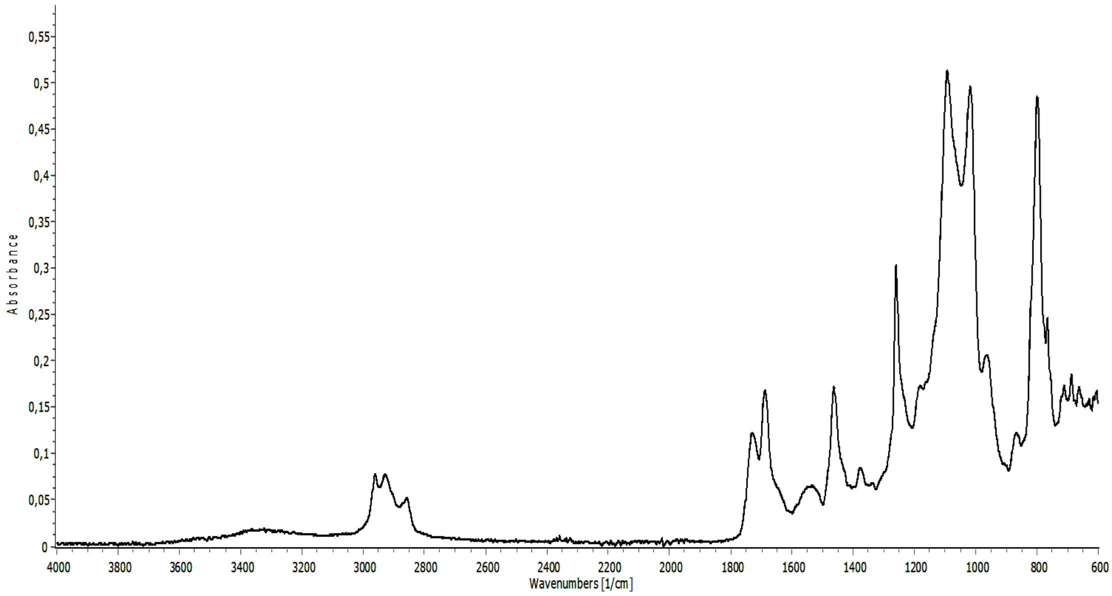


Figure 4-38: FTIR spectrum showing absorbance peaks of TL coating

However, this is not the only possible interpretation of these peaks, because the absorptions at 1092 cm^{-1} and at 1259 cm^{-1} could point out the presence of strong C-O-C absorptions (Paiva *et al.*, 2015). Moreover, the absorption at 798 cm^{-1} was likely to be the same that Defeyt *et al.* (2017) described at 765 cm^{-1} as a marker for the presence of HDI (hexamethylene diisocyanate).

The second area of interest was between 1200 and 1750 cm^{-1} where the absorption of the functional groups C=C-CO-O-R and –CO-NH-C were found. The C-O vibration, identified at 1259 cm^{-1}, was associated with the vibrational absorption at 1728 cm^{-1}, typical of C=O in ester groups. The signal at 1680 cm^{-1} was also attributed to the carboxylic group of an HDI isocyanate. This band has been reported in literature as a distinctive fingerprint absorption of one of the most commonly used diisocyanates for PU formulations (Defeyt *et al.*, 2017).

Further bands of interest were identified between 2800 and 3000 cm^{-1}, typical of CH_2 and CH_3 stretching, and the broad signals around 3320 cm^{-1} were attributed to the stretching of the N-H bond. This observation together with the previous assignments suggest the presence of a PU component in the coating in addition to silicone compounds. Due to the limited penetration of the IR radiation it was difficult to confirm unequivocally if the compound was only present on the sample surface or also within the bulk of the coating. However, it is possible to state that these two components were identified on the TL material.

Peak Location (cm^{-1})	Bond	Type of vibration
3320	N-H	stretching
2960	C-H	asymmetric stretching
2928		
2857	C-H	symmetric stretching
1728	C=O	stretching free
1680	C=O	stretching H-bond
1538	N-H	bending
1462	C-H	bending
1377	C-H	wagging
1259	C-O	stretching
1092	Si-O-Si or C-O-C	stretching
1017	Si-O-Si or C-O-C	stretching
963	C-C	stretching
798	Si-C or C-N-C	stretching

Table 4-3: ATR-FTIR absorption bands, bond and type of vibration found in TL coating

The ATR-FTIR spectrum for the SY coating is presented in Figure 4-39 and the spectra main peaks were assigned in Table 4-4.

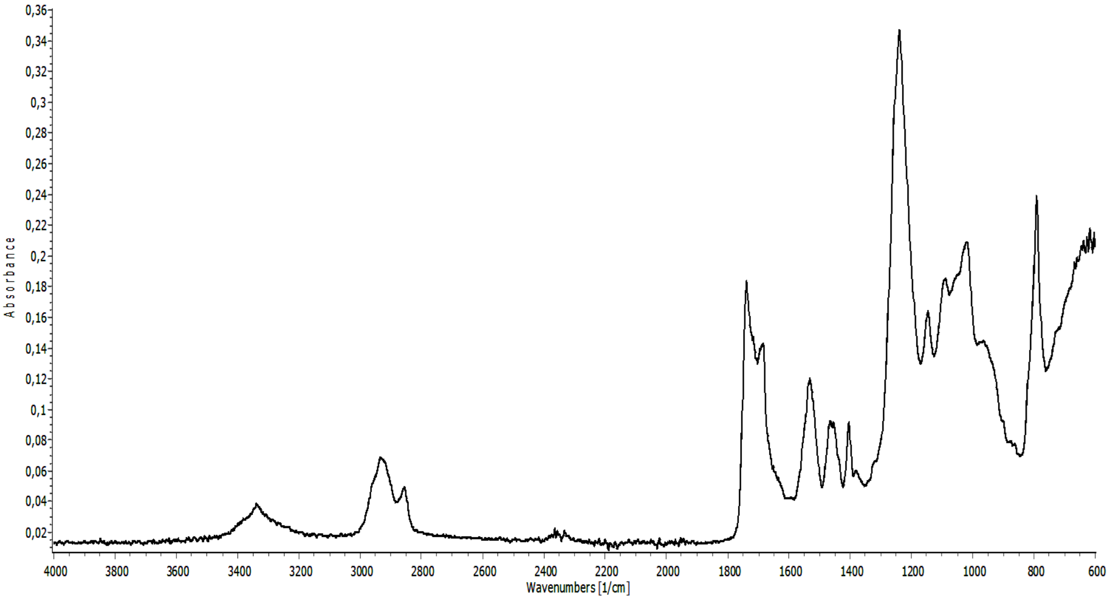


Figure 4-39: ATR-FTIR spectrum showing absorbance peaks of the coated SY material

The PU nature of SY coating became obvious on reviewing the FTIR spectrum. The absorption bands were compared with recent and older published articles on PU coating products used for various application in order to confirm the peak identification (Kaminski and Urban, 1997; Defeyt *et al.*, 2017).

Spectral signals at 3339 and 1531 cm^{-1} indicate the presence of the N-H bond of polyurethane, the former indicating the stretching vibration and the latter the bending of the bond (Chen *et al.*, 2007; van Oosten *et al.*, 2011). The C=O bond associated with the –CO-NH- amide functionality of the molecule was identified due to the absorption at 1683 cm^{-1}. PUs are generated from the reaction of isocyanates and polyols but some characteristics of the original monomers are still recognisable in the final polymer, thus allowing the identification of starting products. At around 1150 and 800 cm^{-1} were the C-N-C asymmetric and symmetric stretching vibrations (at 1146 and 790 cm^{-1}, respectively) related with the isocyanate fraction, in particular the HDI (Defeyt *et al.*, 2017).

Another set of spectral signals were ascribed to the carbamate fraction of the polymer, in particular the vibrations at 1738 and 1238 cm^{-1}, which denoted the presence of C=O and C-O bonds of the carbamate fraction in stretching mode, respectively. The signal at 1238 cm^{-1}, which described the stretching of C-O bond, was the strongest of the spectrum and was characteristic for the presence of a PU (ester) (van Oosten *et al.*, 2011). Peaks between 1100 and 1000 cm^{-1} indicated the presence of the C-O-C group that formed with the reaction of the polyol.

Peak Location (cm^{-1})	**Bond**	**Type of vibration**
3339	N-H	stretching
2934	C-H	asymmetric stretching
2856	C-H	symmetric stretching
1738	C=O	stretching free
1683	C=O	stretching H-bond
1531	N-H	bending
1458	C-H or benzene group	bending
1406	O-H or benzene group	bending
1238	C-O	stretching
1146	C-N-C	asymmetric stretching
1089	C-O-C	asymmetric stretching
1018		
790	C-N-C	stretching
652	C-H	

Table 4-4: ATR-FTIR absorption bands, bond and type of vibration found in the SY coating

These results showed that the TL and SY samples could be identified by collecting ATR-FTIR spectra of their coatings. In fact, the presence of different absorbance bands in the TL spectrum allowed to distinguish the two substrates.

The spectral data of EL2 and EL3 coating are presented in the same figure because their absorbance values overlapped (Figure 4-40) and the main spectral peaks were presented in Table 4-5.

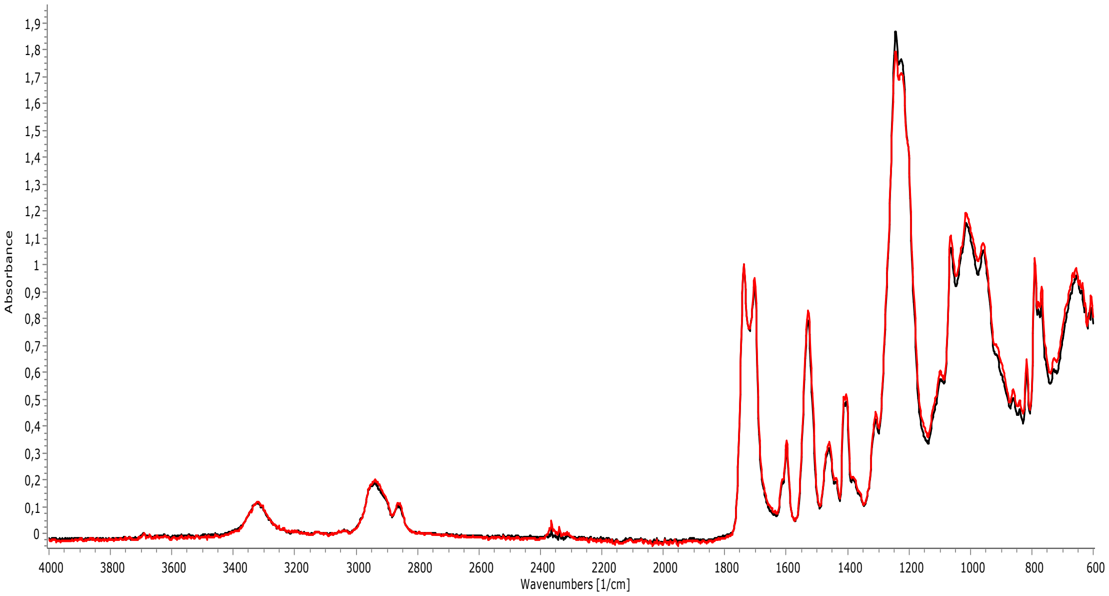


Figure 4-40: ATR-FTIR spectra showing absorbance peaks of the EL2 and EL3 coatings

Initial assessment of the EL2 and EL3 spectra indicated they were almost undistinguishable and they only differed in slight variations in peak intensities. Many absorptions described for SY were also detected in the E-Leather® samples. All the signals associated with the PU macromolecule were found and especially those assigned to the carbamate component, around 1740 cm^{-1} (C=O) and 1240 cm^{-1} (C-O). Again, the salient features of the isocyanate component were recognised in the spectra, particularly the N-H absorption bands at 3332 and 1598 cm^{-1}.

The different intensities in the ester region could be used to distinguish the TL and SY material from the E-Leather substrates. However, it must be noticed that coating formulations change from one manufacturer to the other, thus the TL and SY samples may have different coating compositions compared with other natural or synthetic leathers. For this reason, it would be appropriate to collect the ATR-FTIR spectra of leather-related samples as soon as they enter a collection so that their molecular structure can be studied and compared with that of similar materials. Moreover, it would not be possible to distinguish between EL2 and EL3 because of their identical spectral absorptions.

Peak Location (cm^{-1})	Bond	Type of vibration
3332	N-H	stretching
2939	C-H	asymmetric stretching
2862	C-H	symmetric stretching
1737	C=O	stretching free
1700	C=O	stretching H-bond
1598	N-H	bending
1529	C-H	bending
1460	C-H or benzene group	bending
1405	O-H or benzene group	bending
1244	C-O	stretching
1103	C-O	stretching
1065	C-O-C	asymmetric stretching
1013		
953	C-C	stretching
789	C-N-C	stretching

Table 4-5: ATR-FTIR absorption bands, bond and type of vibration found in EL and EL3 coating

Along with its usefulness in coating analysis ATR-FTIR has been widely used for fibre identification in many fields, from forensic to materials science and, of course, in cultural heritage studies (Richardson *et al.*, 2008; Peets *et al.*, 2017). However, the application of this instrument for characterising composite materials can provide complex results that complicate the substrate understanding. ATR-FTIR was thus used on fibrous layers to demonstrate the ability of the instrumental technique to provide reliable data regarding composite substrates. The spectra obtained from the measurements on all the leather-related materials were then used to assess the possibility of identifying and discriminating the different substrates. Figure 4-41 shows a summary of the absorbance spectra for the TL, SY, EL2 and EL3 fibrous layer.

It was expected that being natural leather, the chemical composition of the TL product would resemble the one of collagenous supports found in literature and that the molecular composition of the SY and E-Leather® products would be more problematic to anticipate. Figure 4-41 presents the ATR-FTIR spectra and highlights the different spectral absorbances of each material.

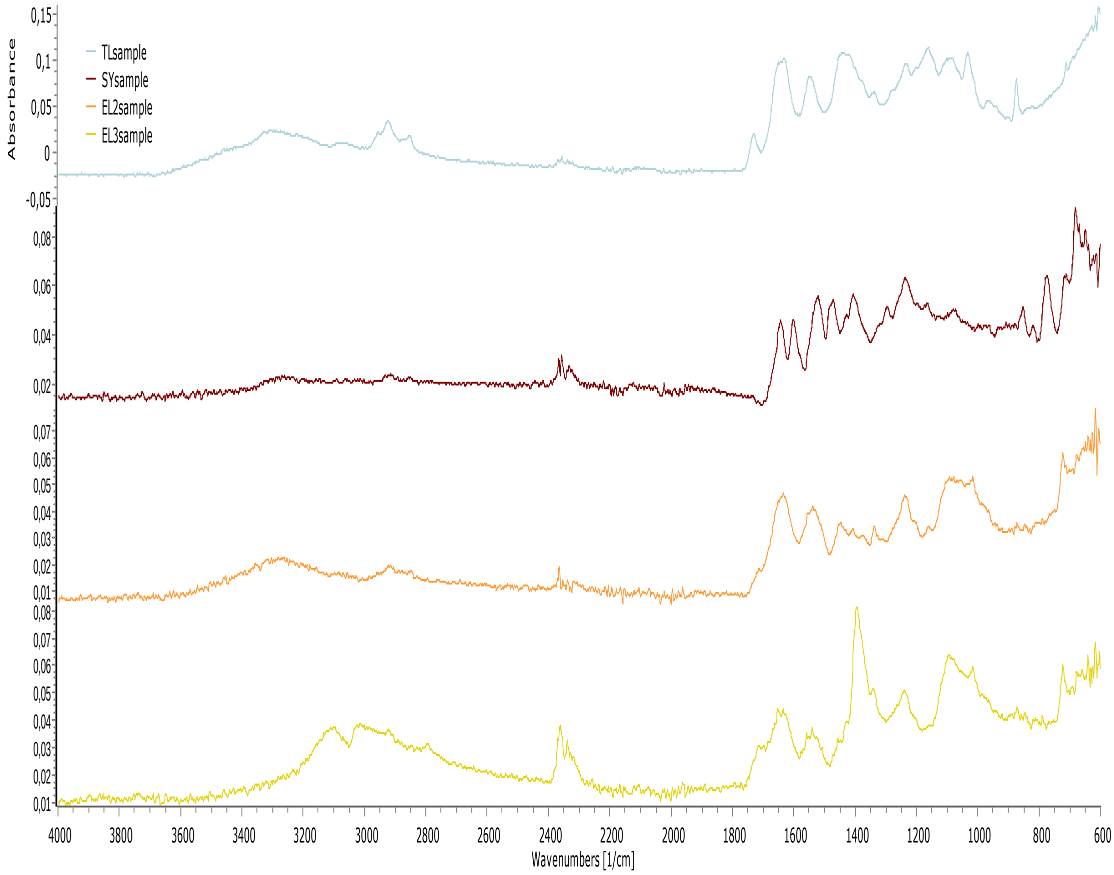


Figure 4-41: FTIR spectra showing absorbance peaks of TL (blue), SY (red), EL2 (orange) and EL3 (yellow) fibrous layer

The absorbance peaks for TL are shown below (Figure 4-42) and the corresponding bands and assignments can be found in Table 4-6.

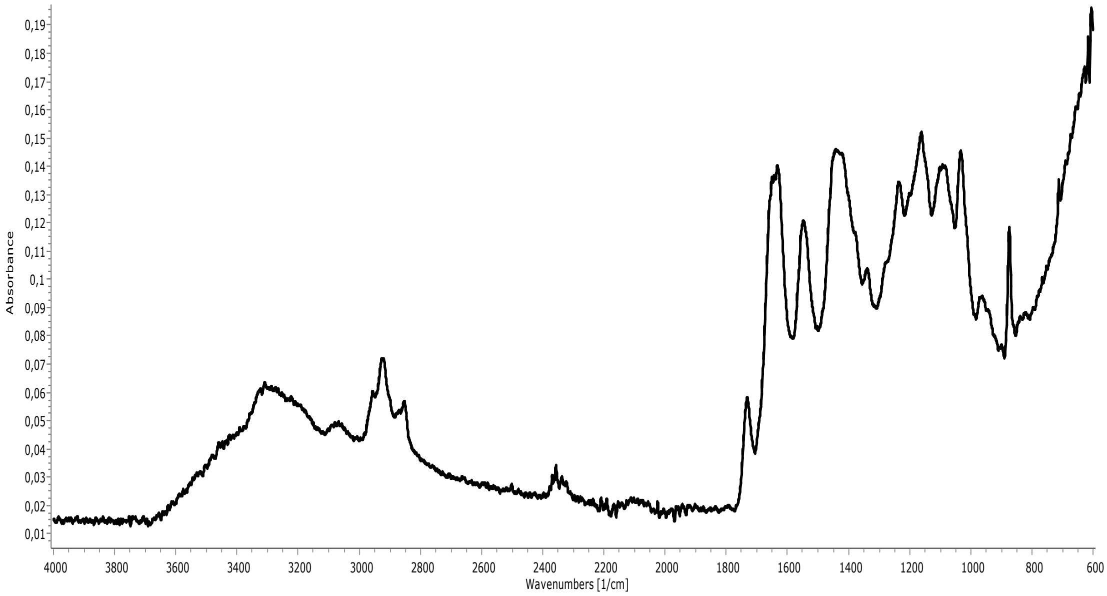


Figure 4-42: ATR-FTIR spectrum showing absorbance peaks of TL fibrous layer

TL exhibited the typical absorption bands of natural leather, in particular cow leather. Bands observed around 3300 and 1550 cm^{-1} were related to the presence of N-H groups of amines and amides, (Shao, 2005). The band of the carbonyl group in the collagen both helical and coiled structures denoted the presence of the amide I vibration (1632 cm^{-1} in Figure 4-42). At 1547 cm^{-1} there was the amide II band, related to the resonance mixing of the N-H bending and C-N stretching vibrations. Research showed that this band tends to change according to conformational variations due to pH and temperature changes (Menderes, 2002), as well as other factors less relevant in this context. The region between 1450 and 1200 cm^{-1} normally contains the signals assigned to the N-H bending and C-N stretching of the amide III group. Around 1340 cm^{-1} was located the peak attributed to the CH_2 group wagging mode, typically associated with proline residues. Bending vibrations at 1279, 1234 and 1203 cm^{-1} were ascribed to the collagen conformation, in agreement with Menderes (2002). Shao (2005) reports that absorptions around 1088 and 1028 cm^{-1} (here at 1091 and 1032 cm^{-1}) are due to C-O group stretching mode and the -C≡S group, respectively.

The difference between cow and other animal leather is normally evident in the region around 1000-1200 cm^{-1}, where bands related to the amide III vibration occur (Shao, 2005). As reported by Mirghani *et al.* (2012) the use of ATR-FTIR and SEM to rapidly discriminate between animal species is useful with the sharp peak in the FTIR spectrum at 1033 cm^{-1} being only found in cattle and goat skins while it is absent in pigskin. They also describe other two spectral regions able to differentiate the leather origin between the three animal species, i.e. at 400-500 cm^{-1} and 600-700cm^{-1}. The latter region was considered of interest, but only a weak signal around 700 cm^{-1} (710 cm^{-1}) was detected and that was not significant. The band at 1033 cm^{-1} was already able to provide the required information to distinguish cow from pigskin; moreover, Figure 4-42 showed that the area between 1000 and 1200 cm^{-1} was characterised by a number of peaks of similar intensities, a feature that enabled the discrimination of cow leather from sheep and goat skin.

Some articles report the use of ATR-FTIR to characterise tannings contained in historical leather after extraction in aqueous solutions (Falcão and Araújo, 2013). Despite the remarkable results achievable by performing the test on the leather extract, this method still remains destructive, reducing its field of application to items that can be sampled. Of course, considering the premises of this thesis, this aspect cannot be of secondary importance because the objective of using FTIR in ATR mode was to avoid material sampling. The possibility of assessing the presence of a tanning agent was investigated by comparing the spectra collected with the literature (Valeika *et al.*, 2010; Nashy *et al.*, 2012). However the lack of raw data did not permit to get homogeneous and comparable spectra to be used as a benchmark to assess the reliability of any hypothesis made on the bases of pure observations of the spectra. Despite this, the spectral peaks of chrome-tanned leather at 1128, 1077 and 1027 cm^{-1} as described by Nashy *et al.* (2012) were not found, confirming that the TL material in this study was not chrome-tanned.

Peak Location (cm^{-1})	**Bond**	**Type of vibration**
3309	N-H	asymmetric stretching
3223	N-H	symmetric stretching
3068	-	-
2985	C-H	asymmetric stretching
2922		
2853	C-H	symmetric stretching
1731	C=O	
1632	C=O	stretching un-ionised C=O
1547	C-N and N-H	stretching and bending
1440	C-H	bending
1338	C-N and N-H	stretching and bending
1234	N-H	bending
1161	-	-
1032	C-O and -C≡S group	stretching
962	C-C	stretching
873	C-H	out-of-plane bending

Table 4-6: ATR-FTIR absorption bands, bond and type of vibration found in TL fibrous layer

SY showed a totally different pattern of absorptions, as clearly visible in Figure 4-43 and Table 4-7. The presence of synthetic fibres as main component of SY substrate was already discussed during morphological, structural analyses and EDX. Though, the identification of the polymer forming the fibres was not possible at that stage because several macromolecules can have features similar to those observed above. The supplier of SY did not provide any information apart from the commercial name of the material, thus the type of polymer used for the fibres was totally unknown. As a result, it was essential to observe not just the presence of specific peaks, but also the absence of others.

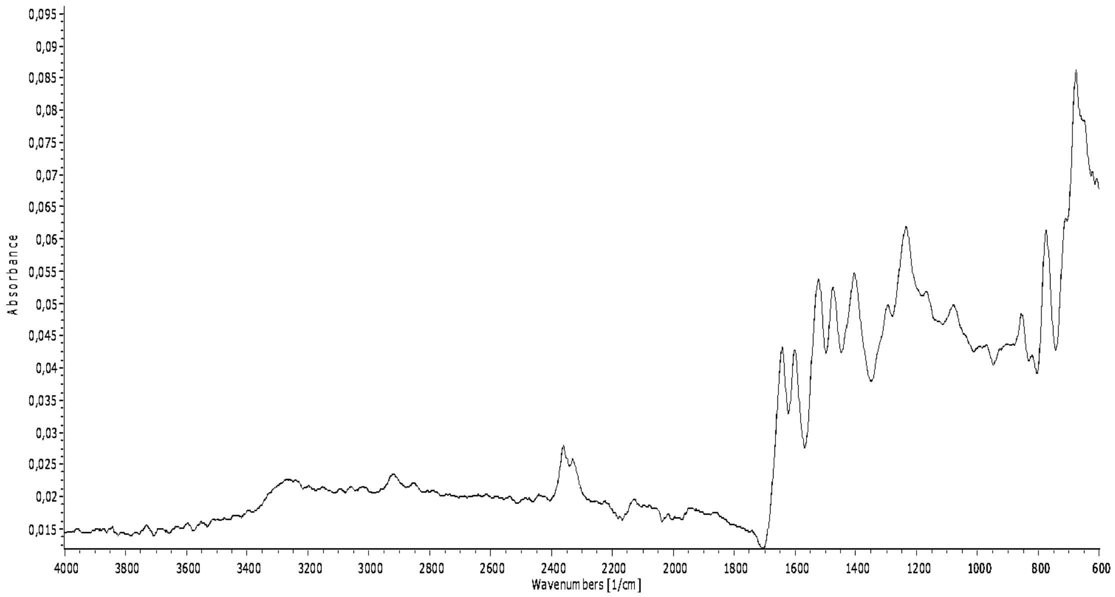


Figure 4-43: FTIR spectrum showing absorbance peaks of SY fibrous layer

Several fibres are characterised by peaks above 1700 cm^{-1}, like cellulose acetates (CA) and polyethylene terephthalates (PET), thus the absence of bands in these regions provided evidence that SY was not made with any of those polymers. However, one peak 1642 cm^{-1} indicated the presence of the carbonyl group typical of polyamides (PA) as reported by previous publications (Chen *et al.*, 2007). Another intense band was at 1234 cm^{-1} possibly related to the C-O-C group stretching. As visible in Figure 4-43, some adjacent peaks within the spectrum were characteristic of aromatic ring vibrations: 1598, 1475, 774 and 677 cm^{-1} absorption bands showed the vibrations of ring structure and C-H bonds. Peaks that could also be informative were at 3265 cm^{-1} (N-H bond stretching), 1522 cm^{-1} (amide II), and 1294 cm^{-1} (amide III). Together with the peak at 1642 cm^{-1} those signals allowed confirmation of the presence of amides. At this point the presence of two important molecular groups was confirmed, that is aromatics and amides, leading to the conclusion that the polymer was an aramid.

Several articles containing aramid ATR-FTIR spectra were examined to confirm possible identification and the outcomes were satisfying. Shebanov *et al.* (2016) described in great detail the absorbance values of five different aramid fibres, and despite some of the bands recorded for SY differed to some extent from the ones reported in the article, the signals did correspond with the assignment described above. The publication of Derombise *et al.* (2009) was also useful to confirm the results obtained and being focused on the degradation of aramid fibres in neutral (and alkaline) environments, it will be also used in the next chapter.

Peak Location (cm^{-1})	Bond	Type of vibration
3265	N-H	stretching
2917	C-H	asymmetric stretching
2846	C-H	symmetric stretching
1642	C=O	stretching
1598	ring	stretching
1522	N-H	bending
1475	N-H and C-H	bending and stretching
1404	N-H, C-H and ring	bending and stretching
1294	N-H and C-H	bending and stretching
1234	C-O	asymmetric stretching
1168	C-H	in-plane bending
1079	C-O	stretching
971	C-C	stretching
855	C-H	out-of-plane bending
774	C-H	out-of-plane bending
677	ring	out-of-plane bending

Table 4-7: ATR-FTIR absorption bands, bond and type of vibration found in SY fibrous layer

The EL2 and EL3 spectral data was presented together during the coating analysis because their spectra were almost perfectly overlapped, but in the case of the fibrous layer it was necessary to describe the substrates separately. Moreover, each of the three spectra collected from all E-Leather® samples presented a number of different absorption bands, probably as a consequence of their composite nature. The aim of this analysis was to describe the functional groups detected from the instrument to assess the possibility to discriminate between the different leather-related materials. Therefore it was decided to report also for EL2 and EL3 the average of the three spectra, as it was done for the other samples, but care must be taken in case of future comparison because the absorbance values of the peaks in each spectrum were relatively different.

The spectrum obtained from EL2 testing is reported below (Figure 4-44) and the absorptions with their assignment are presented in Table 4-8.

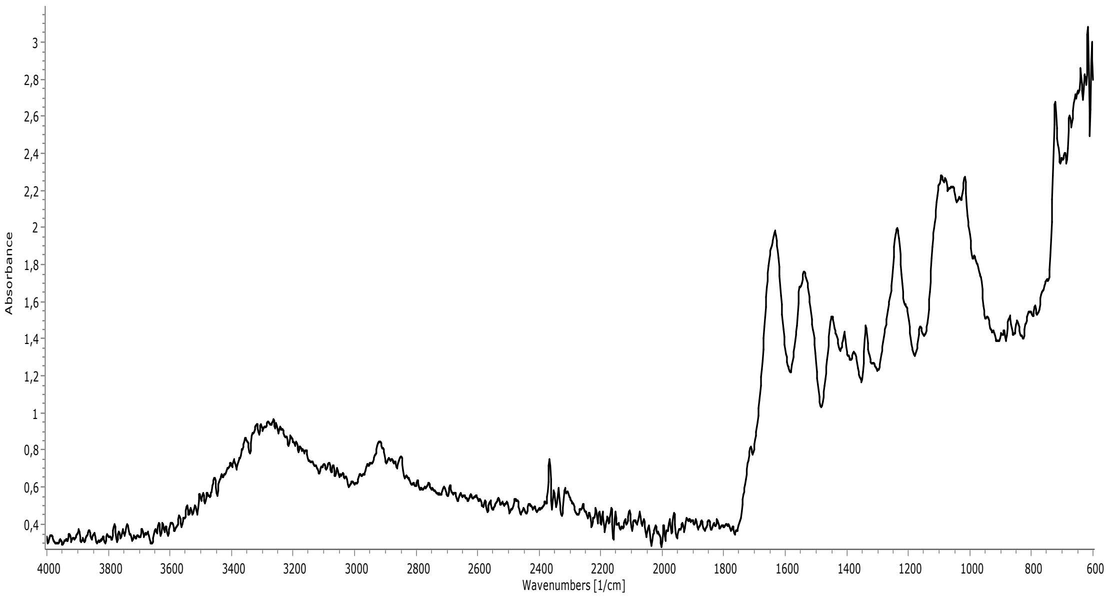


Figure 4-44: FTIR spectrum showing absorbance peaks of EL2 fibrous layer

The presence of leather fibres in the wet blue stage used to make HE web was documented, therefore signals indicating the presence of leather fibres (Menderes, 2002; Nashy *et al.*, 2012) were investigated. A general similarity between this spectrum and the TL spectrum can be noted, thanks to the presence of a wide peak area associated with N-H stretching, above 3200 cm^{-1}, containing a shoulder around 3080 cm^{-1}, and peaks related to the carbonyl (1710 cm^{-1}) and amide (I, 1634 cm^{-1} ; II, 1536 cm^{-1} ; III, 1337cm^{-1} and 1237 cm^{-1}) functional groups (Scott, 2005). The shift of some of these absorptions, e. g. at 1710 cm^{-1} and 1536 cm^{-1}, were likely to be related to interaction of collagen fibres in E-Leather® with the chrome-tanning agent. It is possible that some of the amino acid reactive sites in the collagen molecule reacted to form complexes containing chromium resulting in a shift the peak absorption (Nashy *et al.*, 2012). Peaks at 1158, 1092 and 1053 cm^{-1} could also be indicative of the chrome-tanning of the collagen fibres.

Changes were also observed in the N-H bending peaks, that shifted from 1234 cm^{-1} in TL to 1237 cm^{-1} in EL2, and from 1161 to 1158 cm^{-1}, but in these cases it was not just the change in signal position. In fact, as can be seen by comparing TL and EL2 in Figure 4-41, the shape of some absorbance bands were also visibly different and they also varied in relative intensities. One of the possibilities is that the bicomponent splitting fibre signals were detected along with those of the leather fibres. Splitting fibres, made of PET, were also part of the hydroentangled surface of E-Leather® products, therefore their absorbance values can contribute to the substrate spectrum.

Finally, a weak absorbance attributed to C-H bond occurred at 871 cm^{-1}, whilst in contrast in the TL material the signal was at 873cm $^{-1}$ and was stronger in intensity.

This feature may be connected with the tanning agents used to stabilise the leather or with the re-tanning utilised in TL (Falcão and Araújo, 2013).

Peak Location (cm^{-1})	**Bond**	**Type of vibration**
3280	N-H	stretching
3085		
2916	C-H	asymmetric stretching
2847	C-H	symmetric stretching
1710	C=O	stretching
1634	C=O	stretching un-ionised
1536	C-N and N-H	stretching and bending
1447	C-H	bending
1408	ring	stretching
1377	ring	stretching
1337	C-N and N-H	stretching and bending
1237	N-H	bending
1158	N-H and Cr-complex	-
1092	C-O and Cr-complex	stretching
1053	C-O and Cr-complex	stretching
1016	=CH	in-plane bending
963	C-C	stretching
871	C-H	out-of-plane bending
722	ring	out-of-plane bending

Table 4-8: ATR-FTIR absorption bands, bond and type of vibration found in EL2 fibrous layer

Finally, the spectrum and peaks table for the EL3 substrate are presented in Figure 4-45 and Table 4-9.

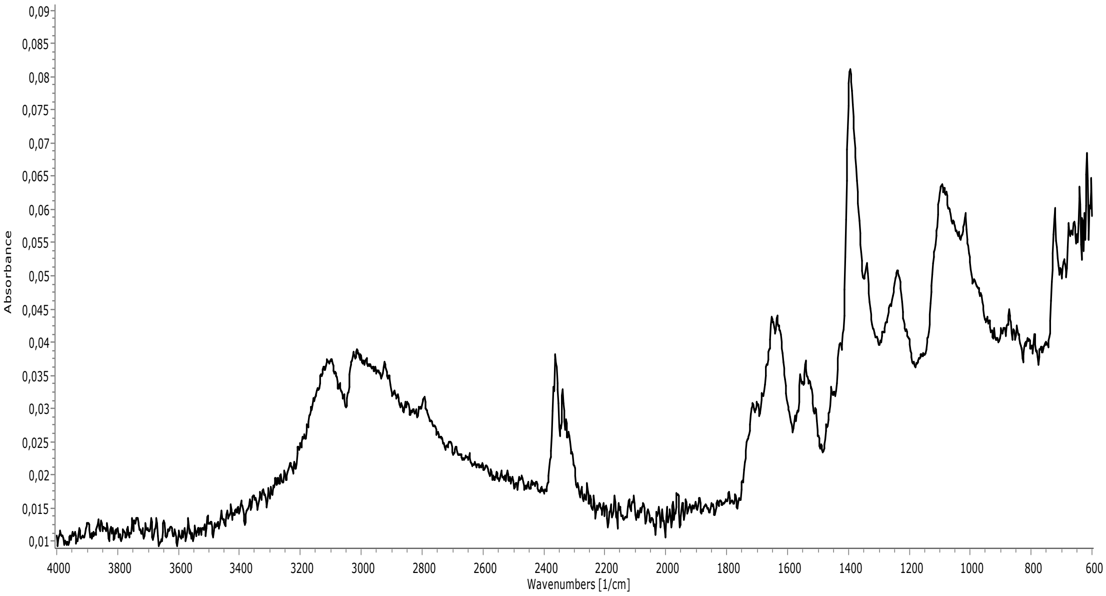


Figure 4-45: FTIR spectrum showing absorbance peaks of EL3 fibrous layer

The spectral region between 3400 and 2700 cm^{-1} was characterised by a very broad peak with other peaks superimposed. This peak profile can indicate the presence of aromatic and aliphatic compounds.

The band at 1713 cm^{-1} assigned to the C=O stretching vibration was relatively weak and it overlapped with the more intense band at 1634 cm^{-1} that confirmed the presence of an amide I C=O bond. This characteristic feature of the two peaks was already noticed in EL2 (Figure 4-44) but with the peaks slightly shifted in EL2 probably due to the structure of the amino acid chains being different.

Signals below 1400 cm^{-1} were difficult to interpret because of the lack of similarities with previous spectra and with the literature data. This region could be related to the interaction of the brominated flame retardant with the collagenous matrix. In particular, the strong absorption at 1394 cm^{-1} had a strong intensity and could be associated to the presence of brominated flame retardant or its interaction with the collagen molecules and melting fibres. The peaks that in EL2 indicated the interaction collagen-chromium were not easily distinguishable in EL3, probably because of the overlapping with other signals.

Peak Location (cm^{-1})	Bond	Type of vibration
3098	ring	stretching
3013	ring	stretching
2923	C-H	asymmetric stretching
2793	C-H	symmetric stretching
1713	C=O	stretching
1634	C=O	stretching
1540	C-N and N-H	stretching and bending
1393	-	
1340	C-N and N-H	stretching and bending
1239	N-H	bending
1093	C-O	stretching
1016	=CH	in-plane bending
872	C-H	out-of-plane bending
721	ring	out-of-plane bending
640	-	
616	-	

Table 4-9: ATR-FTIR absorption bands, bond and type of vibration found in EL3 fibrous layer

In summary, ATR-FTIR was able to provide clear evidences of the different composition of the four substrates. The distinction of the TL, EL2 and EL3 materials, all containing leather fibres, was of particular interest and could be used in future to identify these substrates by means of non-invasive methods.

4.4.3 Discussion of the Chemical Analyses

EDX and ATR-FTIR spectroscopy were demonstrated to be two useful and complementary instruments that allowed the identification of elements and functional groups. Their combined insight and capability provided important data to characterise the samples but also pointed out some limitations.

EDX was valuable in assessing the presence of elements in the coating and fibrous layer and allowed the characterisation of specific additives, such as the beads, which were added to the materials in order to improve performances. The SY coating spectrum highlighted the presence of elements important for the characterisation and, possibly, for the degradation of the material. In addition to confirming the presence of additives the analysis also indicated the absence of specific elements that was important to confirm or deny previous information. For example, the supplier of TL assured that the material was chrome-tanned whilst the results did not detect any trace of chrome. In addition, the use of EDX mapping techniques allowed the distribution of different elements on the superficial and internal part of the layers to be established.

One of the limitations of EDX that partly affected the analyses was that light elements could not be easily identified, in particular when they were present in small amounts. This aspect must be taken in consideration whenever quantitative analysis must be carried out, because otherwise there is the risk of invalidating the recording. Another limitation lies in the fact that EDX is an invasive technique that requires sampling and restricts its application when sampling is not allowed.

ATR-FTIR data allowed the molecular characterisation of samples components but left still open some of the questions regarding the application of the instrument for the study of composites. FTIR allowed the qualitative fingerprinting of fibrous and coating components such as collagen, aramid and polyurethanes.

The EL2 and EL3 materials have never been subject to systematic characterisation or to comparison via ATR-FTIR against leather and synthetic leather substrate. Therefore it was important to investigate the potential of this combined instrument analysis approach. It was found that was difficult to identify all the components of EL3 fibrous layer, possibly as a consequence of the presence of flame retardant. In contrast this issue was not encountered when examining EL2 and its characterisation was effectively conducted.

FTIR instruments are not as expensive as SEM/EDX systems and accordingly tend to be more common in museum laboratories. Moreover the ATR mode guarantees the non-destructivity of the method, meaning that analysis can be conducted without sampling.

Despite the limitations described for both the analytical tools it is important to confirm their ability to provide data that would allow material identification. The presence of specific elements in each material would permit the unequivocal identification of samples. For example only the SY material contained fluorine and antimony, and only TL and SY contained bromine in the coating. In contrast the EL2 and EL3 materials have the same coating composition but their fibrous layer differ for the presence of bromine in EL3. As a result, ATR-FTIR could be helpful to identify TL, SY and E-Leather, though it would be difficult to discriminate between the EL2 and EL3 samples because their coatings have the same spectrum. An examination of EL2 and EL3 fibrous layer would be thus useful in order to decide which of the two materials is under investigation. These aspects could become of key importance in the case of acquisition of E-Leather items by museums in the future.

4.5 Physical Properties

4.5.1 KES-F Bending and Compressional Analyses

The use of the Kawabata Evaluation System (KES) is normally related to academic and industrial studies entailing the characterisation of properties that affect fabric hand (Harwood *et al.*, 1990; De Boos, 2005). To the author's knowledge, only one publication has reported the use of the KES, and in particular the KES-FB3, as a tool to assess properties variations in historical objects (Sato *et al.*, 2011). It is likely that the complexity of the numerical output and obtaining access to the system discouraged the wider application of the KES in this sector. However the potential for the system to be used in museum context is clear, because it does not require sample destruction and only a minor stress is applied to the tested material. Therefore, the possibility of using the KES-FB2, KES-FB3 and KES-FB4 instruments for identification purposes, and in particular the curves constituting the instrument output rather than the numerical output, was investigated.

For KES-FB2 six repetitions, three in the machine direction or parallel to the backbone and three in perpendicular direction or perpendicular to the backbone, were carried out for each material according to the procedure described in the KES manual (Kato Tekko Co. Ltd., 2002). The data output consisted of sets of values that represented the bending moment (M, expressed in gf.cm/cm) and curvature (k, expressed in cm^{-1}), and it also provided measurements of the bending rigidity (B, $gf.cm^2/cm$) and bending hysteresis (2HB, gf.cm/cm) in numerical form.

M and k can be used to plot graphs that allow to visualise the material's behaviour, for example to underline differences before and after treatments (Tsukada *et al.*, 2013). B quantifies the resistance of the sample to flexing and was measured by calculating the mean value of the bending moment-curvature curve slope at two points of the curve (positive and negative sides). 2HB represents the average difference between the loading and unloading curve (positive and negative sides).

All bending curves can be divided in four regions:

- initial loading, from the beginning of the test to the maximum curvature point in the positive side of the x-axis;
- unloading, from the maximum curvature point to the 0-point of curvature, along the y-axis;
- reverse loading, from the 0-point of curvature along the y-axis to the maximum curvature point in the negative side of the x-axis;
- reverse unloading, from the maximum curvature point in the negative side to the end of the test (Lahey, 2002).

The properties of these regions change depending on the material and the treatments it was subject to, therefore the possibility of using bending curves to provide valuable data able to discriminate between different materials was evaluated. Analysis of the curves was considered more significant and direct for the purpose of identification and discrimination. Numerical data output was considered in greater detail during the ageing effect assessment.

The typical curves obtained from the bending tester for TL, SY, EL2 and EL3 are reported in Figure 4-46, where each curve represents one sample per material (in the machine direction or parallel to the backbone).

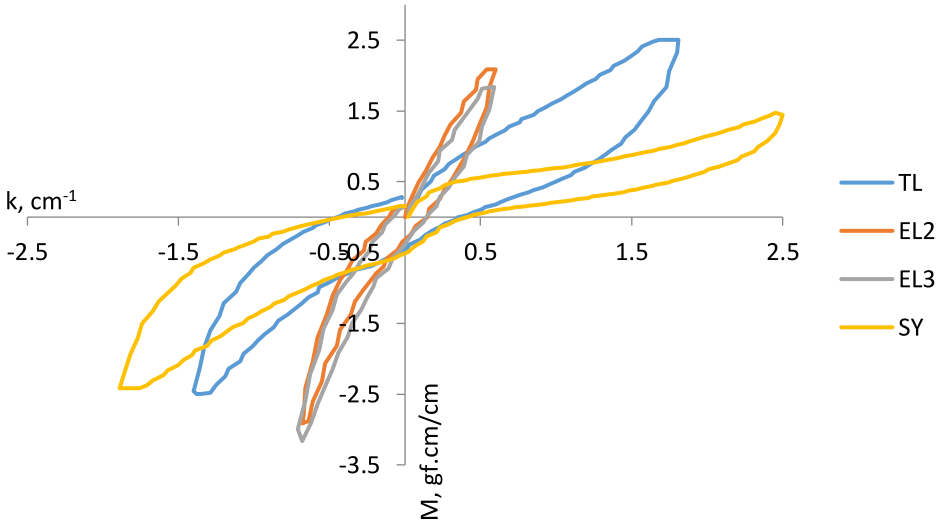


Figure 4-46: Typical KES-FB2 curves for TL (charcoal grey), SY (fog grey), EL2 (silver) and EL3 (cloud grey) tested along the machine direction -or parallel to the backbone for leather

Examination of the data indicates clear differences between natural leather, synthetic leather and composite leather. In fact, the EL2 and EL3 curves appeared almost overlapped and the width of their curves was much narrower than the curves for the TL and SY materials. The samples showed different behaviour immediately after the application of the initial load, as demonstrated by the steep slopes of EL2 and EL3 as opposed to the inclined TL and SY curves. After that stage TL and SY progressively adjusted to the load by reducing the initial slope, but this did not happen in EL2 and EL3. Moreover, the curvature value of the E-Leather materials was significantly lower (0.6 cm^{-1}) than that of the TL (1.8 cm^{-1}) and SY (2.5 cm^{-1}) materials, while their positive bending moment (respectively 2.1 gf.cm/cm and 1.8 gf.cm/cm) was higher than the SY material (1.4 gf.cm/cm) but lower than the TL material (2.5 gf.cm/cm). These results indicated that EL2 and EL3 required higher forces to be bent and highlighted the difference with the other two substrates, TL and SY, which were progressively more bendable.

This difference can be attributed to the type of interaction of the fibres in the four substrates. In the SY samples the fibres were less constrained than in TL because in the latter collagen fibres were chemically bonded to each other and densely packed. Similarly, the bonding and consolidation treatments during EL2 and EL3 manufacturing made the two materials more rigid than SY. However, a significant difference exists between natural leather and the composites under study. The density of the fibre bundles in leather (and TL) and their natural entanglement allowed the substrate to be both flexible and resistant to the application of stresses, whilst this result was not achieved in E-Leather®.

Another interesting aspect of the KES-F data is that all the curves exhibited different ability to bend in the positive and negative direction. This could be attributed to the presence of the polymeric coating on the top of all the samples. In particular for the SY, EL2 and EL3 materials, all reached higher bending moment values in the negative side compared with the values observed on the positive bending side. TL was the only substrate to show the same value on both bending actions, although this behaviour was not visible in all the leather samples. In addition to these considerations, it must be noted that the width of the curve in the two directions only changed distinctly in SY, becoming much wider in the reversal loading/unloading region. This was likely to be related to the higher contribution of SY coating when the sample was bent in the positive side, whilst the fibrous layer was more responsible for the curvature in the opposite direction.

This data showed that the studied substrates performed in distinctly different ways according to their structure. It was not possible to find publications on leather samples reporting the shape of bending curves, but the different behaviour compared with the other substrates was obvious. Similar considerations were valid for the EL2 and EL3 materials that have never been reported through this analytical method. The shape of the SY curve resembled that of the coated fabrics found in literature (Tsukada *et al.*, 2013), probably as a consequence of the similarity between SY fabric and the fabric involved in the study. The polymeric coating on the samples appeared to have an effect on all the materials apart for TL, as highlighted by the distinct shape of the curves in the positive and negative directions. This was probably due to the denser structure of TL material compared with the other materials, which made the substrate less affected by the presence of the coating.

The data suggested that the plot of the KES-FB2 instrument can be successfully used to discriminate between the TL, SY, and E-Leather® materials. Moreover, in this case it was possible to order the materials from the most rigid to the most flexible: EL2 and EL3 were the most rigid substrates, followed by TL and finally SY.

In the case of KES-FB3 three samples per each material were tested for measuring compressional properties. The numerical values associated with the measurement describe thickness (T, in mm) and pressure (P, in gf/cm^2). Initial thickness, namely before compression or T_0, and minimum thickness, namely thickness of compressed fabric or T_m, are automatically collected by the KES-FB3 instrument to derive further material parameters. Compressional energy (WC, in gf.cm/cm^2), resilience (RC, in %) and linearity of compression (LC) were the other measurements provided by the analytical software. WC describes the energy required to compress the sample, while RC refers to the ability of the material to recover after the stress was removed. LC was related to stress and strain, hence when LC was high the linear relationship between stress and strain was equally high (Von Hoven, 2002). Moreover, compressibility (C, in %) can be calculated by using the initial and final thickness values of the sample (Urbanija and Geršak, 2004).

Following the same pattern described for bending curves, compressional curves can be divided in two regions:

- initial loading, from the beginning of the test to the maximum load point;
- unloading, from the maximum load point to the initial position (end of the test).

Typical graphical outputs are presented in Figure 4-47. The graph showed a similar situation to that observed for the KES-FB2 data, where the EL2 and EL3 curves were very close and characterised by similar shapes as compared with the TL and SY material curves. Also in this case the SY substrate was clearly distinguishable from the other samples most likely because of its structural difference. In fact, the thin coating layer applied to the surface of the knitted fabric allowed a certain degree of compressibility to the structure of the material.

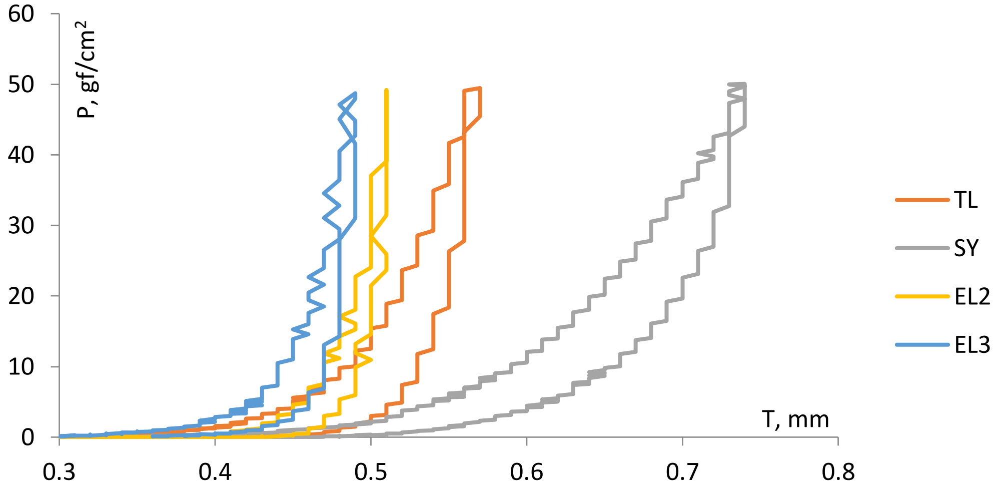


Figure 4-47: Typical KES-FB3 results for TL (charcoal grey), SY (fog grey), EL2 (silver) and EL3 (cloud grey) samples

This was evident looking at the thickness values reached by the SY curve that were much higher than the values of all the other samples at any considered pressure. The maximum value of SY (0.74 mm) was significantly higher than the other samples (TL = 0.57 mm, EL2 = 0.51 mm and EL3 = 0.49 mm), underlining the greater compressibility of the sample. Knitted fabrics are normally more elastic than woven (Mäkinen *et al.*, 2005) and therefore it was expected that SY would show higher values of compressibility.

The curve described by SY was arc-shaped and it consistently increased and decreased in both the loading and unloading regions. EL2 and EL3 followed a different deformation profile pathway, with a steep increase of the pressure values within a very limited thickness. This indicated that the compressibility of the samples was limited, at least if compared with SY and TL. The latter, in fact, exhibited behaviour intermediate to the SY and E-Leather materials. One possible explanation can be found in the presence of leather fibres in both E-Leather substrates and leather. In EL2 and EL3 the contribution of the fibres to the total compressibility, which is added to the contribution of woven core, coating and other treatments, could be in fact responsible for this effect. Further experimentation would be required to elaborate this behaviour and was considered outside the scope of this work.

It is important to recognise that the KES-FB3 data can effectively discriminate between synthetic leather materials having a thin surface coating layer and leather-based materials. In contrast it was noted that distinguishing leather from composite materials was less clear and this could lead to incorrect identification of materials if careful considerations on the shape of the curves was not done.

Another instrument used in this research was the KES-FB4 tool which could measure the geometrical roughness and friction of the sample surface. However, the raw graphical data was not considered in this section and only the average numerical data were evaluated in later sections during the degradation analysis (see § 5.4.4.2.3).

To summarise, both the KES-FB2 and KES-FB3 graphic output may be used to effectively identify leather and related materials. If the identification of synthetic leather was successfully carried out using both the devices, it was more complex to differentiate the composites from natural leather, in particular when KES-FB3 was used.

4.6 Preliminary Summary

The preliminary assessment of the base materials was successful in demonstrating the relevance of some basic analytical tools that provided both physical and chemical information about leather-type materials. The initial findings are:

- The use of inexpensive techniques such as visual investigation of surface and reverse via photography and stereo-microscopy provided material defining information on E-Leather materials. Identification of TL, SY and E-Leather® was possible both using visual photography and microscopy, but some difficulties were found in discriminating between the EL2 and EL3 samples because of their compositional and structural similarities. Identification of these materials could be facilitated through the creation of a directory or database where images of these and other substrates would be collected. During these tests it was noted the importance of assigning the correct name to defects found in coatings because it benchmarks the material and defines the nature and extent of the defect and probable cause of formation. Therefore in any future study it would be advisable to gain experience in this practice before examining coatings and any degradation in order to provide useful data for both museums and other sectors;
- The ATR-FTIR instrumental technique is commonly found in museum laboratories and is relatively cheap. This analytical technique differentiated the differences in both the coating and fibrous layers between TL, SY and E-Leather materials, but it was less successful in discriminating between the EL2 and EL3 materials. Differences in the fibrous layer mainly related to the presence of flame retardant allowed the identification of the two materials;

- The invasive EDX technique was also used to characterise the materials and it was demonstrated to be helpful and complementary in providing useful material characterisation. It was relatively straightforward in identifying the TL, SY and E-Leather materials, in particular the coating layer, but differentiating between EL2 and EL3 materials was again difficult. As in the case of ATR-FTIR, though, testing the fibrous substrate provided significant data to allow materials discrimination. The presence or absence of the flame retardant, together with its interaction with the surrounding components, is likely to be the most important factor that determined the differences between the four materials under study;
- The KES-F graphical output was assessed with a view to its applicability in museum analysis with the aim of discriminating between leather on related materials. The KES-FB2 bending data output was found to be particularly interesting because the structural differences between the substrates allowed the collection of characteristic bending profiles, potentially paving the way to a systematic use of the technique in museum collections. However the EL2 and EL3 materials were again almost indistinguishable because of their structural similarities. This aspect would require further study to investigate the effect that each E-Leather treatment has on the finished substrate. Also the KES-FB3 compressional instrument provided encouraging results, though the mechanical profiles of EL2 and EL3 were similar to the one of TL. This indicated that compressional properties of E-Leather samples were possibly influenced by the leather component, which did not happen in the case of the SY materials. Indeed, bending and compression curve profiles could be potentially used as “user-friendly” tools for identifying unknown leather-type materials.

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Chapter 5 Ageing Simulations in Leather, Synthetic Leather and E-Leather

5.1 Literature Review of Accelerated Ageing Methods

Natural degradation of materials and historic items can occur over a range of time frames depending on various factors and it can be complex to assign the specific nature of the physical and chemical changes in materials due to the combined effect of the individual variables involved in the process. Accelerated ageing techniques are commonly used to reduce the amount of time necessary to mimic the natural degradation of the cultural artefacts (Escobar and Meeker, 2006). Thus, accelerated ageing refers to all those methods that aim to simulate in the laboratory the natural ageing of materials and hence reduce the degradation period necessary to assess comparable "model" materials.

A number of accelerated ageing procedures have been developed and various methods are available today to perform degradation studies, such as high temperature, high temperature and variable relative humidity and light/UV radiation. These procedures rely on models and principles such as the Arrhenius equation, which describes how temperature affects the rate of chemical reactions (Escobar and Meeker, 2006). Despite the widespread acceptance and relevancy of this type of investigations many researchers still view these techniques with wariness and scepticism (Chess *et al.*, 1999).

The actual correlation with natural ageing is not always possible because accelerated ageing often studies one factor at a time, whilst when objects are in use they can be subjected to multiple factors (Chess *et al.*, 1999). This difficulty in assessing relationships between natural and simulated ageing represents the main drawback of studies conducted in this area (Feller, 1994). However, at present accelerated ageing represents the only available alternative to studying long-term behaviour of materials in a limited timeframe and studies on natural/accelerated ageing relationships and associated concerns have been published (Larsen *et al.*, 1994; Pellizzi *et al.*, 2014). These ageing simulations enable obtaining information about the most influential factors that induce degradation. Indeed, this is important to understand how specific factors affect specific materials. Moreover, one can identify degradation due to certain factors at an early stage by studying in advance the impact different factors have on the material under investigation.

5.1.1 Accelerated Ageing Studies on Leather and Coated Fabrics

The need for reliable materials able to withstand certain types of degradative environmental factors has lead a number of industries to develop standards to evaluate their durability in an attempt to predict product lifetime. Automotive and other transportation industries, as well as the textile and footwear industries have proposed and introduced various procedures enabling different materials to be compared and benchmarked under standard conditions (Milligan, 1986). Durability is evaluated by assessing changes in one or more properties and it provides evidence of which products perform better when subjected to specific ageing factors.

Heat, relative humidity and UV radiation have been recognised by many authors as the most dangerous factors which could lead leather and synthetic leathers experiencing faster rates of degradation (Larsen *et al.*, 1994; Ollè *et al.*, 2012; Li *et al.*, 2016). In addition, damage is variable depending on the use of static or dynamic cyclic conditions, thus testing a range of environmental conditions is useful to assess how material performances can vary in use (Meyer *et al.*, 2006; Schröpfer and Meyer, 2012). The studies presented below provide a set of examples that illustrate the importance of the research design and the different uses of the accelerated ageing techniques.

Ollè et al (2011) investigated the effect of tropical conditions (defined as 70 °C and 95% relative humidity) on chrome and vegetable tanned leathers and they compared tear load, fastness, shrinkage and water, fat and chromium (only for chrome-tanned) content of the two substrates. They concluded that the vegetable tanning method made the substrates less resistant to the “tropical” environment. They also observed that chrome tanned leathers showed a progressive reduction of the tested properties immediately after the beginning of the ageing, whilst in vegetable tanned leathers the reduction occurred after seven days from the beginning of the procedure. However, once the degradation was initiated its effect was much greater than in chrome tanned substrates.

Another study was conducted by Ollè’s research group on chrome-tanned and wet-white leathers (Ollè *et al.*, 2012). The analysis of the same properties described for the previous study under different conditions of temperature, relative humidity and UV radiation showed that the relative humidity is the most damaging factor. In particular, wet-white presented greater vulnerability in presence of high relative humidity whilst UV affected chrome tanned leather to a greater extent.

With respect to coated fabrics degradation, Weder (1997) and Eichert (1998) conducted studies to assess the behaviour of diverse coatings under different environmental factors. Eichert’s study was carried out on samples exposed for ten years in different parts of Europe and US characterised by specific types of climates (Eichert, 1998). He underlined how the effect of UV radiation alone did not affect the strength of the tested composite but rather it was the combined action of radiation and humidity together that produced obvious deterioration.

Along with assessing the effect of certain factors on the material, the correlation between product performances before and after exposure are important. Potočić Matković *et al.* (2014) tested the effect of outdoor exposure on the thermal properties of PU-coated knitted fabrics and noted that after three months the thermal resistance reduction did not correlate with parameters of the knitted substrate before ageing. This lead to the conclusion that the polymeric layer was much more compromised than the fibrous layer, meaning that the rate of degradation of the two layers interacted differently with the surrounding environment.

Similar procedures have been used in cultural heritage. Early studies referencing accelerated ageing in the heritage sector appeared in the early 70s (Delacorte *et al.*, 1971; Baer *et al.*, 1972). At the time the main ageing parameters used to conduct the procedures were temperature and humidity in static or cyclic mode. Today accelerated ageing is increasingly used and is becoming a useful tool to test the effect of specific factors on heritage materials. Its applicability is normally restricted to the following types of studies:

- sampling is allowed and the long-term effect of ageing factors or consolidation treatments is tested on the sampled surface (Larsen *et al.*, 1994);
- the effect of consolidation treatments are tested on materials that replicate the materials used in collections but are not part of the collection (Pellizzi *et al.*, 2011);
- degradation studies are conducted on samples that are not part of museum collections but that replicate them (Lovett and Eastop, 2014; Pellizzi *et al.*, 2014).

In spite of the amount of publications on accelerated ageing in the heritage field, none focuses on chrome tanned leather and there is only a limited amount of investigation on synthetic leathers. This lack of information constitutes a threat for the future preservation of these materials in the context of museum.

Bechthold *et al.* (2006) investigated PU-coated textiles used in 1960s furniture describing the mechanisms of degradation of the fabric and pointed out the need for development of preventive conservation practices. However, in order to successfully identify preventive conservation plans, it is necessary to assess the degradation mechanisms that mostly affect materials. The only study found in this area was by Lovett and Eastop (2014), where variable amounts of oxygen and relative humidity were used to evaluate the change in mechanical properties of PU-foam structures. Also in this case, the high relative humidity was identified as a detrimental factor for the preservation of PU. It must be noted that the material chosen to conduct the accelerated ageing study was a foam and not a sandwich structure as in the original dress.

The need for more accelerated ageing studies on leather-related materials is evident and the benefit of coupling methods used in industry and heritage becomes obvious. If accelerated ageing is applied today to study materials before they enter museum collections, the future of preserved items will be less unpredictable. Moreover, conducting this study before degradation will reduce the need for sampling at a later stage. In addition, while a number of invasive techniques allow the identification of ongoing degradation, it is less common to use non-invasive techniques to achieve the same purpose. For this reason, it is recommended that the development of alternative non-invasive methodologies able to provide similar results is undertaken.

5.2 Accelerated Ageing Techniques

Instruments and parameters used to conduct accelerated ageing have been described in Chapter 3. In this section the selected procedures are described in more detail and the reasons for their choice are given.

5.2.1 Parameters

As already stated heat, relative humidity and UV radiation are among the most deleterious factors which could lead leather and PU coated materials experiencing faster rates of degradation. It was hence decided to perform a series of tests using these factors, focusing on precise values, to assess their effect on the four leather-related substrates under examination. The experimental conditions were selected to purposely increase the reaction rate to induce and identify early degradation markers.

Previous research reports indicate that different ageing factors can induce different phenomena in materials or, in some cases, similar effects but in a longer or shorter time frame (Ollè *et al.*, 2011). For this reason, the study of various factors at increasing times was examined to investigate similarities and differences in sample behaviour. Moreover, because the focus of this research was on the detection of the early signs of degradation, the intervals for the repeated analysis were selected in order to both allow degradation to occur and to avoid too drastic changes without the possibility of effective documentation.

5.2.1.1 Heat Ageing

Heat plays an important role in the deterioration of any material and the extent of this deterioration is variable depending on chemical composition and physical properties of the tested item. The Arrhenius equation (Equation 5-1) underlines the strong relationship between heat and degradation as a consequence of the increased reaction rate (Celina *et al.*, 2005), stressing the ability of heat to induce structural disorder and increase activation energy,

$$k = Ae^{-\frac{\Delta E_a}{RT}} \tag{5-1}$$

where k is the reaction rate constant, E_a is the activation energy, R is the gas constant and T the absolute temperature of reaction. A is the pre-exponential factor and is related to molecular collisions.

Broadly speaking, and is apparent from the equation, the extent of reaction that can occur doubles by increasing the temperature by 10 °C. It is interesting to note that, despite the great influence of heat on materials degradation, most of the publications in the field of leather and synthetic leather reported on deterioration after heat and relative humidity (Ollè *et al.*, 2011; Lovett and Eastop, 2014; Li *et al.*, 2016). Therefore, in this study different temperatures and low humidity were considered to evaluate how the former impacted on the samples.

Several standards for heat ageing are available for leather and coated textiles, with some used for specific applications such as footwear and automotive. The EN 12280-1:1998 standard defines the parameters to test the effects of accelerated ageing on rubber- or plastics- coated fabrics (British Standards Institution, 2010). It sets the test temperature at 70 °C and states that 168 hours is the minimum interval for the test. The minimum interval was considered of great importance in this study, because after the selected amount of time (168 hours) changes in the material might have already occurred. Similar considerations can be done for the Sahara test, that was proposed in the car industry to test fabrics for car interiors (Milligan, 1986). In this case the temperature is set at 115 °C for 144 hours. Of course, considering Equation 1 it is expected that the rate of chemical reaction in the case of ageing at 115 °C is greater than the rate at 70 °C, and consequently a greater degradation would be expected in the first case.

Standard procedures for leather are described in the BS EN ISO 17228:2015 standard, indicating timeframes and temperatures to conduct the test (British Standards Institution, 1992). Conditions vary according to the final purpose of the product and they can run for as short as four hours or as long as 168 hours; also temperature is variable depending on the application, from 60 °C (general-purpose) to 120 °C (automotive).

5.2.1.2 Heat and Relative Humidity

The presence of heat alone is rather unconventional in ordinary conditions while the presence of a variable amount of relative humidity represents the normality. As a consequence, most of the reactions that occurs in an air atmosphere and lead to degradation stem from the combination of heat and relative humidity. This is likely to be the reason for the greater number of publications focused on the co-application of the two factors compared to those on heat alone.

The EN 12280-3:2002 standard defines conditions for accelerated ageing procedures referred to as environmental ageing (British Standards Institution, 2002). The temperature is also in this case at 70 °C but, differently from the standard for heat ageing, in this case the relative humidity must be set at 95%. Since the procedure is specified for coated fabrics and is commonly carried out on man-made products, it would be expected that the effect on leather, being a natural proteinaceous material, is greater. However, comparison between leather and synthetic leather during degradation has not been documented. Likewise, E-Leather® has not been subject to this procedure in a systematic way and information on its behaviour when the substrate is under stress is not available.

5.2.1.3 UV Irradiation

UV radiation comprises the region between 10 and 400 nanometres of the electromagnetic spectrum. This radiation is sub-divided into smaller spectral regions, such as UVA and UVB that can interact with some components of objects, e.g. polymers and dyes. As a result, the exclusion of UV radiation is of primary importance in museums and is also central in other contexts. For example, car seats can be exposed to it when they are parked in the open sun and in some cases this can lead to photolysis of dyes (Timar-Balazsy and Eastop, 1998). Moreover, UV is able to induce what is called photooxidative degradation in polymers that in extreme cases results in destruction of the polymeric chain (Yang *et al.*, 2002; Zhang *et al.*, 2013).

UV is able to damage the aesthetics of leather and related materials by modifying the colour of exposed surfaces. Authors reported on this topic for both leather and synthetic leather (see section 5.1.1) but, again, no comparison between the substrates has been published. Moreover, there is no evidence of E-Leather® studies on this subject and accordingly it is important to understand how sensitive the material is to UV radiation.

5.2.1.4 Test Conditions within this Project

The first accelerated ageing test was carried out following the Sahara temperature test conditions (115 °C) but limiting the test time to 56 hours. This was done before defining the length of each interval in order to evaluate whether the 56 hours timeframe was appropriate to induce any damage on the substrates. Also, some of the samples were overlapped during the first experimental procedure to macroscopically evaluate possible issues encountered during the following accelerated ageing tests. After this test, the following temperatures were selected for the study:

- 70 °C;
- 115 °C;
- 150 °C

For clarity, these treatments will be named H70, H115 and H150 from this point forward. The decision of including an accelerated ageing at 150 °C was taken to evaluate if drastic changes happened in all the studied materials once they were subject to extreme conditions. This temperature does not typically occur under normal usage conditions, but it is interesting to understand how the materials would react and how they will potentially behave in the long-term.

Four measurements were collected to conduct the investigations on the samples at increasing times and each interval had the length of 56 hours up to 168 hours. All the samples were removed from the ageing chamber after each interval and kept at standard conditioning temperature and humidity prior to further analyses.

This enabled the first signs of degradation to be established and to evaluate whether the changes were occurring at a constant rate or not. In addition, by selecting three intervals it was possible to follow the evolution of the degradation and assess whether or not changes occurred within that small range of time.

To assess the effect of high temperature and relative humidity the following parameters were selected:

- 70 °C and 90% RH.

For clarity, this treatment will be named H+RH from this point forward. Four measurements at intervals of 56 hours were collected as in the case of heat ageing in order to perform comparisons between the values of each procedure. All the samples were removed from the ageing chamber after each interval and kept at standard conditioning temperature and humidity prior to testing.

Finally, the irradiance value for the UV test was selected as 0.77 W.m^{-2} with a lower temperature and relative humidity compared with the studies previously described. These conditions were considered more appropriate in order to limit changes in the substrates due to factors other than UV. The black panel temperature was set at 23 °C and it reached 50 °C within the first hour from the beginning of the test. The relative humidity in the apparatus was set at 50%. Also in this case four measurements at intervals of 56 hours were collected as in the case of heat ageing up to 168 hours. Likewise, all the samples were removed from the ageing chamber after each interval and kept at standard conditioning temperature and humidity prior to testing. For clarity, this treatment will be named UV from this point forward.

5.3 Early Accelerated Ageing Simulations

Initial tests to assess the effect of ageing factors on the different materials were conducted in a convection oven. Heat ageing was conducted on samples of TL, SY, EL2 and EL3. Dry heat affected to some extent all the leather-based substrates (TL, EL2 and EL3) while it had a limited impact on synthetic leather.

Figure 5-1a and Figure 5-1b show two samples of leather before and after the early accelerated ageing procedure (115 °C for 56 hours), respectively. The samples on the right side of each picture were not aged whilst the material on the left was subject to the Sahara Test.

a) b)

Figure 5-1: Samples of TL cut for visual (a) and crumple-flex (b) before (right) and after (left) Sahara test.

An obvious reduction in the samples size was noticed following heat ageing and it is clearly visible in Figure 5-1. Except for the top coating TL was almost entirely made of leather, tanning agents and a limited amount of additional components. Size reduction was thus considered as a macroscopic evidence of the changes in collagen fibres and dry heat can be responsible for this kind of phenomenon (Schröpfer and Meyer, 2012). However, evaluations of the size before and after heat treatment and its importance for the assessment of conservation state are rarely reported. Permanent area loss, defined by Schröpfer and Meyer (2012) as the area of the leather sample subject to the dimensional variations, was calculated by measuring the size of unaged and aged samples. The permanent area loss (PAS, see Equation 5-2) was 8.7%.

$$\mathrm{PAS} = \frac{(\text{Area before treatment} - \text{Area after treatment})}{\text{Area before treatment}} \times 100 \qquad (5\text{-}2)$$

Heat deterioration occurs within a wide range of temperatures and according to a number of variables, such as water content in the sample, tanning method, relative humidity in the testing environment. TL size reduction was attributed to the effect of dry heat on the leather. In fact, Schröpfer and Meyer studied the effect of dry heat and climate variations on leather size and shrinkage temperature and underlined that dry heat is the main responsible for the breakage of hydrogen bond that stabilise the structure leading to deterioration (Schröpfer and Meyer, 2012). When water in the mesopore regions of the collagen fibrils evaporates, following an increase in temperature, the whole structure contracts and shrinkage occurs. This happened because of the collagen triple helix denaturation during heat treatment, when hydrogen bonds are broken and the structure is subject to compressional forces (Schröpfer and Meyer, 2012). Further effects associated with the degradation of collagen fibres are mass and thickness variation and increase of bending stiffness. KES-FB2 and KES-FB3 were selected to investigate variations of these properties after ageing (see section 5.4).

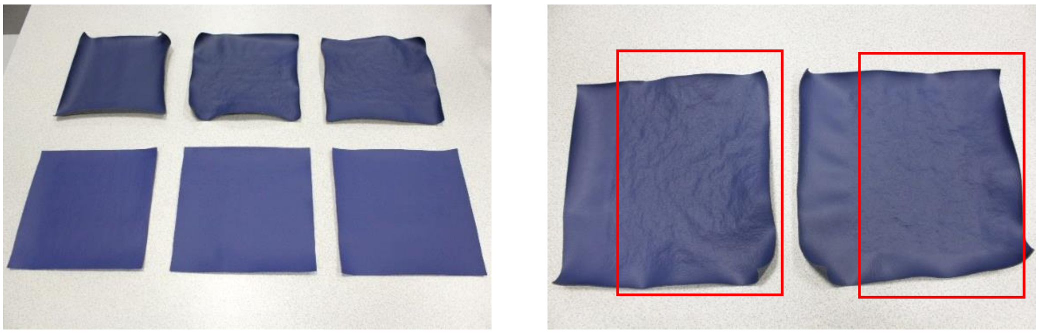
The shrinkage of TL samples, tanned by chrome-free method, indicated that dry heat had a clear effect on the fibrous substrate. The behaviour of chrome and chrome-free leather is different, the former being more stable in presence of humidity and the latter less influenced by dry heat (Meyer *et al.*, 2006). The effect of dry heat was thus considered of particular interest for the comparison of TL and E-Leather® samples because of the different tanning method used for the leather production.

Despite the size reduction being clearly visible in all TL samples, the area of the skin where the samples were taken from had a great effect. This was particularly clear on samples cut for crumple-flex testing (Figure 5-1b) because they required large areas of material and, despite the effort to sample in accordance with the standards, the leather available did not permit this sample size. As a consequence, intrinsic irregularities lead to different deformations related to the direction of the fibres in the skin. Sampling location for the TL mechanical tests, in particular for tensile tests, were kept consistent for the following accelerated ageing in order to minimise this issue.

Colour variation is another indicator of changes occurring within materials and is of primary importance in museum contexts. According to Ollè *et al.* (2012), UV is the parameter that mostly affects chrome-tanned leathers, while humidity modifies to a greater extent wet-white. In TL material subjected to H115 a colour change was visible to the naked eye but in this case this was only attributable to high temperature. The reason of this change could have been associated to factors such as alteration of the coating chemical structure or less likely transformations of the pigment and none of these reasons could have been excluded without thorough examination. Assessment of the colorimetric values and ATR-FTIR were considered as valuable techniques to evaluate possible causes of this phenomenon.

Synthetic leather was expected to be more stable under moderate heat ageing than leather and, in fact, SY did not show any appreciable change in appearance after the modified Sahara test. However, it was not possible to state that heat had not produced any other effect on mechanical and chemical properties. The use of ATR-FTIR, tensile tests and KES in the following stages of the research was considered beneficial to assess the actual mechanical behaviour of leather and fabrics during the ageing process.

The preliminary examination of E-Leather® accelerated ageing comprised the analysis of thickness, bending and extension variation. This was decided to address the problem of lack of data on the degradation of leather composites. EL2 and EL3 were placed in the oven distributing the samples so that some of them were overlapping with each other. This position would reproduce situations where two overlapped pieces of E-Leather® are laid on a surface under hot conditions, e.g. in train or car seats under the sun. The effect of this ageing on the samples is presented in Figure 5-2.



a) b)

Figure 5-2: a) EL3 (top) and EL2 (bottom) after heat ageing at 115 °C. b) EL3 (top) after heat ageing at 115 °C showing the typical "elephant skin" effect.

EL2 (Figure 5-2a, bottom) presented a flat, nearly unchanged in colour coating on those areas where samples were not overlapped, while the surface was slightly rougher in the overlapping regions. In addition the samples seemed less flexible than before, probably as a combination of the stress collagen fibres were subject to after water desorption and rearrangements of the polymeric coating.

Among the four tested substrates EL3 was the material that showed the greater changes after dry heat degradation. First of all, a colour difference was noticed and the overlapping samples showed marked ripples in the overlapped areas accompanied by signs of stress along the borders of these areas. This is particularly evident when assessing the sample on the right in Figure 5-2b. The size of the samples seemed different, smaller if compared with the unaged samples, but the sample rippling effect did not allow an accurate measurement. Moreover, all the samples were rigid, in particular the overlapped ones, and much less flexible and less soft to the touch than the unaged substrates.

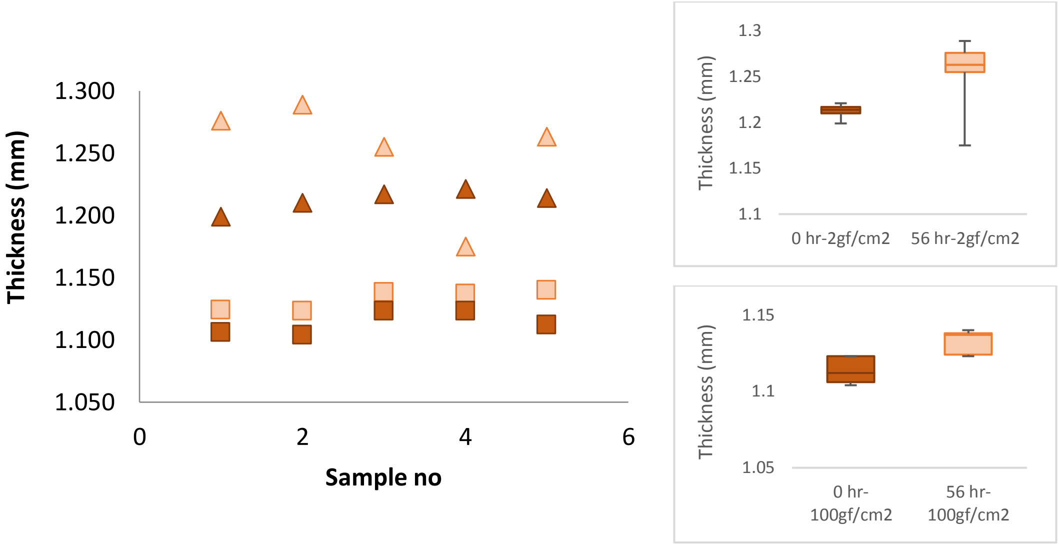


Figure 5-3: Results of FAST 1 conducted on EL2 before (dark orange) and after ageing (light orange), using two pressures: 2 gf/cm², triangular markers, and 100 gf/cm², square markers. The scatterplot shows all measurements (left); the box-and-whisker plots show the difference in the mean thickness values

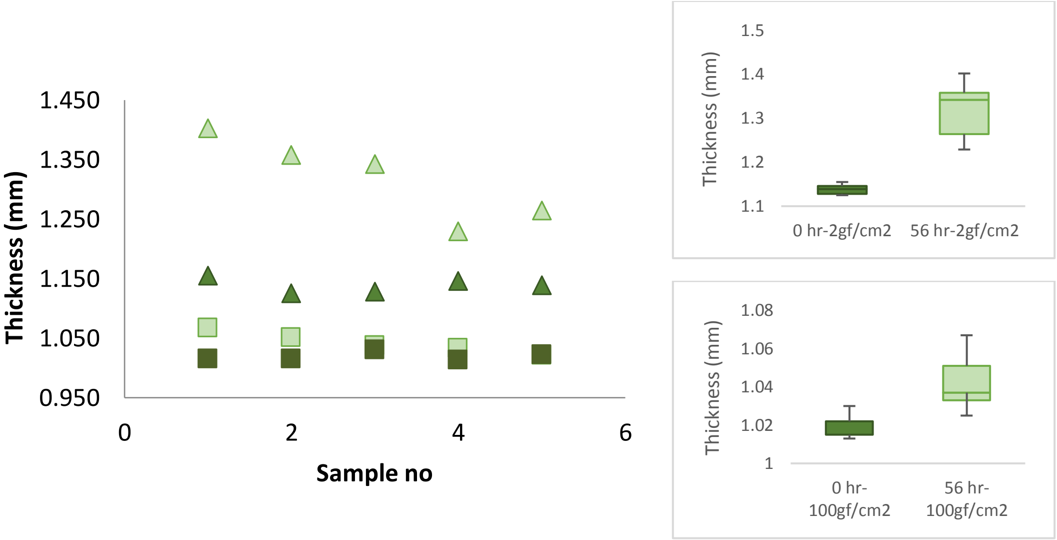


Figure 5-4: Results of FAST 1 conducted EL3 before (dark green) and after ageing (light green), using two pressures: 2 gf/cm², triangular markers, and 100 gf/cm², square markers. The scatterplot shows all measurements (left); the box-and-whisker plots show the difference in the mean thickness values

Due to the total lack of literature regarding composite leather fibre products, a preliminary study of E-Leather® was carried out by using the FAST system. Results of the FAST-1 evaluation before and after the modified Sahara test on EL2 and EL3 are presented respectively in Figure 5-3 and Figure 5-4. Five repetitions for both EL2 and EL3, in warp and weft direction, were performed. Thickness values before ageing were generally consistent and characterised by low variances. These values were representative of the whole roll of composites and this constitutes a significant difference when compared to leather. In fact a research conducted on ovine leather by using the FAST system has pointed out the differences in thickness, as well as other properties, depending on the distance from the spine and the sampling orientation (Lange *et al.*, 1999).

A general increase of the mean values of thickness was measurements on both EL2 and EL3 samples after the modified Sahara test. Moreover, if before ageing the variance of the thickness values was limited, this difference also tended to increase after the procedure. These variations were likely to be due to the increased roughness and stiffness of the samples, particularly in the case of EL3. In fact for the EL2 sample the thickness increased from 1.212 mm to 1.250 mm and from 1.113 to 1.132 after the application of 2 gf/cm^2 and 100 gf/cm^2 measurement force, while in EL3 it increased from 1.138 mm to 1.319 mm and from 1.019 mm to 1.046 mm, respectively. The analysis was complicated by the sample rigidity despite the application of a load.

The bending test analysis provided inconsistent results characterised by great variability within the same set of samples both before and after ageing. Accordingly a greater number of repetitions was required. The FAST-2 analysis requires each sample to be placed between a flat surface and a metal plate and it must slide over the flat surface while a wheel measures the movement and the length of the fabric when detected by the sensor (see Chapter 3). However, E-Leather® did not slide properly and it was difficult to keep the samples in place. EL2 was found to have slightly decreased its bending length in the machine direction (MD), from 46.33 mm to 41.50 mm, while it was almost unchanged in the cross-machine direction (CD, from 40.50 mm to 41.00 mm). EL3 presented much lower values than EL2 in the MD (11.33 mm) and similar values in the CD 42.33 mm. After ageing, the bending rigidity was so high in the CD that it was not possible to conduct the test, and a marked reduction of bending length was also registered in the CD (10.33 mm).

The FAST-3 Extension analysis, with the measurements performed at 5 and 20 gf/cm, did not provide any valuable information (0.0% extension). This made irrelevant the comparison of formability before and after ageing, because formability is calculated by using the two initial extension values in combination with bending rigidity (De Boos and Tester, 2005). However the third measurement, at 100 gf/cm, provided some significant differences. The extensibility of EL2 remained unchanged in the MD and dropped from 1.13% to 0.7% in the CD. EL3 showed a limited extensibility increase along the MD (from 0.2% to 0.4%) and a marked reduction in the CD (from 1.27% to 0.8%).

Some preliminary conclusions were drawn after these early results. The colour of the coating was moderately different compared to the unaged sample and also the fibrous layer colour became yellower. Analysis of the colorimetric values and ATR-FTIR were considered appropriate to quantify these variations and provide answers to questions regarding colour change. Measurement of pH was also considered important to evaluate possible acidification or basification processes occurring within the samples after ageing and possibly related with changes of the fibrous layer.

A general increase in the surface irregularity was noticed after ageing, and one of the possible reasons for this irregularity was identified in the stiffening of the fibrous layer. Both EL2 and EL3 presented a certain degree of surface irregularity, but it was much more obvious in EL3. It is possible that partial denaturation of the collagen molecule took place during the dry heat ageing procedure, but this was unlikely to be the only phenomenon able to produce that type of damage. In fact, if the effect was only due to the collagen molecule, the deterioration of EL2 should be comparable to the one of EL3.

A possible reason for the enhanced effect was the presence of flame retardant in the EL3 matrix which induced the greater damage in both the fibrous layer and coating. When samples were overlapped, the volatile fraction of the flame retardant in the bottom sample was not able to ‘escape’ from the surface top coating because it was trapped by the fibrous layer of the upper sample (Figure 5-5).

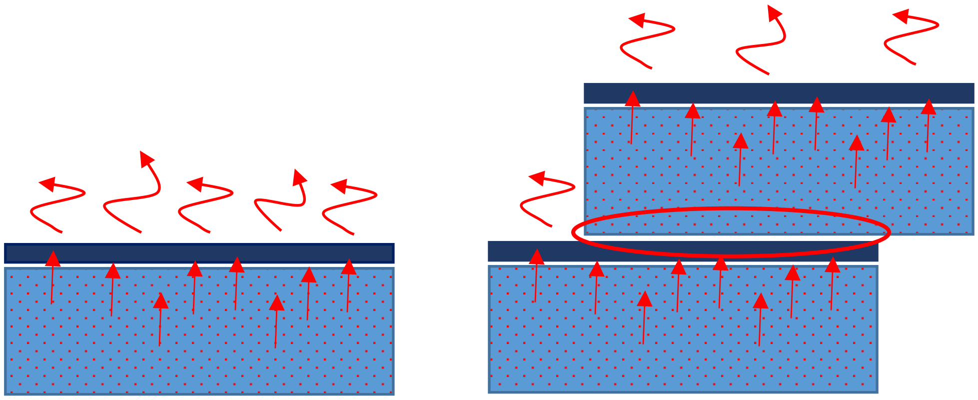


Figure 5-5: (Right) Schematic representation of EL3 cross-section with volatile component of flame retardant (red arrows). (Left) Two overlapping EL3 samples and area of higher damage in evidence.

Further research undertaken suggested that this hypothesis can be confirmed but unfortunately the results cannot be reported for confidentiality reasons. Even if the thickness variation was measured and it was possible to quantify the change of this parameter, it was noticed that the unevenness of the substrate made the test more difficult and a large number of measurements were collected before obtaining a satisfactory level of consistency. For this reason, image processing and KES-FB4 were selected to quantify the roughness change in the following research stage whilst KES-FB2, KES-FB3 and tensile strength were selected to quantify bending, compression and tensile properties more accurately.

5.3.1 Crumple-flex Tests

Examination of the combined effect of crumpling and flexing on the both unaged and aged samples showed that the TL material performed worst on this preliminary test, while the other substrates were able to preserve their integrity despite some minor issues.

Fatigue tests are especially important in industry because they assess the time durability of the materials performances (Milašienė and Bubnytė, 2007). Crumple-flex provides an insight into the serviceability of products used for car seats and garment. After 9,000 crumple-flex cycles, the PU laminated fabrics studied in previous research presented the first evident signs of deterioration with small cracks formed in the corresponding alignment with the pits in the lamination layer (Padleckienė and Petrulis, 2010). It was expected that leather and synthetic leather were more durable than the laminated fabrics by virtue of their thicker and denser structure. Likewise, it was expected that TL performed better than SY because of the compact nature of the collagenous fibrous layer. However, other factors influence the length of use, such as the presence of persistent wrinkles that can be detrimental for products appearance.

A summary of the damage status of each sample, determined on the basis of clause 6 on the relative standard (British Standards Institution, 2009) and classified accordingly (0, none; 1, slight; 2, moderate; 3, severe), is reported in Table 5-1.

	Before ageing			After ageing		
	5000	9000	13000	5000	9000	13000
TL	1	1	1/2	1/2	1/2	2
SY	0	0	0	0	0	0
EL2	0	0/1	0/1	0/1	1	1
EL3	0/1	1	1	1	1/2	2

Table 5-1: Flex resistance of TL, SY, EL2 and EL3 samples at increasing number of crumple-flex cycles

With the exception of SY, that was unaffected before and after the ageing procedure, the resistance of all samples to crumple-flex decreased after ageing. TL started to show initial signs of bending lines and wrinkles after visual inspection at 1,000 cycles and this was confirmed after inspection after 5,000 cycles. At that stage the surface was carefully inspected and it was assessed that despite the wrinkles no cracks were present. The same happened after 9,000 cycles that, as described above, is a crucial step for coated and laminated materials. A further increase in TL wrinkling was noticed after 13,000 cycles, but also in this occasion it was possible to assess the coating integrity. TL, consisting of treated animal skin, is naturally flexible and resistant to continuous flexing stress (Milašienė and Bubnytė, 2007). However, the appearance of permanent wrinkles that remain after the stress has been removed is often considered an unpleasant characteristic. These wrinkles form in the areas most exposed to continuous movement and tend to persist after a certain number of repetitions (Padleckienė and Petrulis, 2010).

After the modified Sahara test the substrate seemed partially damaged and prone to cracking, though it did not happen. In general, the trend of the damage was consistent with that observed before ageing, with the only difference being that the values were increased of half unit in the damage scale. Normally, higher temperatures introduce greater stresses within polymer coatings applied to leather that then become more prone to damage (Milašienė and Bubnytė, 2007). It is likely that the conditions TL was subject to were still too mild to trigger significant fatigue degradation in the samples.

SY was the material that performed better in terms of damage ranking because it did not show any evidence of damage or persistent wrinkles. Not only all the samples before ageing were consistently flat and even after 13,000 cycles, but the same pattern was repeated after ageing. This demonstrated that SY was able to maintain an outstanding fatigue resistance after being exposed to heat ageing.

EL2 and EL3 performed in a way that can be considered intermediate between TL and SY, with EL2 closer to SY performances and EL3 to TL. EL2 passed the initial inspection stages without any major sign of bending lines and wrinkles and only started to exhibit permanent wrinkles after 9,000 cycles. Moreover the same wrinkles found at 9,000 were also present after 13,000 cycles and no cracks were detected. The same trend noticed before ageing was identified after it, but as in the case of TL the ranked score was half unit higher. EL3 exhibited the first bending lines after 1,000 cycles and persistent wrinkles after 3,000. The damage assessed until 9,000 cycles tended to increase and then it reached a plateau. This trend changed in the aged samples, where the damage increased steadily until the final stage at 13,000 cycles.

It was noticed that the reverse side of E-Leather® samples presented areas where the fibres seemed looser than before the crumple-flex test. These areas corresponded almost exactly to the bending lines noticed on the coating side (Figure 5-6). SEM images underlined the presence of areas characterised by fibre looseness that can become a weak point in the fabric structure.

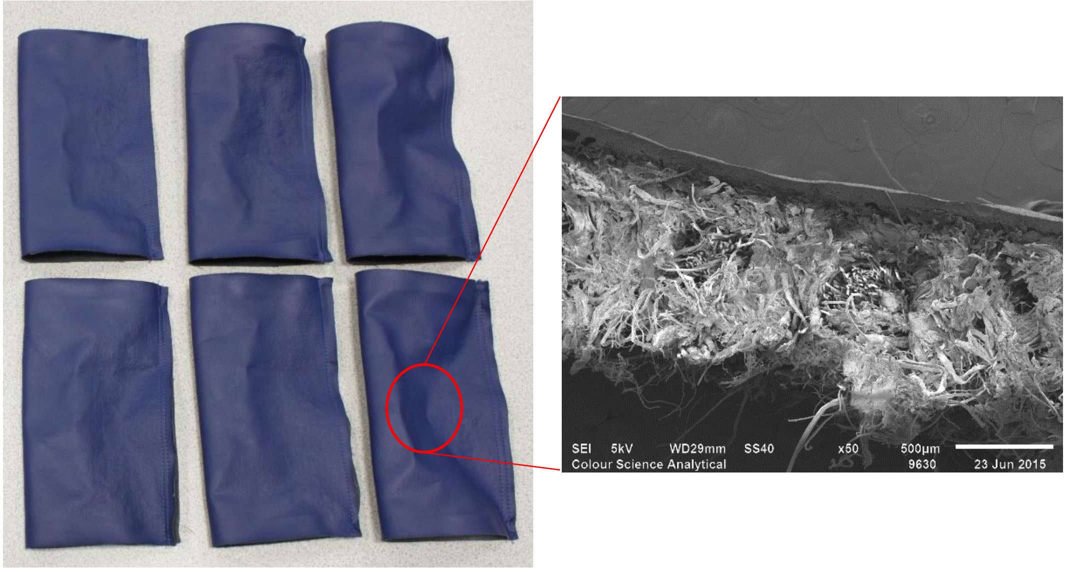


Figure 5-6: EL3 samples after crumple-flex test and cross-section showing loose fibres in correspondence of bending lines

The nature of these fibrous layer areas within the composite structure suggested that items made of E-Leather® might present a visibly intact surface after use, but their sub-surface fibrous layer might be in highly damaged condition. This result is particularly important for museum objects, and even more in the case of objects that cannot be sampled, because the integrity of the fibrous layer cannot be assumed even if the surface coating is in a good conservation state.

Crumple-flex test permitted the assessment of the overall appearance of the samples after fatigue testing. Factors such as the presence of bending lines and wrinkling were estimated and it was found that cracking, flaking and discoloration did not occur. This indicated that a greater number of cycles would be required to increase the degree of damage, but this would be out of the purpose of this thesis. Furthermore, a large amount of material was necessary to conduct the test and, as seen in the case of TL, it was not always possible to conduct the test on samples collected following the official standard position. Because of these reasons it was decided to preserve the available material to conduct consistent investigations and comparison of all the substrates, hence removing crumple-flex from the list of the tests to be carried out. However, the procedure provided valuable results that permitted the comparison of the substrates performances and highlighted possible weaknesses of E-Leather®.

5.4 Accelerated Ageing on Leather and Related Materials

5.4.1 Appearance Observations and Analysis

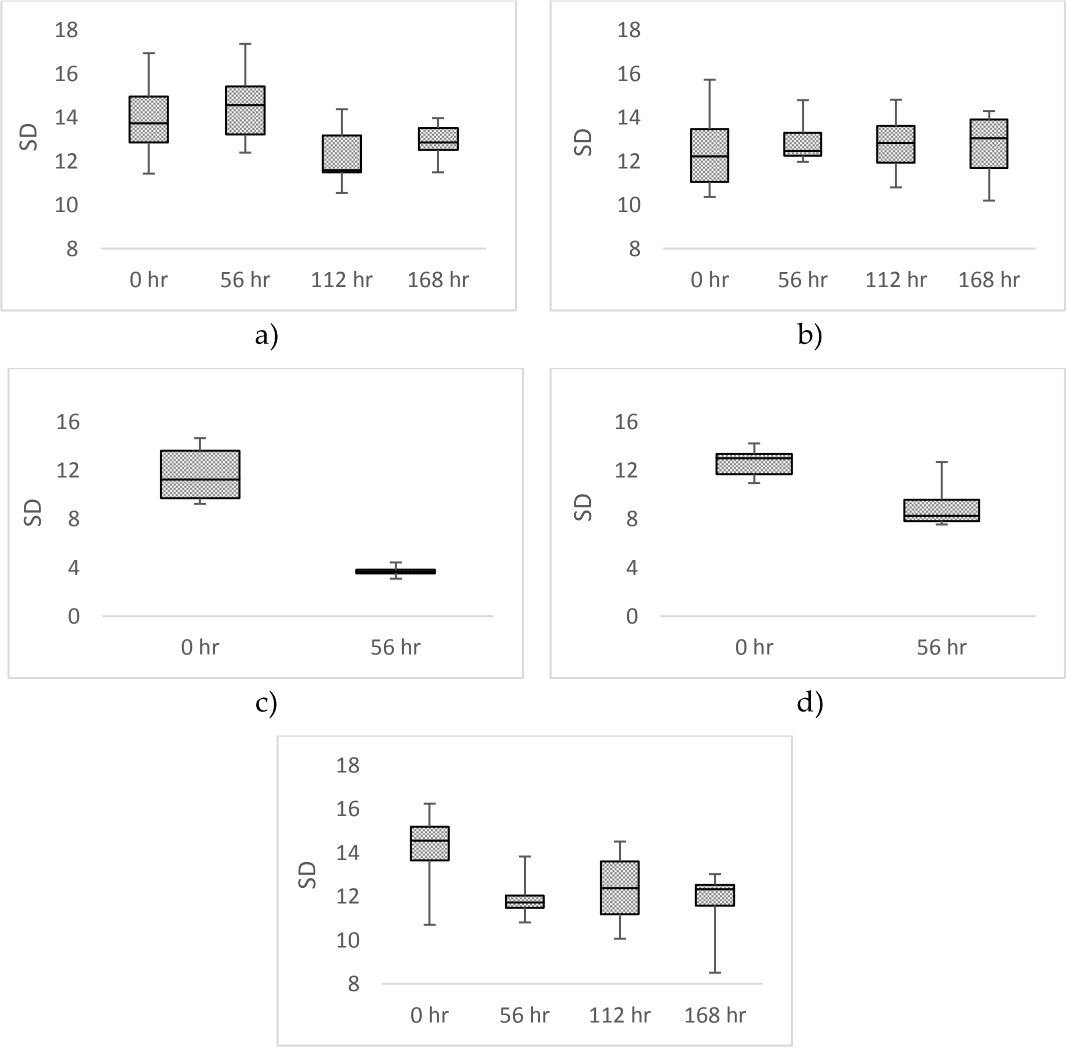
5.4.1.1 Roughness Detection via Image Capture and Simple Processing

The roughness of materials can be characterised by means of image processing techniques and was examined in this study to assess appearance changes in samples after accelerated ageing. Gore *et al.* (2004) previously discussed the use of image capture and processing techniques to investigate leather surface while Mhute *et al.* (2016) reported on the use of profilometry for diagnostic analysis of leather. The macroscopic change in leather surface with ageing, however, has been rarely studied. Wýstenbecker *et al.*(1997) presented one example of this type of study where topographic analysis was conducted via surface profiling devices to detect changes in artificially aged leather samples. Applying photography and image processing to detect changes in surface profiles could be useful to identify roughness variations due to deterioration.

Thornbush (2014) applied digital photography and image processing to evaluate roughness on geological samples exposed outdoors. She stated that the standard deviation values of lightness are related to surface texture, which allows users to evaluate and compare similar samples under different conditions. There is a potential for this approach to be used in leather and textiles context, therefore the current study started from this point with the objective to simplify the procedure and assess its reliability.

Three measurements were taken from each sample (bottom, median and top positions) before and after accelerated ageing and the resulting grey scale values, measured on screen, were used to obtain the greyscale standard deviation (SD) values. Figure 5-7, Figure 5-9, Figure 5-11 and Figure 5-12 show the box-and-whisker plots of the different leather-related materials. Differences in the absolute SD values for unaged samples (0 hr) are seen in some cases and are particularly significant for leather specimens (e.g. Figure 5.15). These variations are due to the variability of the material. However, these variations do not impact on the validity of the study since the recorded values for aged samples for each ageing condition also includes the recorded value for the exact same sample before ageing (0 hr). Therefore, SD values within each condition are directly comparable, and trends across ageing conditions are also comparable irrespective of staring (unaged sample) SD value.

Figure 5-7 reports the values of SD for TL samples at different ageing times and after being subject to different ageing conditions. The box-and-whisker plots showed that the effect of accelerated ageing on the sample roughness was particularly evident in samples after H+RH ageing and severe heat (H150). Also t-tests conducted on the roughness results demonstrated the significance of the change (p-value < 0.05). These two results should be interpreted as a reduction of the coating roughness due to the ageing treatment. In the case of H150 this observation was in agreement with the appearance to the naked eye of the samples, and in fact the coating appeared smoother.

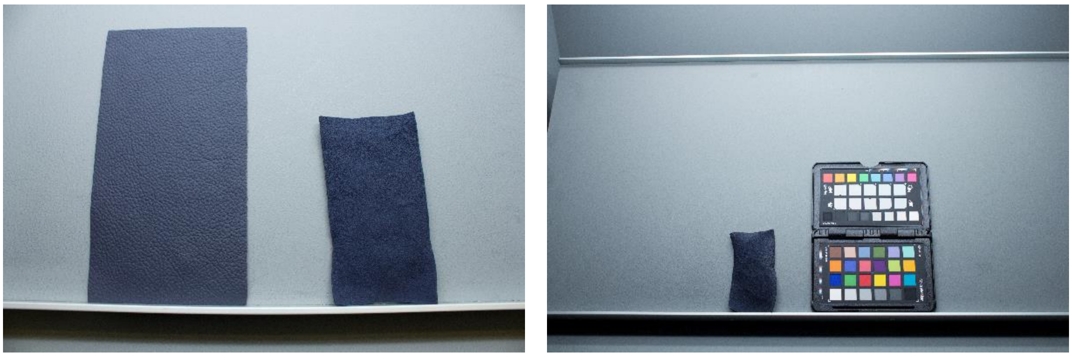


a) b) c) d) e)

Figure 5-7: Box-and-whisker plots of roughness (via picture capture and image processing) on TL samples at different stages of accelerated ageing. a) H70, b) H115, c) H150, d) H+RH, e) UV ageing

Moreover, the specimens were slightly convex and less flexible to the touch. This was interpreted as the result of a weak shrinkage on the fibrous layer that was counterbalanced from the coating. The loss of water type II and type III that are respectively responsible for the interaction between collagen fibrils and allow collagen fibres to move, and between “free water” and collagen fibres (Reich, 2005) could be responsible of this behaviour.

The effect of the combined heat and humidity exposure produced a marked shrinkage that resulted in a totally different morphology of the surface coating and a modification of the physical properties. The ageing test, that was planned to continue for further 112 hours, was suspended after the first exposure period. Macroscopic visual inspection of the samples was useful to assess the severity of the change not only in the coating but also in the fibrous layer aspect (Figure 5-8).



a) b)

Figure 5-8: a) TL samples before (left) and after (right) 56 hours of H+RH ageing. b) TL after H+RH ageing with ColorChecker

This observation, coupled with the roughness values results (p-value < 0.05), provided evidence of a drastic change in the material. The shrinkage of the collagenous substrate had in fact induced a great change in the coating appearance that was distinctly different to that exhibited after H150 ageing. The reason for the similarity of the roughness results despite differences in the appearance could be found in the change of the roughness periodicity. Bhushan (2000) explained that changes in height parameters, such as SD or roughness coefficient, refer to the variation of the profile in the vertical direction but they do not provide information regarding the horizontal contribution to the profile. This means that data regarding the frequency of the asperities or their shape and slope are not derived from the same parameter. Indeed, this represented a limitation of the method that can be partly overcome by considering multiple factors during the investigation, e.g. the peak density (Bhushan, 2000). This improvement to the method could provide further new research directions in the future.

The role of water was considered essential also in H+RH ageing. Chahine (2000) reported that in severely deteriorated leathers the water content was very low and that part of the water acting as triple helix stabiliser, type I according to Reich’s definition (Reich, 2005), can be subject to modification. The destabilisation of chrome-free leather in conditions of high temperature and humidity was already reported in Ollè *et al.* (2011). The latter also mentioned that, while the properties of chrome-tanned leather gradually worsened, in chrome-free samples the decrease was rapid and it resulted in carbonised leather after 14 days. These studies mainly looked at leather from a microscopic point of view, but the macroscopic appearance of the samples subject to those tests was not discussed. Therefore the results of this work could constitute the macroscopic manifestation of the phenomenon generally studied in a different scale.

The remaining accelerated ageing had a lesser impact on the roughness of the samples. The results of H115 ageing seemed to have influenced the material less than H70, which was the opposite of the behaviour expected. The former presented a gradual increase of the roughness median value that in the long term did not affect the material appearance (p-value > 0.05). The latter showed an initial increase of SD followed by a decrease. After statistical comparison of the datasets at different ageing times, it was noticed that the only significant difference occurred in the interval 56 – 112 hours. This means that the ageing affected the samples to a greater extent in that time frame, but finally the variation returned to standard values.

UV ageing was also responsible for gradual reduction of SD values from an initial 14.18 to 11.67 grey value units. This trend is likely to be connected to the flattening of the leather fibrous layer during the ageing procedure. Samples were in fact mounted on the sample holder that secured the specimen in a flat and vertical position, introducing a consistent constrained compression of the fibrous layer. This type of stress, in the presence of heat and humidity within the chamber, can be responsible for the flattening of the fibrous layer and, at the same time, of the coating. During humidification, a treatment used for flattening or moisturise fragile textiles and leathers, tensioning is accepted as a common practice to control water evaporation avoiding the fibres sticking together (Woods, 2011).

The TL results were different from those of the SY samples. Figure 5-9 reports the box-and-whiskers graphs for synthetic leather. At a first glance the roughness variation of the samples seem to be much less affected by the accelerated ageing procedures than in leather samples. H150 was the only ageing treatment that produced drastic changes in the coating, while H70 and H+RH showed less obvious variations of the SD value. H115 and UV ageing did not affect significantly the roughness of SY, apart for the final stage of the UV procedure (p-value slightly below 0.05).

Heat ageing at 70°C, H70, induced significant changes during the third stage of the ageing but the distribution of the results before and after this stage remained almost unchanged. Variations in the coating after H+RH were much more obvious. Differences in the material behaviour when subject to this type of ageing could be caused by hydrolytic breakdown that has been recognised by many authors as the predominant degradation pathway of ester-based PUs (van Oosten et al., 2011; Lovett and Eastop, 2014). Even though it was not possible to confirm the occurrence of the hydrolytic chemical degradation of the coating at this stage, it was possible to state that indicators of roughness changes started to be visible within the interval 56 – 112 hours and that remained unchanged after the following interval. While in TL the fibrous substrate was considered as the main responsible for the roughness variation, it was rather unlikely that a similar pattern was valid for SY. In fact, aramid fibres that constitute the supporting fabric of SY have been described as resistant in the short term and long term to hydrolysis (Derombise *et al.*, 2009).

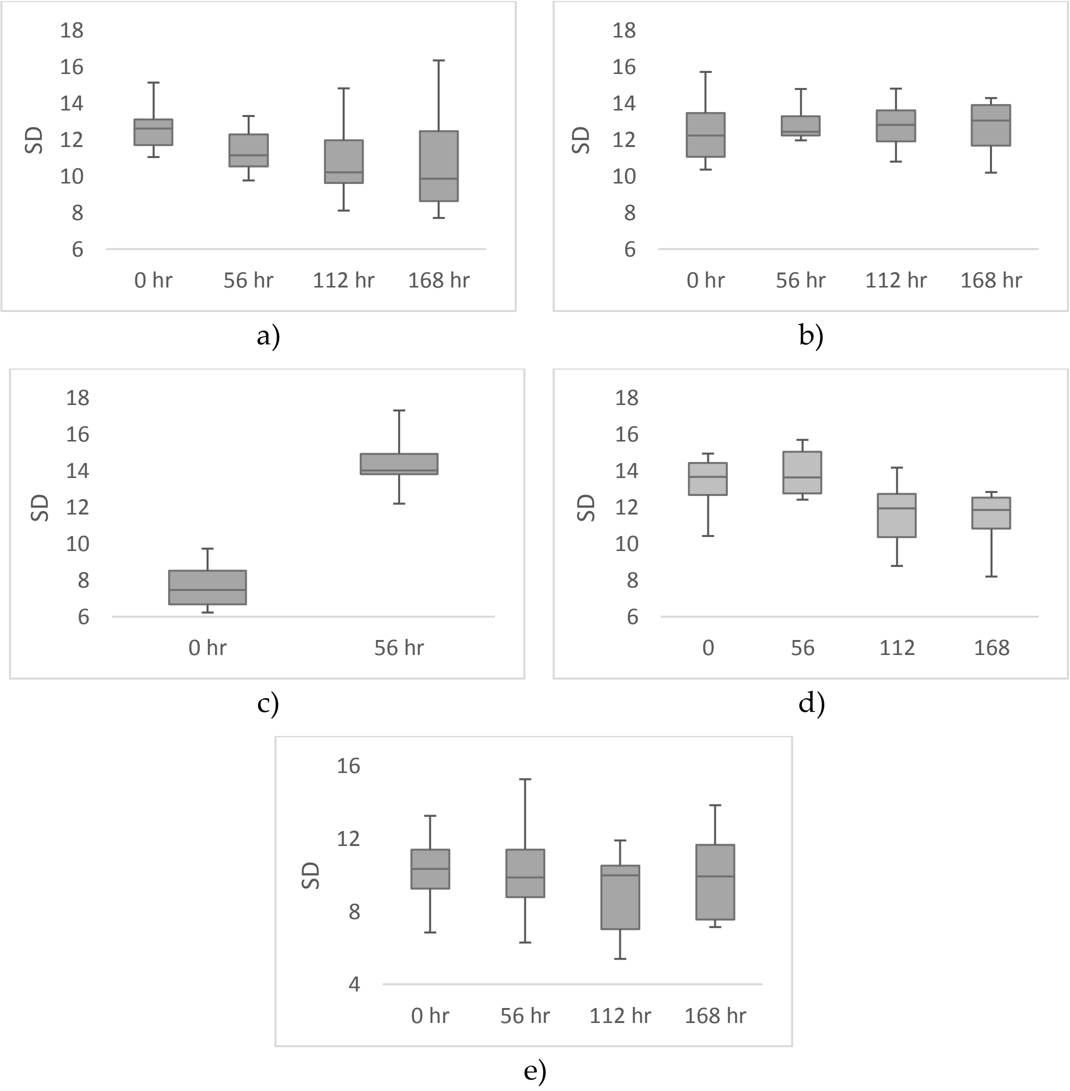


Figure 5-9: Box-and-whisker plots of roughness (via picture capture and image processing) on SY samples at different stages of accelerated ageing. a) H70, b) H115, c) H150, d) H+RH, e) UV ageing

The H150 ageing provided an example of how synthetic leather can deteriorate and to what extent the deterioration can affect the final appearance (Figure 5-10). The first important observation was related to the appearance of the supporting fabric geometry on the coating layer. Figure 5-10b indicated it was possible to recognise the pattern of the fabric underlying the coating and that after accelerated ageing it appeared to be in closer contact with the top surface. In addition, the coating was clearly glossier than before the treatment, producing the opposite effect of fading and blooming that generally leads to gloss loss.


a)

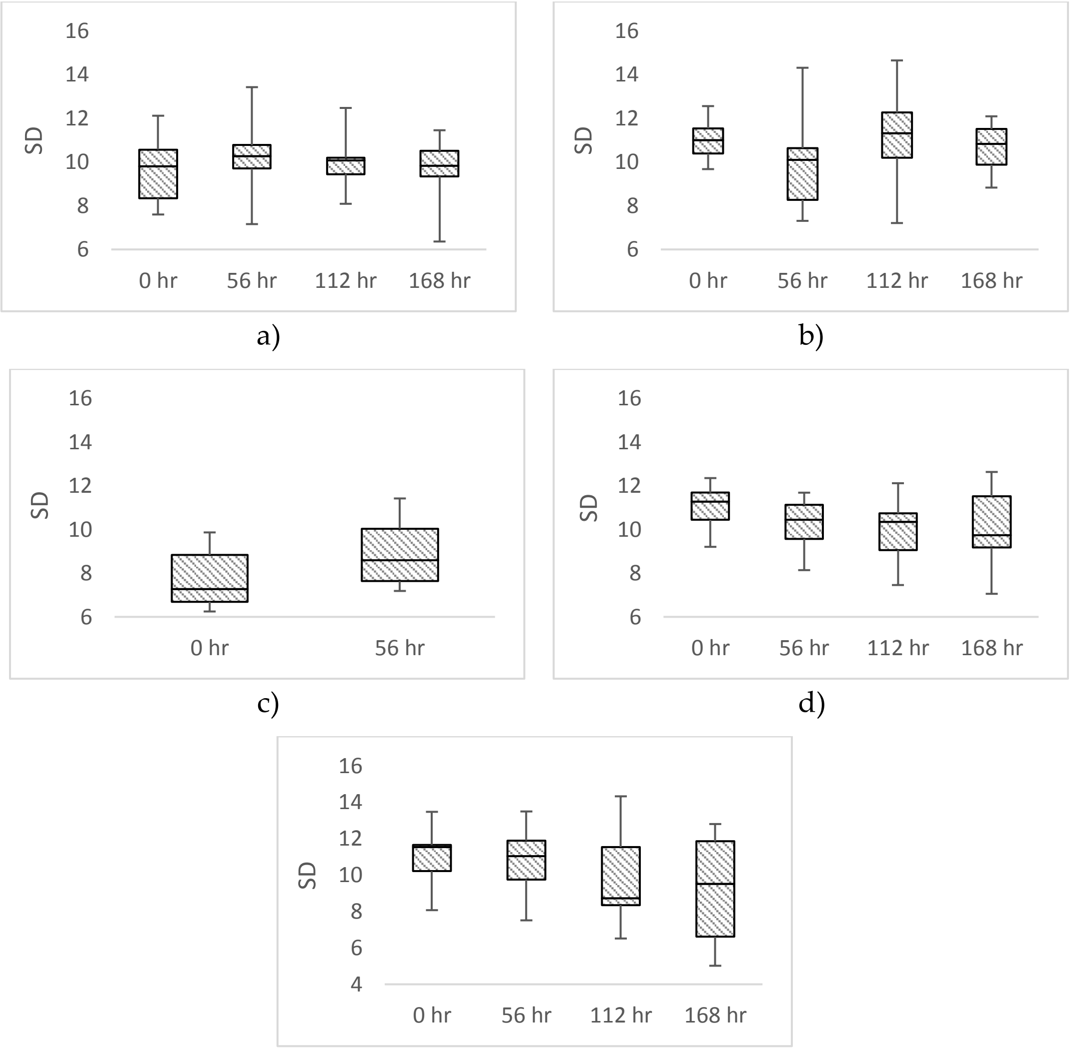
b)

Figure 5-10: SY before (a) and after (b) 56 hours of heat ageing at 150 °C

Previous studies (Hu *et al.*., 2009) demonstrated that the gloss values of some PU coatings tend to increase during the first period of exposure to artificial ageing in the presence of light and UV when mild heat and water are also present. The authors suggested that the gloss increase, related with surface roughness decrease, could be due to internal adjustments of the coating structure during the first period of exposition (Hu *et al.*, 2009). However no evidence was found in the literature of gloss increase after exposure to severe heat ageing, as observed in this work. In addition, according to the recorded SD values the roughness parameter increased from 7.73 to 14.30 grey value units, thus making the samples coarser and not smoother. The increased gloss seemed thus in contrast with the coarser surface.

Partial melting of the coating due to additives or its intrinsic chemical characteristics could provide a possible explanation for the increased roughness observed after H150, even if this would not explain the higher gloss value. However as previously seen in the case of H+RH ageing in TL samples, drastic changes in the periodicity of the roughness could produce inaccurate results when the predominant surface variation is in the horizontal direction, rather than in the vertical direction. Further work to confirm the correctness of the above hypothesis will need to be undertaken.

With respect to EL2, the results in Figure 5-11 show an overview of the roughness values after accelerated ageing. It is interesting to report that only two ageing conditions produced significant changes in the top coating, that is H150 and H+RH, with p-values of 0.05 and < 0.05, respectively, while the remaining ageing conditions did not cause substantial roughness variations.



a)

b)

c)

d)

e)

Figure 5-11: Box-and-whisker plots of roughness (via picture capture and image processing) on EL2 samples at different stages of accelerated ageing. a) H70, b) H115, c) H150, d) H+RH, e) UV ageing

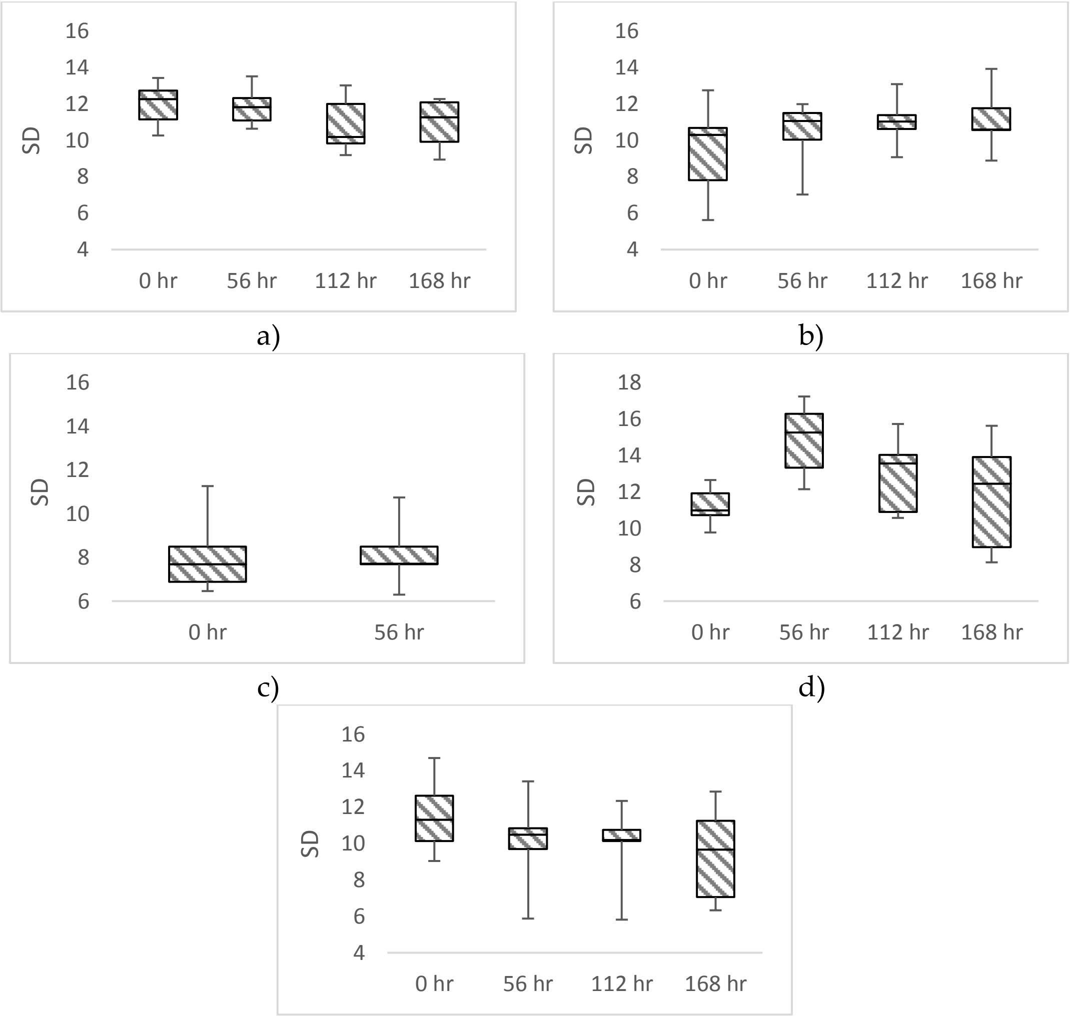
The appearance of H150 samples changed during the initial 0 – 56 hours period resulting in a "wavy" surface. This change was visible to the naked eye and was in fact successfully detected by the camera, though the difference between the roughness values was not as marked as in the previous cases. H+RH samples presented a consistent decrease in SD from the beginning of the test, but the change became statistically significant only after the second interval, between 56 and 112 hours. Despite this variation, the SD value after 168 hours was not statistically significant from the initial value, indicating a possible rearrangement of the coating during the last exposure period.

On reviewing the data some similarities emerged from the comparison of the SY (Figure 5-9) and EL2 data (Figure 5-11). Both substrates were generally less affected than the TL material by accelerated ageing procedures and, most importantly, by H+RH ageing. Interestingly, EL2 showed higher stability during ageing procedures when compared to TL. This was particularly true for the samples after H+RH procedure, where the TL material shrank after 56 hours.

This finding was relatively unexpected, because the presence of leather fibres in EL2 suggested some structural changes in the substrate as in the case of TL. In contrast to the TL material, however, the E-Leather® collagenous fibres derived from chrome tanned leather and should behave differently from chrome-free leather (Ollè *et al.*, 2012). Furthermore, the presence of a fabric core and synthetic fibres will provide strength to the fibrous layer of the composite, where the leather fibres would otherwise be loose and weakly entangled (Bevan, 2005). Even if leather fibres are an essential component of E-Leather® manufacturing process, the actual importance of chrome-tanned leather fibres in reducing the ageing mechanism cannot be assessed at this stage. It is likely that they played a part in stabilising the fibrous substrate, but the presence of the woven core was also possibly involved in this aspect.

The second substrate provided by E-Leather®, EL3 (Figure 5-12), showed a different roughness behaviour compared to EL2. The H150 results presented surprisingly very similar values before and after ageing, which considering the appearance of the samples was not expected. In fact, similar to the case of EL2 after H150 ageing, the EL3 coating appeared wavy and the smoothness properties of the substrate affected. As already explained in the case of TL, variations in roughness periodicity were not detected through the evaluation of standard deviation. Thus, other parameters would be necessary in case the variations occurred in the horizontal direction rather than in the vertical direction.

H+RH ageing of the samples provided the greatest damage visible to the naked eye. The samples showed an uncommon trend, in part similar to the one exhibited by SY during H+RH, where the SD tended to increase in the first interval and then decreased in the following two periods. The median grey value passed from 11.28 to 14.94 units between 0 and 56 hours, 13.02 units after 112 hours and 11.84 units after 168 hours, indicating that following the initial steep increase the mean values gradually decreased. ANOVA analysis confirmed the significance of the change in the SD values ($p = 0.002$) and paired t-tests were used to assess which ageing steps were the most detrimental for the samples. It was thus possible to confirm that the first two intervals were the most deleterious for the material. At a first glance the effect of this ageing procedure could appear surprising, because the same treatment did not have a comparable effect on EL2.



a) b) c) d) e)

Figure 5-12: Box-and-whisker plots of roughness (via picture capture and image processing) on EL3 samples at different stages of accelerated ageing. a) H70, b) H115, c) H150, d) H+RH, e) UV ageing

However, the main difference between the two substrates in terms of composition lies in the presence in EL3 of a brominated flame retardant. As already seen with the formation of the “elephant skin” during the initial accelerated testing, it seemed clear that a component of EL3 was negatively interacting with other components of the sample under ageing conditions. Further studies on this subject will be reported in the following sections.

Also with the H115 ageing conditions there was a roughness increase (Figure 5-12b) that was also clearly perceptible to the naked eye. ANOVA analysis was also conducted for the samples after H70 and UV ageing and it was demonstrated that the roughness values before and after ageing were not statistically different (p-value > 0.05).

These results showed that the use of simple image capture analysis, with defined settings and in presence of appropriate reference materials could be effectively used as a mean to assess an object's conservation state or test the progress of their deterioration. The method was tested on flat, not-in-tension samples, because the analysis of 3D objects would require more sophisticated calculations that could become a deterrent, for example, for small institutions undertaking this analysis. In fact, polynomial texture mapping (PTM) and reflectance transformation imaging (RTI) are examples of image capture and processing techniques that are becoming increasingly popular in heritage studies (Dellepiane *et al.*, 2006; Earl *et al.*, 2010). These techniques allow the tri-dimensional reconstruction of entire artefacts and provide indispensable information for documenting current conservation state. However extremely large datasets need to be manipulated (Earl *et al.*, 2010), hence expert professionals and powerful computers are required to conduct analysis. The use of a common documentation tool, photography, as a reliable means to detect degradation signs would permit virtually any museum to carry out preliminary, consistent investigations of samples using a limited budget.

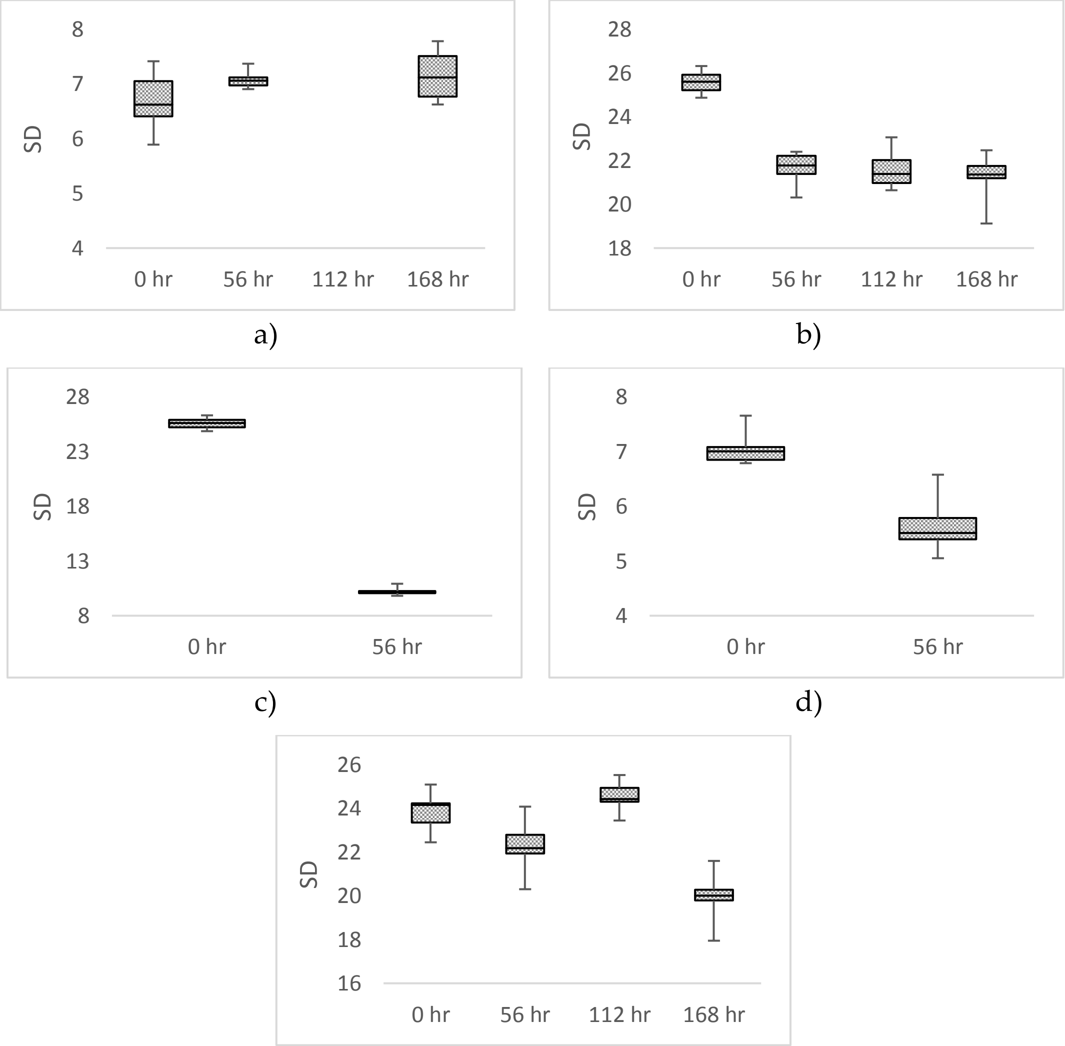
5.4.1.2 2D scans

Scanning technologies are widely used to conduct studies on artworks and museum objects, particularly in the case of library materials (Brown and Seales, 2000). In the last two decades, efforts have been made in order to improve the quality of digitalised images and improve collections accessibility. This has produced a shift from 2D images to 3D imaging techniques that are now under investigation in many conservation fields (Barone *et al.*, 2012). Despite their undeniable importance and the need for continuous research in this area, the 3D imaging is still rather expensive and cannot be used by many institutions. The application of flatbed 2D scanners in this context, as in the case of photography, could help to identify initial morphological changes while documenting the state of preservation of collections.

The same principle described to measure the roughness after photographic analysis was applied for 2D scans. In this case nine measurements were collected for each sample after each accelerated ageing interval, instead of three measurements on three different samples, and the resulting grey scale values were used to obtain the standard deviation (SD) values. Figure 5-13, Figure 5-14, Figure 5-15 and Figure 5-16 show the box-and-whisker plots of the different leather-related materials. Differences in SD values of unaged (0 hr) samples and corresponding aged samples have their origin in the modification of the exposure values of the scanner (see Section 3.2.2.1.2). However SD values within each condition are directly comparable, and trends across ageing conditions are also comparable irrespective of measured absolute SD value.

Figure 5-13 reports the box-and-whisker plots of TL samples after ageing and the results were compared with those obtained after photographic analysis. The effect of high heat and humidity ageing and severe heat affected leather the greatest (p-values < 0.05), as already pointed out by the photographic analysis. Also in this case the roughness reduction after H150 ageing was in agreement with the hypothesis of a shrinkage on the fibrous layer being counterbalanced by the surface coating, and macroscopic observations of the samples confirmed a surface smoothing.

The material shrinkage resulting from H+RH ageing, which changed the coating appearance, was also detected through 2D scans. The change in roughness periodicity, already discussed above and in agreement with Bhushan (2000), affected the test and underlined the need for further studies to include variations of the period in the roughness calculation.



a) b) c) d) e)

Figure 5-13: Box-and-whisker plots of roughness (via 2D scanning) on TL samples at different stages of accelerated ageing. a) H70, b) H115, c) H150, d) H+RH, e) UV ageing

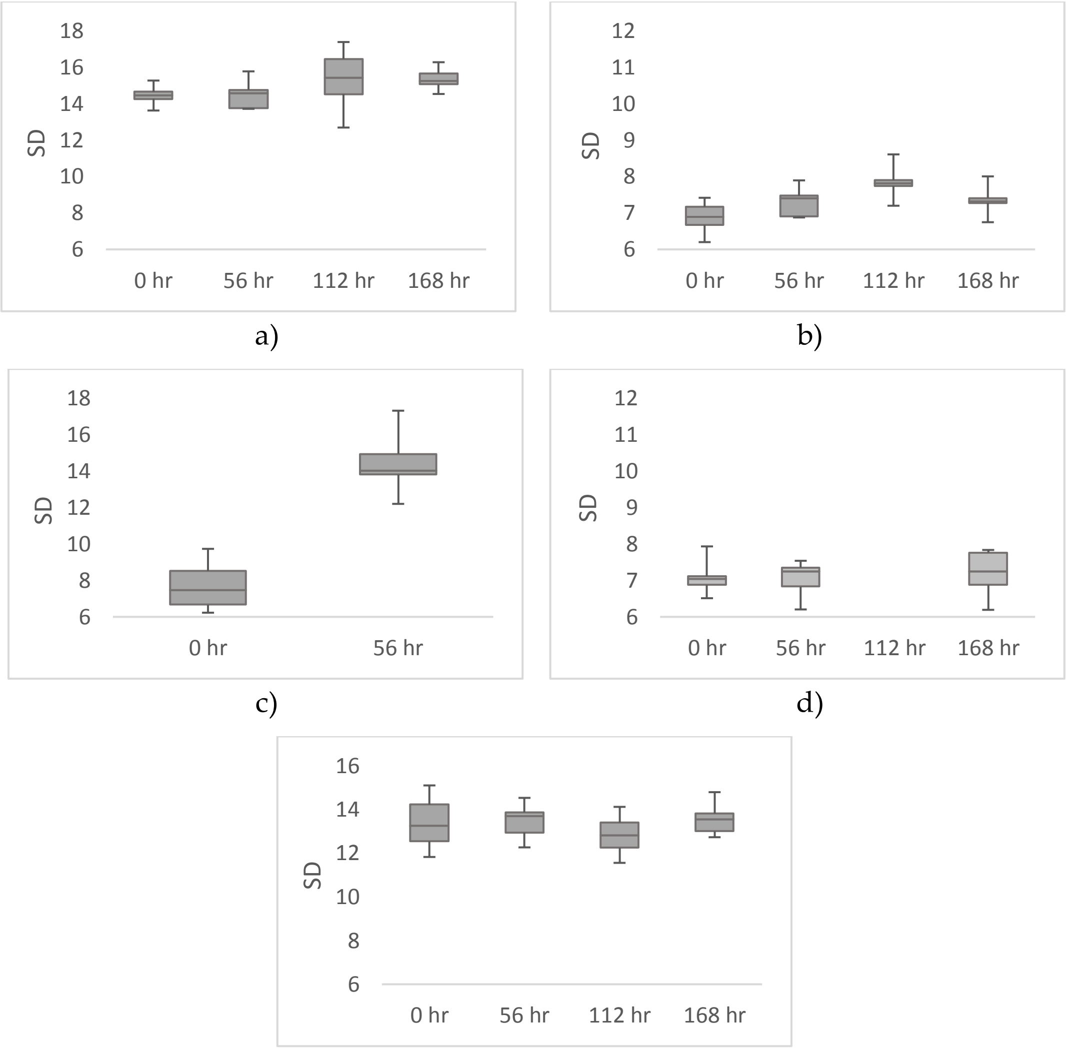
Scans of samples subjected to H70, H115 and UV ageing presented slightly different roughness variation patterns compared to those measured via photography. The H115 samples showed a significant drop in roughness after the first 56 hours interval and the mean values remained almost unchanged throughout until the end of the exposure period. ANOVA analysis indicated the high significance of the variation ($p = 2.27 \times 10^{-13}$) and t-test conducted on the values after each ageing stage confirmed that the variation occurred mainly within the first interval. Initially this result might seem in contrast with the photographic test analysis, but it must be noted that 2D scans provided more detailed images (600 dpi) compared with the captured images (240 dpi). It is therefore possible that less obvious variations of the roughness were not detected during photographic tests while they were distinguished via 2D scanning.

In contrast the H70 exposure resulted in an increase in the roughness after the initial ageing stage, as also noticed in Figure 5-7a, but then remained almost unchanged after 168 hours. This indicated that the different results can be due to two reasons: again, the greater precision of 2D scanning or, in alternative, the use of different samples in 2D scanning instead of repeated tests on the same samples in image capture and processing. Similarly the results of UV ageing were not in complete agreement with the image capture and processing data. In particular the measurements collected after 112 hours presented higher values than the others probably for the same reason described above.

Synthetic leather (Figure 5-14) showed minimal roughness changes based on the 2D scanning data, as reported after photographic analysis. The only procedure that induced an obvious change in the roughness was the H150 ageing, while H70 and H115 ageing showed less significant changes.

The fluctuations noticed after H+RH ageing during photographic analysis were not present in this case, therefore it was not possible to confirm the presence of an ongoing coating degradation. UV ageing left the coating apparently intact, indicating that no damage measurable via 2D scanning was ascribable to this radiation exposure within the selected time frame.

It is interesting to notice that H70 ageing increased the roughness mainly after the second interval, with an opposite trend compared with photographic analysis. Similarly, H115 presented increased roughness until 112 hours and then the trend reversed. These observations pointed out that some form of phenomena might have occurred at those stages, but that their entity must be further investigated to assess if physical properties were also affected.



a)

b)

c)

d)

e)

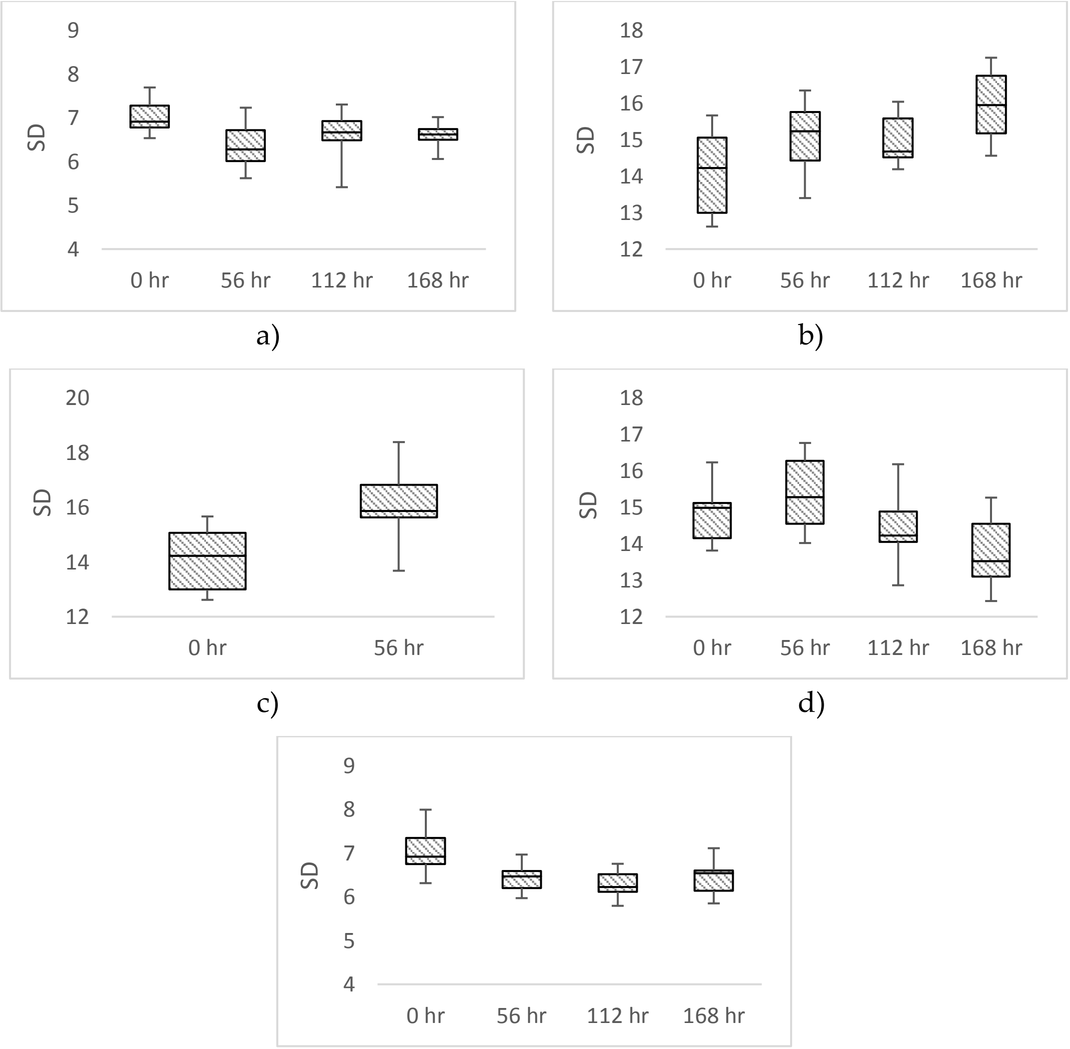
Figure 5-14: Box-and-whisker plots of roughness (via 2D scanning) on SY samples at different stages of accelerated ageing. a) H70, b) H115, c) H150, d) H+RH, e) UV ageing

The effect of H150 on the coating has already been discussed together with the appearance of the supporting fabric geometry (Figure 5-10). Also 2D scanning provided the evidence of an increase in the roughness (p-value < 0.05) indicating a coarser surface. The fabric pattern became even more evident than in photographic analysis, making stronger the theory that part of the coating structure went through a softening process resulting in a partial penetration through the underlying fabric.

2D scanning on EL2 samples mainly reflected the results obtained during photographic analysis with the difference that, in the former, roughness changes were also detected after H70 and H115 ageing. The box-and-whisker plots in Figure 5-15 report these results.

H70 ageing produced an initial significant reduction of the SD value resulting in a flatter surface, but after the second interval the SD values were closer to the initial values. Similarly, UV ageing made the surface flatter after the first two ageing steps and then the SD values decreased. ANOVA analysis conducted on these data confirmed the effect of the two ageing procedures ($p < 0.05$ in both cases).

A much more obvious variation was detected after H115, H150 and H+RH ageing. SD changes were registered already within the first 56 hours in all of the three procedures but only in the case of H150 were they significant ($p = 0.004$). Moreover, H+RH showed a different trend if compared with H115; the former induced an initial increase in the roughness and then decreased in the following stages, the latter increased constantly. Interestingly, the changes detected via image capture and processing also showed a decrease in the roughness values within the second interval (56-112 hour), but there the final SD was not statistically different from the original. Also in this case it is possible that the greater resolution of 2D scanning played an important role in better detecting surface variations.



a) b)

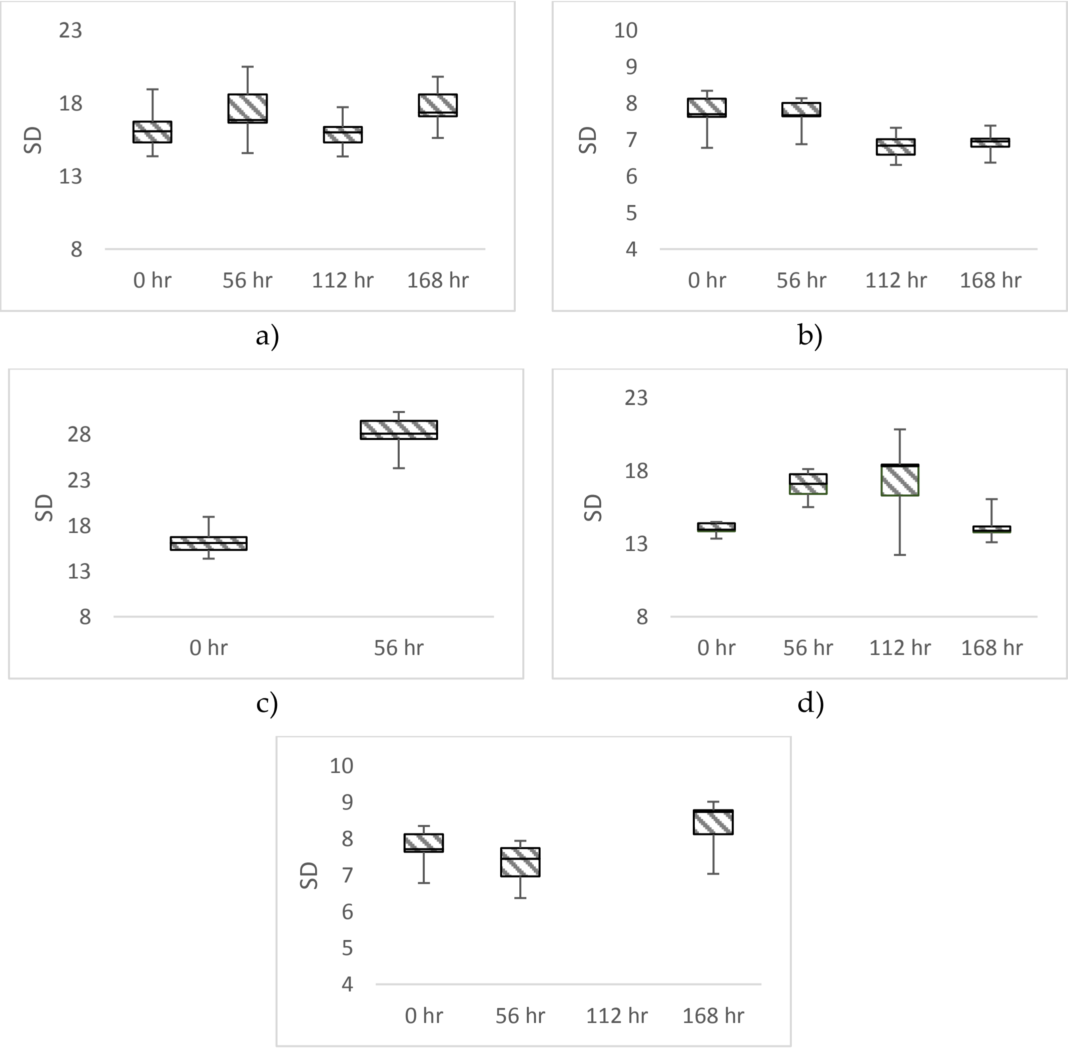
c) d)

e)

Figure 5-15: Box-and-whisker plots of roughness (via 2D scanning) on EL2 samples at different stages of accelerated ageing. a) H70, b) H115, c) H150, d) H+RH, e) UV ageing

The lower susceptibility to ageing of EL2 samples compared to TL was confirmed by these analyses. However, if during photographic analysis only two exposure conditions produced a variation of the SD values (H150 and H+RH), this was not the case in 2D scanning. EL2 values demonstrated that changes in the coating occurred after every exposure condition, even if they affected the surface to a variable extent. These findings suggested that the presence of leather fibres in E-Leather samples might have an important role in their ageing behaviour, as in the case of TL. Nonetheless, the composite structure of EL2 was likely to provide higher stability to the substrate, as also wet-blue leather fibres withstood ageing procedures differently from chrome-free leather (Ollè *et al.*, 2012).

In comparison to EL2, EL3 was characterised by a different behaviour. The box-and-whiskers plots in Figure 5-16 show the roughness at different stages of accelerated ageing.



a) b)

c) d)

e)

Figure 5-16: Box-and-whisker plots of roughness (via 2D scanning) on EL3 samples at different stages of accelerated ageing. a) H70, b) H115, c) H150, d) H+RH, e) UV ageing

Apart from UV and H70, which exhibited less significant variations, all of the ageing procedures exhibited highly significant variations of SD values. Photographic image capture and processing indicated H150 ageing seemed not having a significant effect on the coating substrates, and was not in agreement with the substrate appearance. 2D scanning successfully detected the coating roughness fluctuations and t-test pointed out the significance of these fluctuations ($p = 4.34 \times 10^{-11}$). It is likely that also in this case the greater detail of 2D scanning was able to capture the differences between the coating before and after ageing.

After the second interval of the H115 ageing the samples seemed flatter, which contrasted with the observations conducted via photographic analysis. It must be noticed that EL3 exhibited a marked bending after this ageing procedure (see Figure 5-17) that introduced new tension into the sample.

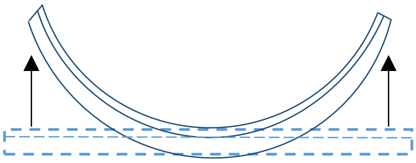


Figure 5-17: Schematic representation of EL3 bending after H115 ageing

Despite this problem also being present during photographic analysis, it is likely that in that case the pressure of the wooden frame used to keep the samples flat had a different impact on the sample compared to the pressure applied by the scanner cover. In the former the coating was compressed because the wooden frame only pushed down the samples edges, resulting in higher roughness, while in the latter the scanner cover subjected EL3 to higher pressure in the centre of the samples leading to superficial flattening.

H+RH ageing affected the roughness to a great extent, with samples showing increased SD values after the first and second interval. In spite of this, after the third interval SD mean values returned to figures comparable with those before ageing. This result was surprising because the samples appeared clearly damaged even after the third interval, though it was also in agreement with the observations reported after photographic analysis. In fact, also in that case the initial roughness increase was followed by a return to values close to the original material. A possible explanation is that after the material had lost its original flexibility, particularly on the fibrous layer side, its internal structure went through mechanical phenomena that lead to readjustments of the fibrous substrate. This explanation will be further investigated in the following paragraphs focusing the attention on properties related to flexibility, such as bending and tensile strength as reported in previous studies (Urbanija and Geršak, 2004).

To summarise, all the materials exhibited high sensitivity to severe heat exposure. However, every substrate presented typical degradation patterns and sensitivities to the different ageing procedures. These differences, if confirmed by further analyses, could be potentially used to differentiate the factor that might have induced the degradation in the first place. Variations occurred between one ageing step and the other can be worrying signs of changes in the substrate, though in some cases they only indicate that there is an initial structural change then resulting in less obvious modifications. The roughness fluctuations assessed on EL3 through 2D scanning confirmed the different behaviour of the two substrates provided by E-Leather®.

It is worth noting that not all the roughness measurements conducted via 2D scanning (Figure 5-13 to Figure 5-16) correlated with the ones via photographic picture capture and image processing (Figure 5-7 to Figure 5-12). For this reason it would be useful, whenever possible, to use both the techniques in order to get more reliable and definitive information regarding roughness variations.

5.4.1.3 Spectrophotometry

The centrality of colour and colour difference for the industrial and heritage sectors has been discussed in Chapter 2. It is well-known that the application of coatings or protective layers to cultural heritage substrates can result in variations in colour properties (García and Malaga, 2012; Koochakzaei *et al.*, 2014). Similarly, degradation can affect materials by changing their colour and, in accelerated ageing studies, alterations of chromatic properties are normally related with ongoing phenomena within the substrate (Gargano *et al.*, 2017). During these studies the phenomena can be linked to the environment surrounding the samples, therefore reporting on the effect of each factor on the colour of leather and related materials was considered of importance in this thesis.

Despite colour difference can be detected to some extent to the naked eye providing a subjective way to identify changes in objects' appearance, less evident variations can only be detected using digital tools. Spectrophotometry is often used for this purpose (Lorusso *et al.*, 2008; Koochakzaei *et al.*, 2014) and it was used also in this context.

Colour values of coated and fibrous layers were measured in the colour space CIE L*a*b* before and after each ageing procedure. Ten measurements per each sample and three repetitions were collected at each ageing stage to assess the variability between samples. The calculation of the ΔE* was indispensable in providing a quantitative indication of the difference between the values before and after ageing.

$$\Delta E^* = \sqrt{(L_2{}^* - L_1{}^*)^2 + (a_2{}^* - a_1{}^*)^2 + (b_2{}^* - b_1{}^*)^2} \qquad (5\text{-}3)$$

ΔE* describes the total colour difference between two objects – or two areas of the same object – by assessing the distance of their colour parameters in the selected colour space (see Equation 5-3). The higher the ΔE* value the easier is detecting visible colour differences. However, it is well known that colour changes can be perceived better by the human eye when they occur in some regions of the electromagnetic spectrum, thus it can be easier or more difficult to identify some variations according to the colour of the surface. As a consequence, the interpretation of the colour change is not straightforward and the threshold above which the change is perceivable to the naked eye depends on the context of the study. For example, the limit value for anti-graffiti coatings used for cultural heritage exposed outdoor is 5 units (García and Malaga, 2012), but other threshold values can be used in different areas of conservation. In this work ΔE* = 1 was identified as the threshold for the colour change perception.

Figure 5-18 illustrates the effect of the ageing procedures on the colour coordinates a* and b*, respectively associated with red/green (positive = red, negative = green) and yellow/blue (positive = yellow, negative = blue) colours.

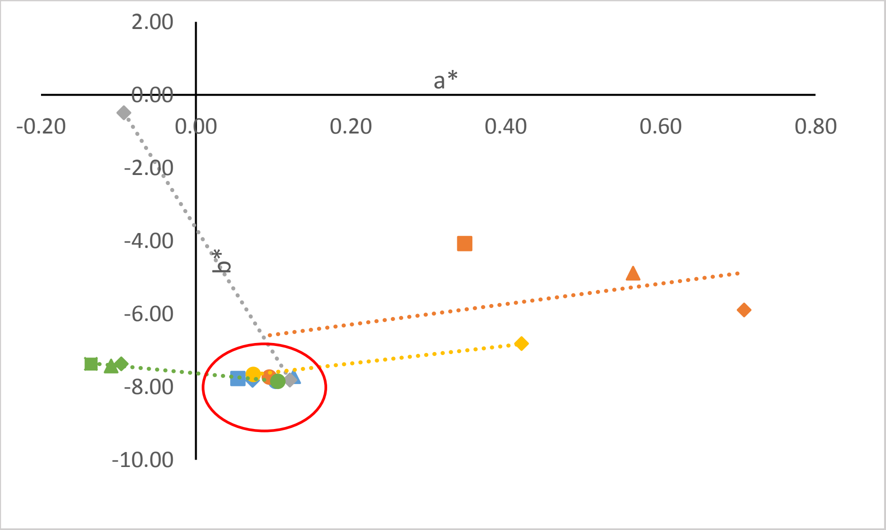


Figure 5-18: a* and b* values of TL coating subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours. The oval shape defines the initial colour values interval

TL coating was affected by every ageing procedure in a different way and the only procedure with a limited impact was H70 ageing. The unaged samples, together with the samples subject to mild heat ageing, constituted the most populated cluster of the graph. The effect of UV ageing, described in literature as the most damaging factor for chrome-tanned leather and less influential for chrome-free leather (Ollè *et al.*, 2012), exhibited a shift in the coating colour towards the green while leaving almost unchanged the values along the b* axis. Also H150 ageing produced a greener coating, but in this case the yellowing was much more pronounced (coordinates -0.09, -0.49), being the highest of all the aged samples. H115 ageing resulted in a significant shift along both a* and b* values (coordinates 0.71, -5.90) after the first interval, then the gap along the b* axis tended to reduce with the samples becoming yellower. H+RH ageing had a similar effect on the samples, shifting the colour to more yellow and redder values within 56 hours.

These results indicated that the coating behaved in a similar way when subject to the H115 and H+RH ageing. Likewise, the H150 and UV procedure presented variations that were different in intensities, similar in direction but opposite to the H115 and H+RH ageing. It is possible that the H150 and UV treatments determined changes in both the coating – causing yellowing – and dyes structures, while the other treatments only affected one of the two components.

To better understand the effect of the ageing procedures on colour parameters, Figure 5-19 presents the variation of lightness values for the samples. It is possible to assess that the most damaging procedure was the one that combined high temperature and humidity, resulting in a 31 % decrease of the sample lightness.

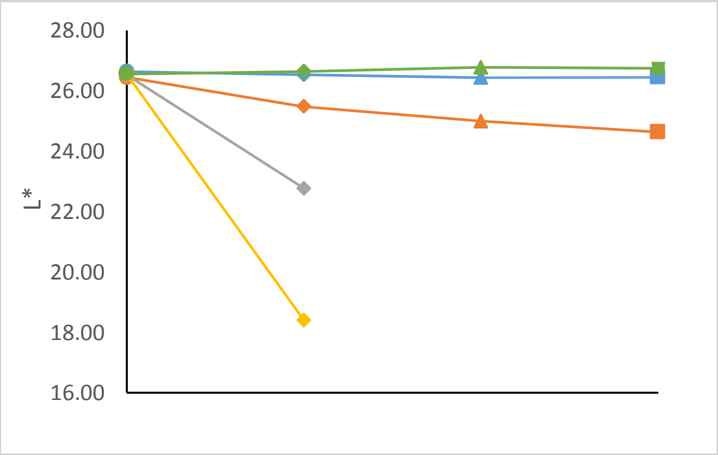


Figure 5-19: L* values of TL coating subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours

The effect of H150 ageing also produced a marked decrease (14 % decrease) in lightness, while H115 showed a smaller change (4 %). Both H70 and UV presented negligible lightness variations. The darkening of leather is a phenomenon documented by many authors (Thomson, 2005; Axlesson *et al.*, 2016), therefore it was not surprising that the H115, H150 and H+RH procedures determined a decrease of the L* values. These values could be the result of the associated darkening of coating and fibrous layer, because it must be noted that the results reflect the behaviour of the thin coating of the TL material and are not necessarily or exclusively related with the fibrous layer.

The same measurements conducted on the coating were repeated on the fibrous layer to evaluate possible differential behaviour of the two sides of the samples. The results are illustrated in Figure 5-20.

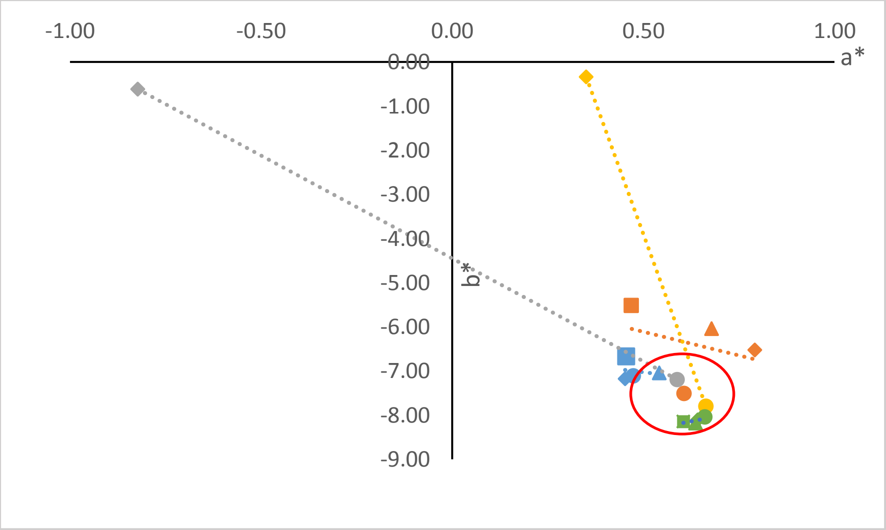


Figure 5-20: a* and b* values of TL fibrous layer subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours. The oval shape defines the initial colour values interval

H150 was undoubtedly the ageing condition that produced the greatest variation in a* and b* values, shifting the coordinates from (0.59, -7.20) to (-0.82, -0.62). This resulted in a colour shift towards yellower and greener values away from the original ones. H+RH exposure made the samples yellower, though the value along the a* axis shifted only slightly. H115 ageing produced an initial increase of the a* values followed by a reduction whilst the b* values tended to increase. Mild ageing produced a small change on the samples but perceivable because of the continuous reduction of the b* values. UV ageing had a limited effect, as it was expected, because the samples were only irradiated on the coating side. Despite this some changes were detected, probably as a consequence of the temperature and relative humidity conditions chosen to perform this type of ageing.

Research conducted on parchment has demonstrated that untreated collagen fibres subject to dry heat have colour coordinates that shift towards the yellow and red values (Axelsson *et al.*, 2016). In the case of the TL material the collagen fibres were subjected to dyeing procedures, therefore the shift of the a* and b* values was possibly determined by variations of both the collagen fibres and the dyes.

The lightness values (Figure 5-21) also highlighted it is possible to identify similarities, particularly in the trends already observed during the coating examination, and differences between the ageing procedures.

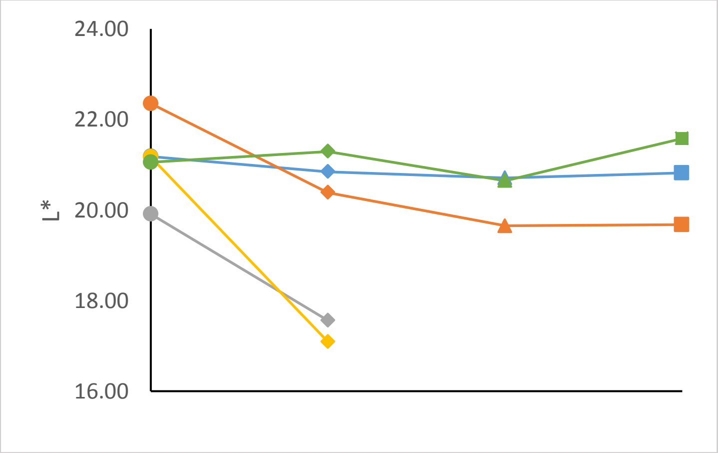
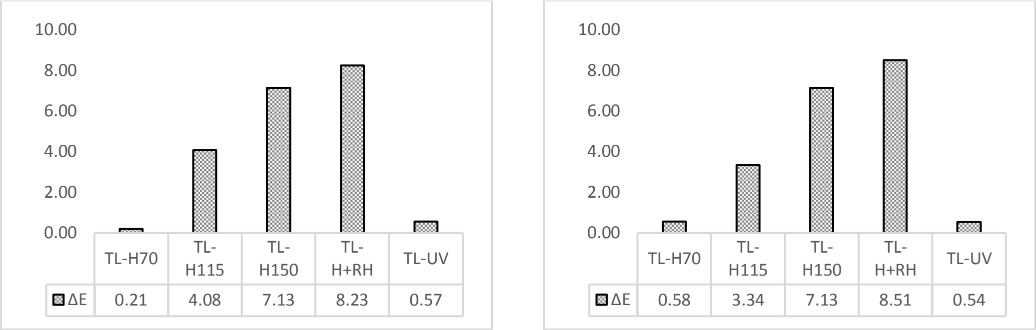


Figure 5-21: L* values of TL fibrous layer subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours

H115, H150 and H+RH exposure induced lightness changes within the first exposure periods, though the extent of these variations was different from the comparable ageing on the coating face. A 9 % decrease of the lightness values was already registered after the first 56 hours of H115 ageing and after 168 hours a 12 % reduction was registered. This same reduction was also measured after 56 hours of H150 ageing, while a more significant 19 % was registered after 56 hours of H+RH ageing. These measurements suggest that the TL fibrous layer was affected by the three most aggressive ageing procedures, H115, H150 and H+RH, after just 56 hours of exposure.



a) b)

Figure 5-22: ΔE values of TL coating (a) and fibrous layer (b) at the end of the accelerated ageing procedure

As demonstrated by the ΔE* values (Figure 5-22), the effect of the ageing processes on the two sides of the samples was strongly correlated (r = 0.99). H+RH ageing led to the greatest change (ΔE 8.23 and 8.51), followed by H150 and H115 ageing, while UV and H70 ageing produced a negligible change.

Figure 5-23 indicates the a* and b* values measured on synthetic leather samples and, compared with TL, clear differences in the coating behaviour are obvious. In the case of TL the coating was affected to some extent by all of the accelerated ageing procedures, while in SY the coating mainly suffered during the application of UV radiation and severe heat.

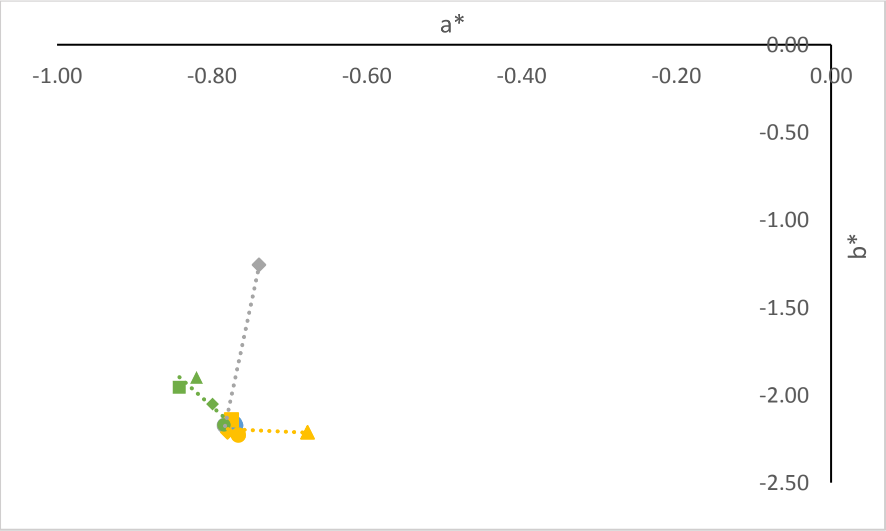


Figure 5-23: a* and b* values of SY coating subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours

The graph shows that H+RH ageing produced a marginal change with the a* chromatic parameter moving towards the red after 112 hours of ageing. Similar behaviour was observed for the UV ageing that induced a gradual but small shift of the coating towards greener and yellower values. Only the H150 test conditions resulted in a more pronounced change, shifting the b* value from -2.18 to -1.26.

The use of different dyes to colour the coating of the SY material may be identified as the main reason for the lower variation of the a* and b* values. For example, in this material TiO_2 was possibly used as both a colouring agent and stabiliser because the colour of the end-product was light grey. In contrast, the use of the same additive in the TL material was limited because a dark blue colour wanted to be achieved.

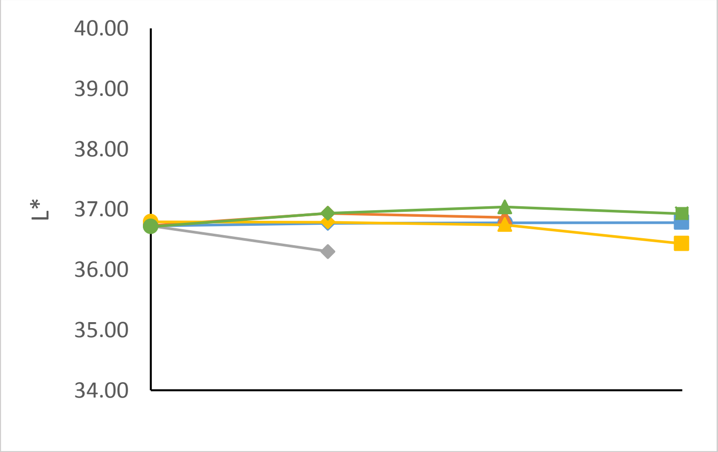


Figure 5-24: L* values of SY coating subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours

Lightness values were stable during all the ageing procedures (Figure 5-24). H150 showed the greater reduction in the short interval (1 %) and H+RH reached similar values after 168 hours of exposure.

The fibrous layer of SY showed minor variations in the a* and b* values after all the experimental conditions (Figure 5-25).

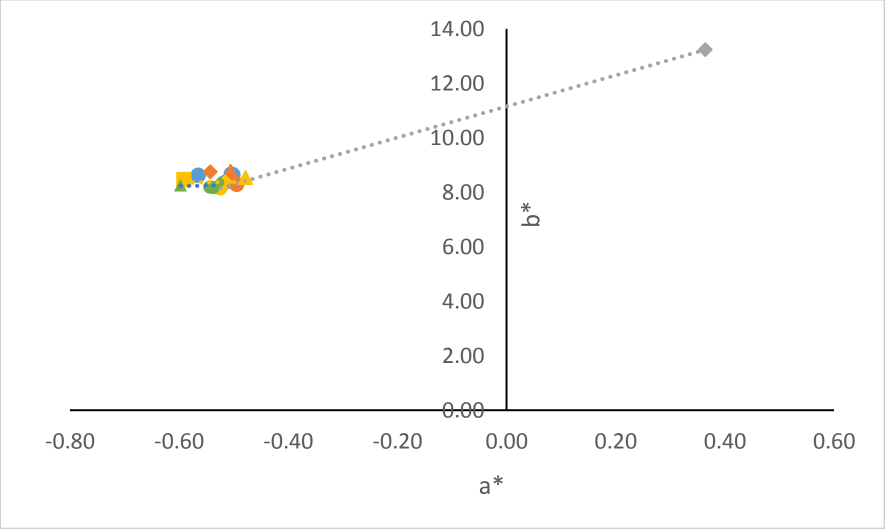


Figure 5-25: a* and b* values of SY fibrous layer subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours

H150 constituted the only accelerated ageing able to modify the aramid fibres of the supporting fabric, making them redder and yellower. A similar pattern was evident for the L* values (Figure 5-26) that decreased markedly after 56 hours of severe heat ageing. This result pointed out that high temperature affected aramid fibres more than the combined action of heat and humidity.

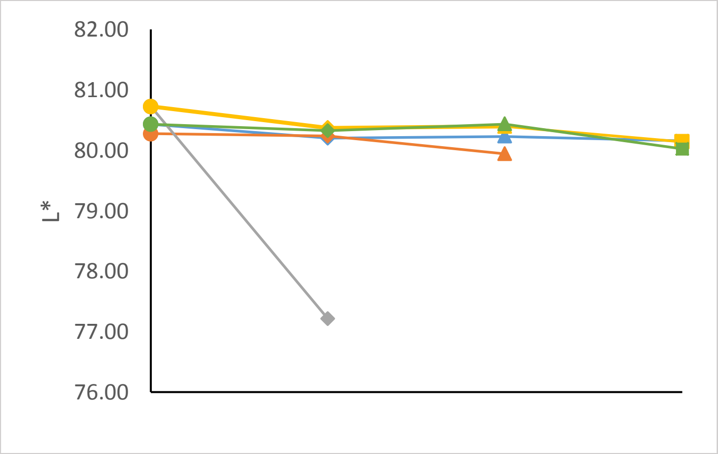
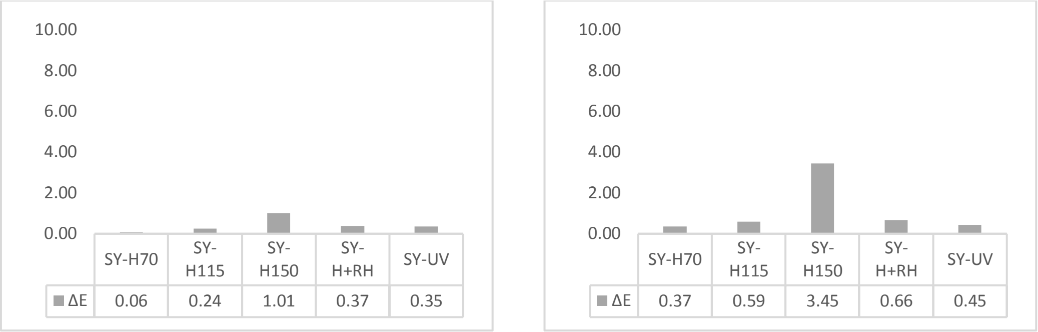


Figure 5-26: L* values of SY fibrous layer subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours

The general stability of SY was also supported by the ΔE* values (Figure 5-27), that were equal to or lower than 1 on the coating side. Nonetheless, the effect of H150 ageing on the fibrous layer was underlined by the ΔE*. The correlation between the variations on the two sides of the samples was strong also in this case (r = 0.95).



a) b)

Figure 5-27: ΔE values of SY coating (a) and fibrous layer (b) at the end of the accelerated ageing procedure

Despite the fact that a colour variation does not necessarily correlate with mechanical properties changes, the findings of the H150 procedure were interesting because aramid fibres are used in those applications where high performance fibres with thermal resistance are required (Fung, 2002). Therefore it was considered of primary importance to establish whether colorimetric variations corresponded to changes of mechanical properties or not. Heat resistance of aramid fibres has been widely studied and it depends on the position of the substituents in the molecular structure (Bourbigot and Flambard, 2002; Perepelkin *et al.*, 2003). Dimensional changes, in particular elongation, have been reported to occur when the temperature is increased, though below 400 °C these changes did not exceed 2 % (Perepelkin *et al.*, 2003). As a consequence, it was considered unlikely that variations of the chromatic parameters in SY fibrous layer were associated with fibres deformations or mechanical changes because this would have required extremely high temperatures. This assumption will be further investigated through the mechanical analysis (see § 5.4.4).

The composite materials EL2 and EL3 behaved differently during ageing both regarding the coating and the fibrous layer side and therefore, also in this occasion, they are presented separately. Figure 5-28 represents the graph of the a* and b* values referred to the EL2 coating after accelerated ageing.

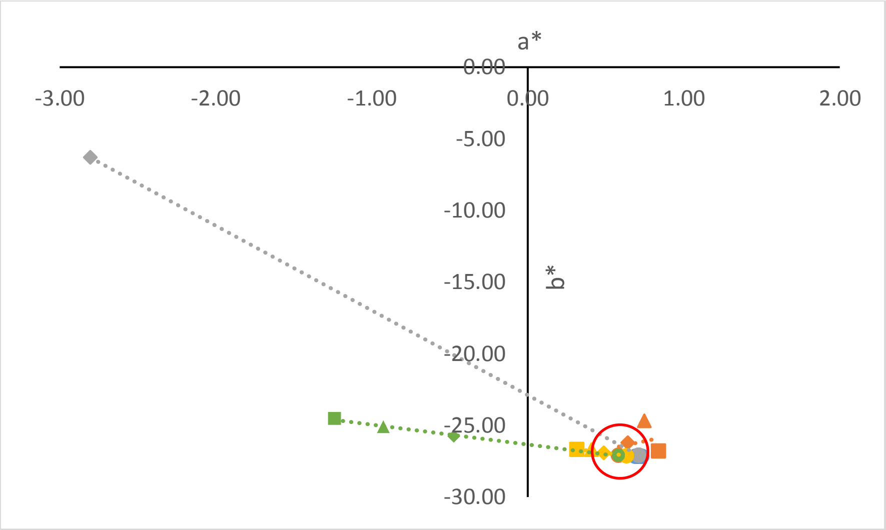


Figure 5-28: a* and b* values of EL2 coating subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours. The oval shape defines the initial colour values interval

H150 ageing was again the most damaging procedure, resulting in a vigorous yellowing of the samples and shifting the a* values towards the green side. Also UV ageing caused a transition towards green and a yellowing effect that started to become significant after 56 hours of exposition. H115 gradually shifted a* and b* towards positive values resulting in a perceivable variation of the colour.

Lightness (Figure 5-29) seemed to be less affected by accelerated ageing, showing a pattern that resembled SY. In EL2, as in the synthetic leather samples, L* considerably decreased (9 %) after H150 ageing, but it remained almost unvaried after the other ageing procedures.

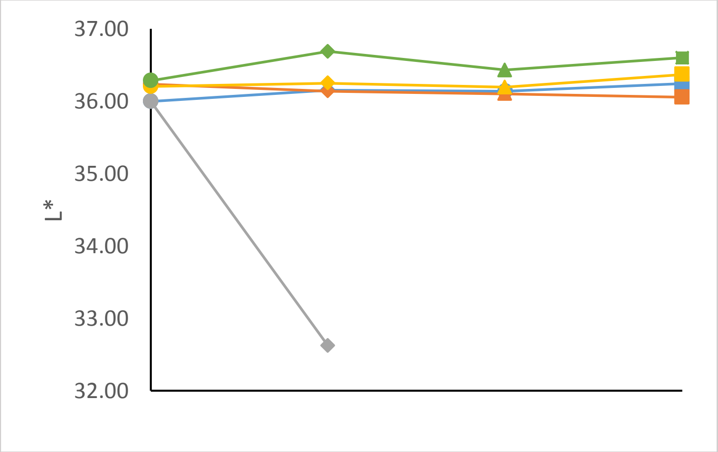


Figure 5-29: L* values of EL2 coating subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours

The fibrous layer was much less resistant to colour change, and all the accelerated ageing procedures except for H70 caused a shift of the chromatic parameters (Figure 5-30). As already seen in the previous samples, H150 ageing significantly shifted the values along both axes.

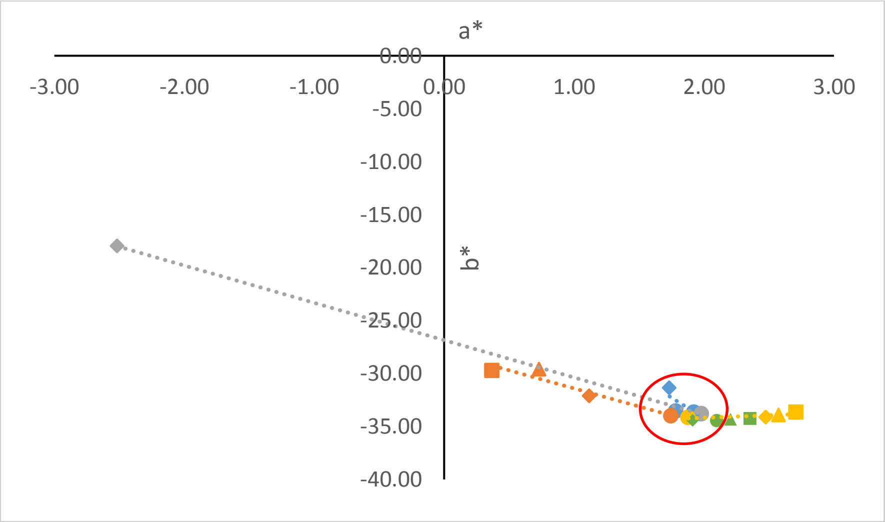


Figure 5-30: a* and b* values of EL2 fibrous layer subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours. The oval shape defines the initial colour values interval

Similar but to a lesser extent, the H115 exposure shifted the colour to the yellow and green side. UV and H+RH showed an opposite trend compared with the other procedures, with the fibrous layer colour turning gradually redder. Also in this case the change was attributed to variations of both collagen fibres, resulting in yellowing, and dyes.

H70 and UV ageing left almost unaffected the lightness parameters of EL2 on the fibrous layer side, even if after the first 56 hours the samples seemed to have higher L* values that decreased after that stage (Figure 5-31). In contrast a marked reduction of lightness was noted after the first ageing stage of the other accelerated ageing procedures. A 10 % decrease was measured after H150, while a 6 % (5 % after 56 hours) and a 4 % (5 % after 112 hours) were recorded after H+RH and H115 ageing.

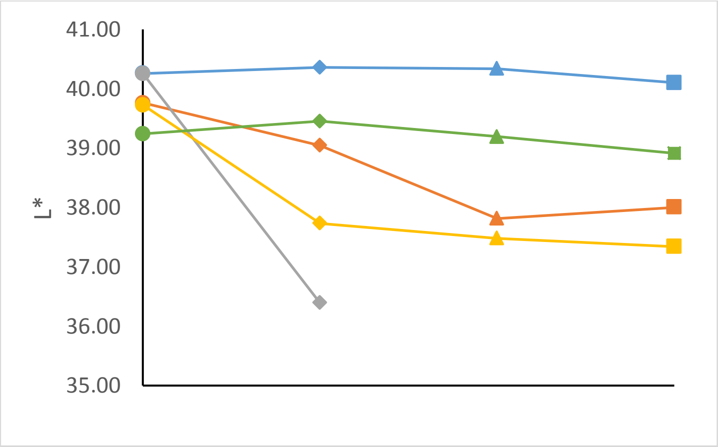
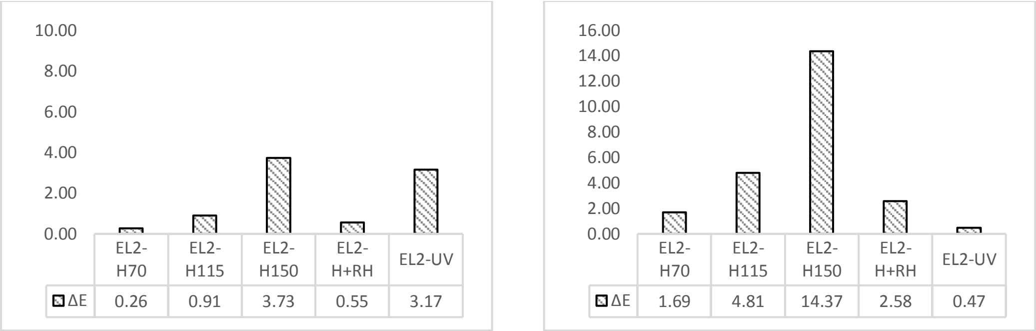


Figure 5-31: L* values of EL2 fibrous layer subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours

The results of the measurements on the fibrous layer pointed out that the impact of H+RH ageing on the bulk material was not so drastic, in terms of colour change, as compared to TL. The latter, in fact, exhibited a 19 % decrease of the lightness value after 56 hours of exposition to high temperature and humidity, whilst EL2 showed a L* reduction in the first interval that continued in the following intervals but this reduction was not as steep as that observed for TL. Similarly decreases in L* after H115 and H150 ageing were consistently more marked in TL than in EL2.



a) b)

Figure 5-32: ΔE values of EL2 coating (a) and fibrous layer (b) at the end of the accelerated ageing procedure

The different behaviour for the coated and fibrous layer to the accelerated ageing was underlined by the ΔE* exhibited by the samples. H150 and UV ageing were the most damaging procedures for EL2 coating, though UV ageing did not affect the fibrous layer that was much more degraded by all the other procedures. There was a moderate correlation between the two sides (r = 0.56), but it was not as strong as in TL and SY samples.

Observing the values of ΔE* on the fibrous layer side it is evident that UV ageing had a minimal impact on the substrate compared with the other procedures. Previous studies described the effect of UV radiation on leather samples as more damaging than heat and humidity ageing (Li *et al.*, 2016). However, the presence of a polymeric coating on the grain side has an obvious influence on the colour variation and acts as a protective layer. In this work the higher stability of the substrate was due to the fact that UV only reached the coating and this allowed the fibrous layer to be exclusively affected by temperature and humidity.

The colorimetric parameters measured on coating and fibrous layer of EL3 are shown in Figure 5-33 to Figure 5-36. The only accelerated ageing that did not have an impact on the EL3 coating was H70, which had values in the same range of unaged samples. This was likely to be due to the fact that the activation energy required for the reactions to take place was not reached under mild heat conditions. The other exposed samples colour values shifted towards lower a* and higher b* values.

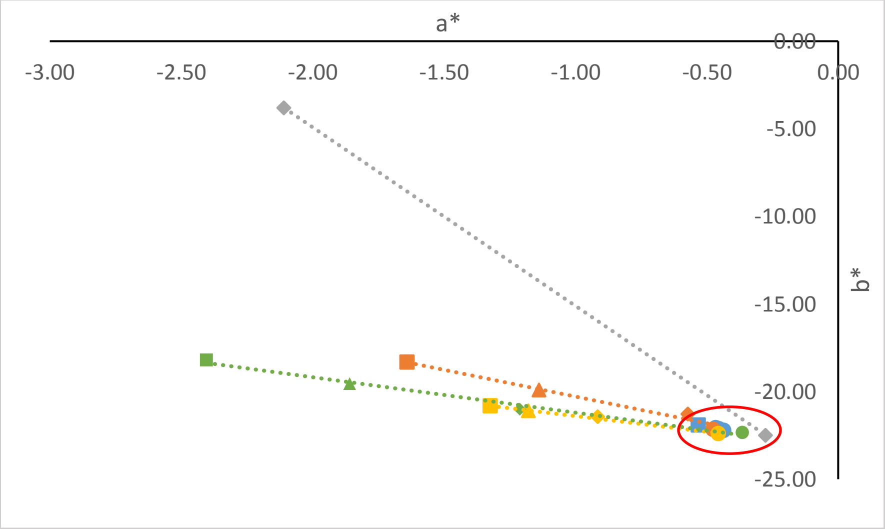


Figure 5-33: a* and b* values of EL3 coating subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours. The oval shape defines the initial colour values interval

H+RH and UV ageing had the same behaviour, even if the rate at which the coating became greener was higher in the case of UV ageing. H115 ageing also exhibited a similar trend, but samples had their b* values shifted towards positive figures when compared to the previous procedures. The H150 ageing conditions produced the highest level of degradation, resulting in a strong yellowing and shifting the values towards the green within 56 hours. These variations in the a* and b* parameters did not correspond to an equally great change in L*, that only presented a significant decrease after H150 ageing (Figure 5-34).

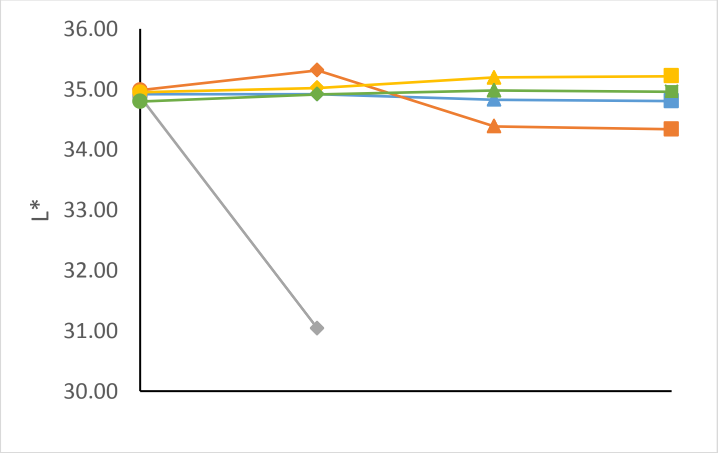


Figure 5-34: L* values of EL3 coating subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours.

The behaviour of the fibrous layer of EL3 samples was considered noteworthy because it was visible to the naked eye that it tended to become darker after moderate heat treatment. Also, the change registered for the chromatic parameters confirmed that the leather fibre composite was sensitive to the H115, H150 and H+RH procedures (see Figure 5-35).

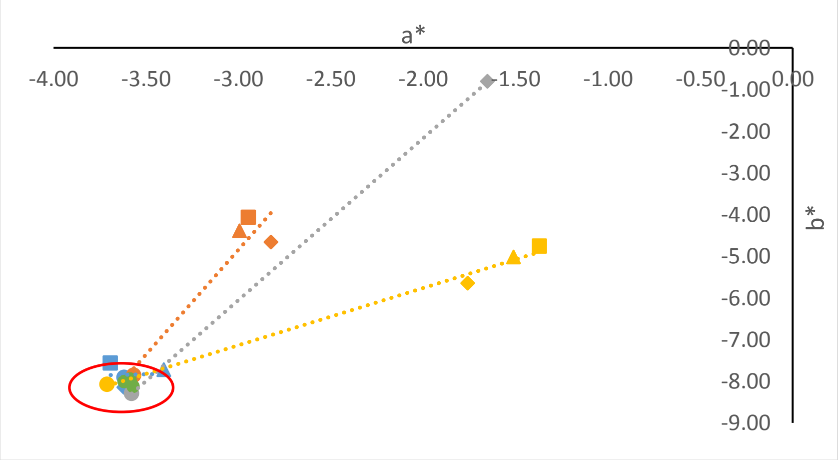


Figure 5-35: a* and b* values of EL3 fibrous layer subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours. The oval shape defines the initial colour values interval

The colour coordinates recorded for the H150 aged samples shifted significantly towards redder and yellower values from (-3.58, -8.30) to (-1.65, -0.81) in agreement with the results reported in literature (Axelsson *et al.*, 2016). H115 and H+RH ageing exhibited values with similar trends to the H150 materials, towards the yellow and red, even though with lower figures. The former produced a steep increase of the b* values and a mild increase of the a* values, while the opposite happened during H+RH ageing.

The lightness parameter, in this case, was also greatly affected by the different ageing procedures. The strongest reduction of the L* value was registered on samples measured after H150 and H+RH ageing. It is interesting to point out that almost the same reduction percentage was recorded after the first interval of both ageing (35 % and 34 %, respectively). It is also worth noticing that the first interval of H+RH ageing was the one responsible for the greatest change on the substrate. A 14 % reduction was registered on samples subject to H115 ageing for 168 hours, indicating that EL3 fibrous layer was more sensitive to thermal ageing than TL (12%).

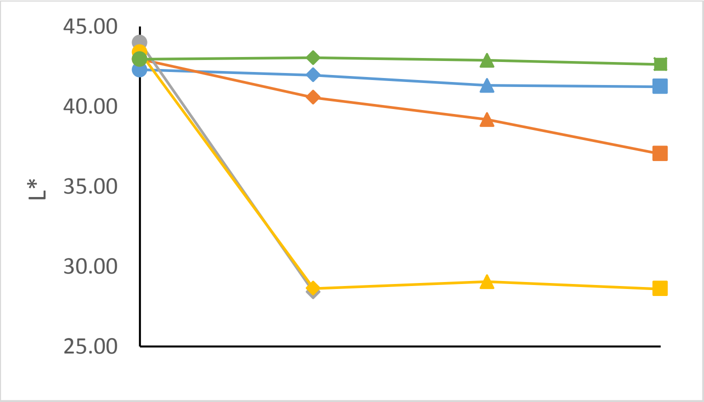
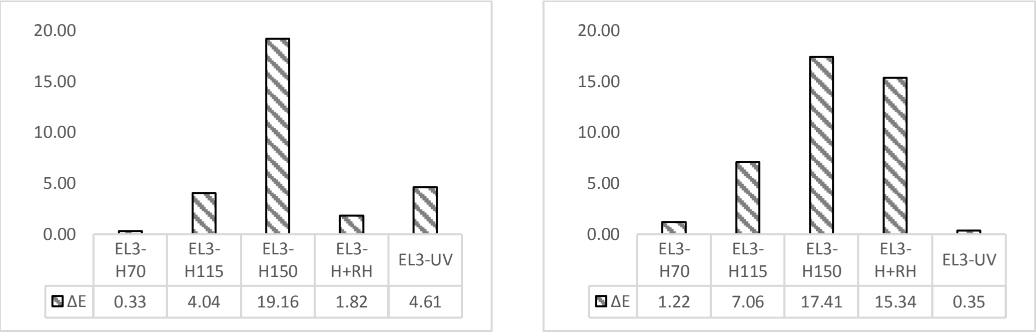


Figure 5-36: L* values of EL3 fibrous layer subjected to different ageing procedures. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing; green markers: UV. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours

As partly seen in the case of EL2, the difference between the parameters registered on the coating did not perfectly correlate with the ones registered on the fibrous layer. EL3 coating was highly damaged by H150 and UV ageing, as in EL2, but also H115 produced a conspicuous increase of the ΔE*.



a) b)

Figure 5-37: ΔE values of EL3 coating (a) and fibrous layer (b) at the end of the accelerated ageing procedure

The leather fibres substrate was mainly affected by high temperature (H115 and H150 ageing) and by the combined effect of heat and humidity. The correlation between the variations of the registered parameters on the two sides, however, was moderate ($r = 0.60$).

To sum up, the substrate that presented the highest ΔE* was EL3 after H150 ageing. This highlighted that TL was more resistant, in terms of colour change, than the manmade material EL3. Normally colour changes in the leather and coated fabrics top layer can be related to two main reasons, that is variations in the polymeric coating or in the type of pigments used (Li *et al.*, 2016). The results in this paragraph highlighted that moderate and severe heat (H115 and H150, respectively) and UV radiation were the main responsible for shifts of the chromatic values and the darkening of the coating, possibly affecting both the polymer and the dyes structure. The H+RH procedure also affected the colour but only for the TL and EL3 materials.

The fibrous layers presented different sensitivities to the ageing factors compared to the coatings and, in particular, the UV treatment did not produce any marked colour change. The H+RH ageing had the worse effect on the TL samples, whilst the H150 ageing determined the greater colour variation (ΔE*) in the SY, EL2 and EL3 materials. In the latter substrates these variations were attributed to both collagen (yellowing and darkening) and dyes.

5.4.2 SEM observations

SEM has been used for the analysis of leather and parchment because of its ability to provide images with high definition and remarkable detail down to the level of the collagen fibrils (Larsen *et al.*, 2005). When an environmental SEM that allows testing without the need for sampling is not available, the application to cultural heritage is again limited to those cases where sampling is allowed. Therefore, most of the published work in this area was carried out on model replicas –for museum objects (Larsen *et al.*, 1994) or new samples to test their properties for specific applications, i.e. industrial products (Siddique *et al.*, 2015).

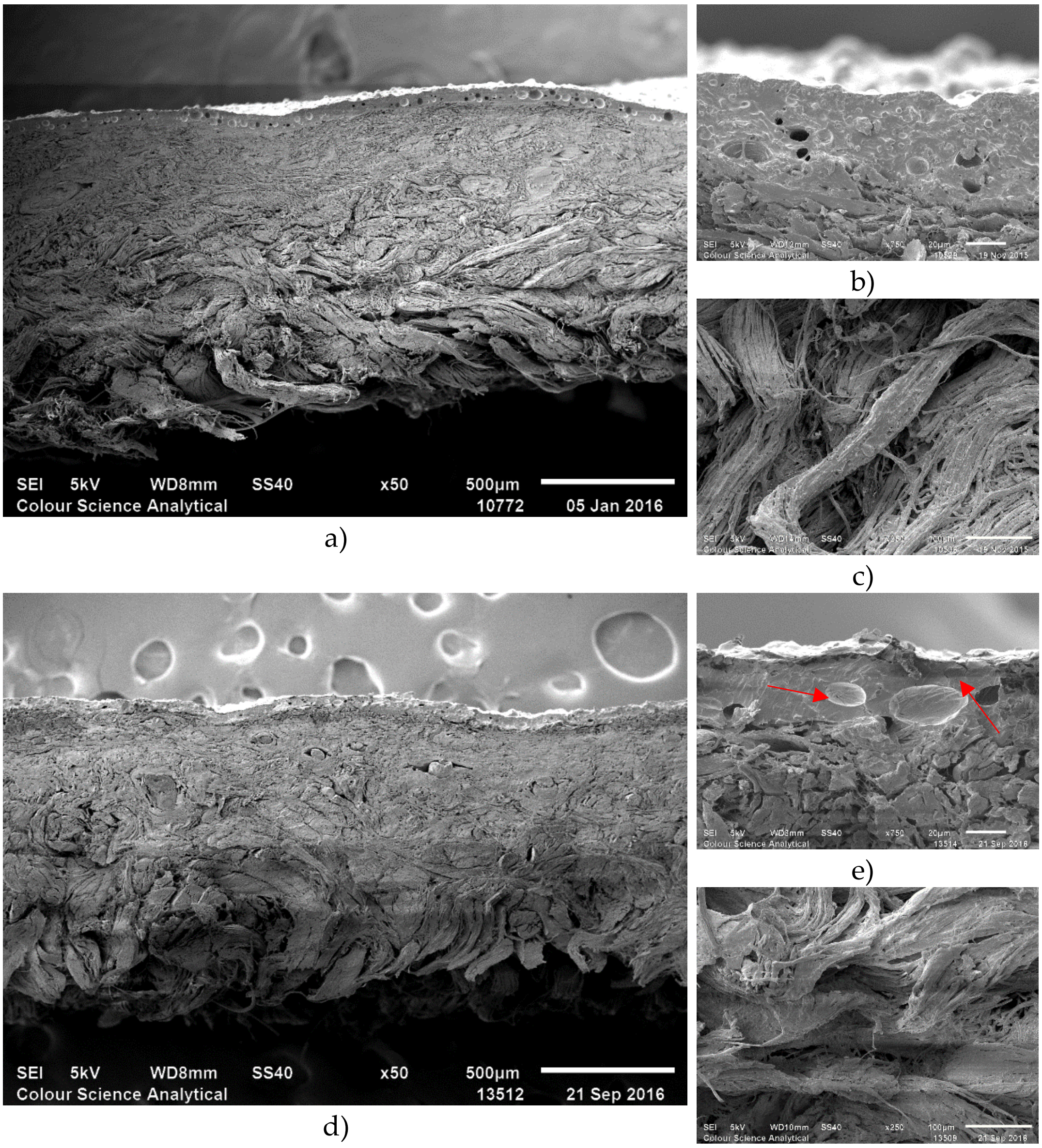
SEM has been used to compare morphological characteristics of natural and synthetic leathers (Chen *et al.*, 2007; Qu *et al.*, 2008; Sudha *et al.*, 2009). In addition, initial studies on the change of morphological and structural properties of leather during accelerated ageing have been also conducted (Ollè *et al.*, 2011; Li *et al.*, 2016). They confirmed the usability of SEM as a powerful tool to detect variations especially in the distribution of fibre bundles.

The studies conducted on synthetic leather in museum context did not use SEM, but rather optical microscopes (Bechtold *et al.*, 2006). However, other PU materials such as foams have been observed with this method (Pellizzi *et al.*, 2014). Publications focused on the study of synthetic leathers by using SEM are limited also in other fields, though the data available provide information difficult to obtain with a different technique, such as looseness of fibres bundles and clear definition between the different layers of the material (Chen *et al.*, 2007; Sudha *et al.*, 2009). Moreover, studies have been conducted to evaluate changes on coated fabrics subjected to degradation cycles (Padleckienė and Petrulis, 2010; Potočić Matković *et al.*, 2014) but not on synthetic leather. The application of this technique to assess the SY degradation was hence considered worthwhile.

Samples of leather, synthetic leather and E-Leather® were assessed before degradation and after each degradation interval. After observation of all the data collected it was decided to include only those images that illustrated significant changes of the substrates.

TL did not show signs of damage after mild heat ageing and after UV ageing, indicating that both the coating and leather substrate were able to withstand the thermal stress induced by those treatments. However, after H115 exposure both layers started to exhibit significant damage. The cross-sections (Figure 5-38a and d) indicated the evolution of the damage that increased with the exposure time. This can be noticed by looking at the increased level of fibres compactness, for the fibrous layer, and the reduction of the coating thickness that passed from 53.24 ± 6.68 μm at 0 hours to 42.31 ± 8.57 μm after 168 hours.

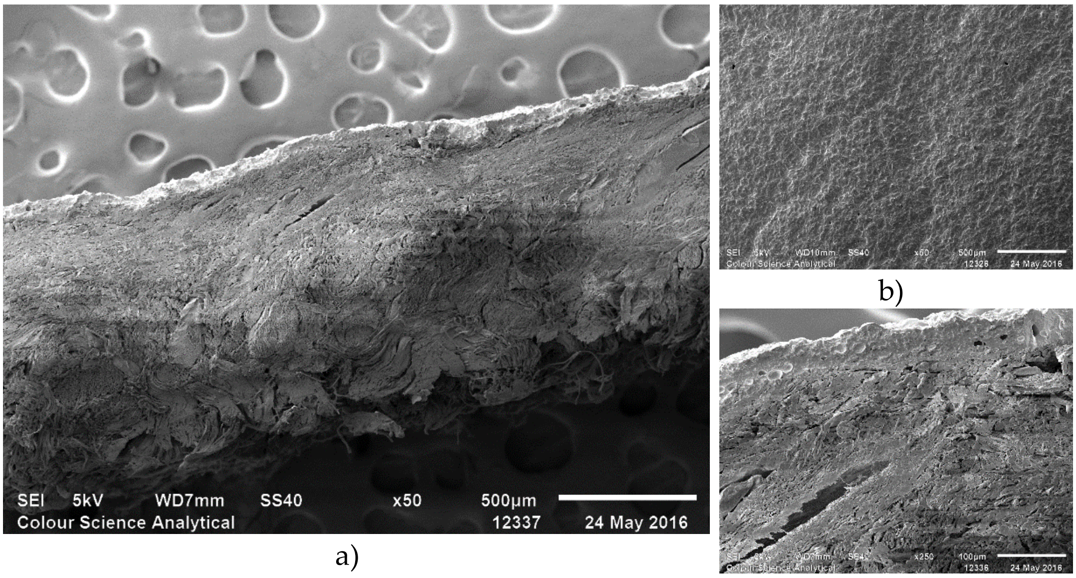
Detachment of the collagenous matrix and coating were noticed after the second interval (112 hours), probably as a consequence of the high stress caused by the variation of temperature and humidity. The different sensitivity to thermal stress of the leather and polyurethane, confirmed by studies conducted on the thermal behaviour of the two materials (Chahine, 2000; Pellizzi *et al.*, 2014), may be both responsible for the partial detachment of the coating and the formation of small cracks (arrows in Figure 5-38e). These cracks were noticed only after the third ageing interval but it is likely that in the long term they would have induced aesthetic damage visible to the naked eye.



a) b) c) d) e) f)

Figure 5-38: SEM images of TL samples before (a, b, c) and after (d, e, f) H115 ageing. Details show coating cross-sections at mag. 750x before (b) and after (e) ageing and fibres bundles at mag. 250x on the reverse side before (c) and after (f) ageing

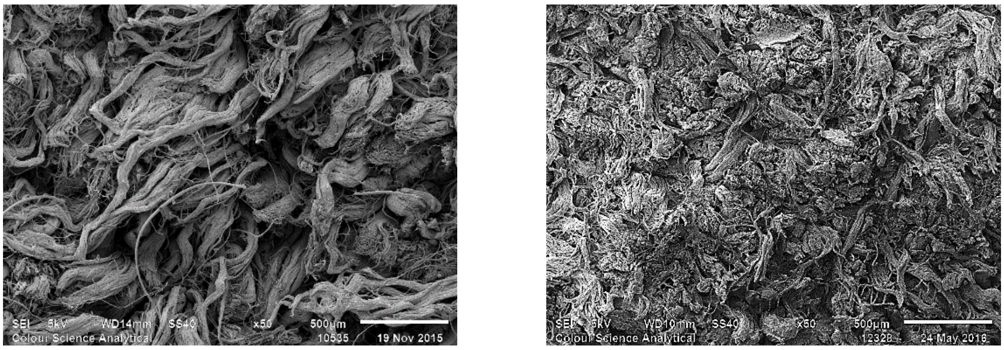
Even greater damage was visible after H150 ageing, where the coating appeared rougher and the compactness of the leather fibres increased (Figure 5-39). The coating thickness decreased to 44.90 ± 7.99 µm and became more compact. This was evident observing images of the cross-section at higher magnification (Figure 5-39c), where the amount of bubbles was lower possibly as a consequence of the combined effect of coating softening and leather shrinkage.



a) b) c)

Figure 5-39: SEM images of TL samples after H150 ageing. Cross-section at mag. 50x, details of top coating at mag. 50x (b) and cross-section at mag. 250x (c) after ageing

The fibrous layer appeared more compact than before ageing and the fibre bundles seemed to stick to each other both on the grain and corium layers. This observation was confirmed by the comparison of the leather fibres on the reverse side of the samples (Figure 5-40b) and was in agreement with previous work conducted by Li *et al.* (2016). The level of organisation of the collagen fibre bundles seemed decreased after H150, indicating that part of their stability was lost and a reorganisation of the structure took place. This lower organisation was attributed to the partial denaturation of the collagen molecule.



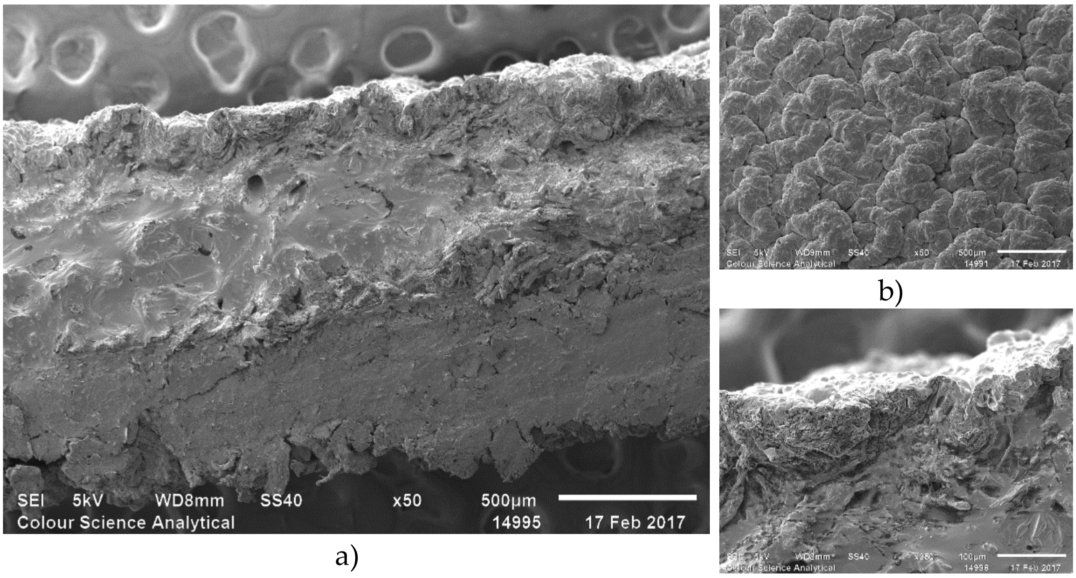
a) b)

Figure 5-40: SEM images of leather fibres in TL samples at mag. 50x before (a) and after (b) H150 ageing

The correlation between shrinkage and denaturation is well documented and it is known that heat is one of the main factors that cause collagen denaturation (Wright and Humphrey, 2002; Meyer *et al.*, 2006). Collagen can go through renaturation in presence of water, though the type of bonds that are formed when the protein is in the amorphous state are different from the ones formed in the organised structure

(Wright and Humphrey, 2002). The stability of these bonds formed with water is lower than the bonds typically found in virgin leather. This aspect would determine long-term instability of the material that may become more susceptible to moisture and less resistant to physical damage.

H+RH ageing revealed the instability of TL samples to high temperature and humidity, as visible in Figure 5-41. The change of the top coating morphology was drastic and the structure of the fibrous support was almost not recognisable.



b)

a)

c)

Figure 5-41: SEM images of TL samples after H+RH ageing. Cross-section at mag. 50x, details of top coating at mag. 50x (b) and cross-section at mag. 250x (c) after ageing

Leather fibres were still visible in a few areas of the samples, while the rest of them seemed to have compacted forming a continuous material. Thomson (2005) reported that hardening takes place in historical samples as a consequence of fluctuations in the relative humidity, because water brings in solution compounds that are present within leather and once the humidity decreases moisture and compounds move towards the surface. He wrote that these compounds accumulate where fibres are denser and with time they reduce the flexibility (Thomson, 2005). In this study the author's considers this behaviour was only partly responsible for TL hardening for two reasons. Firstly, the structure of TL (Figure 5-41a) seemed consistent throughout its thickness, thus it was unlikely that the accumulation of compounds occurred only on the outer surface. Secondly, TL was made of newly produced leather and was tested immediately after ageing, hence it was different from naturally aged samples. A possible explanation for the structure of the sample was that collagen fibres went through partial denaturation in presence of high temperature and humidity forming a gelatinous material. Once the samples returned to standard conditioning temperature the gelatinous materials solidified and acted as a collagenous glue among the fibres. This would explain the increased hardness of TL samples and it would be in agreement with the observations of the fibre shrinkage and clustering noticed on the reverse side (Figure 5-42).

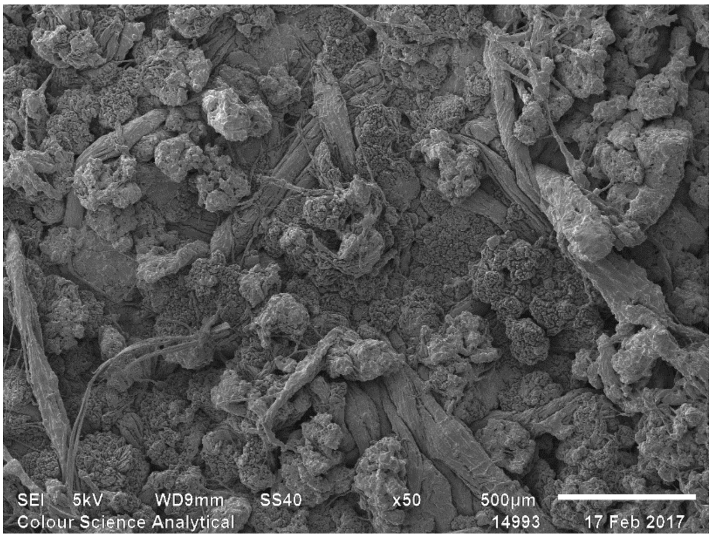
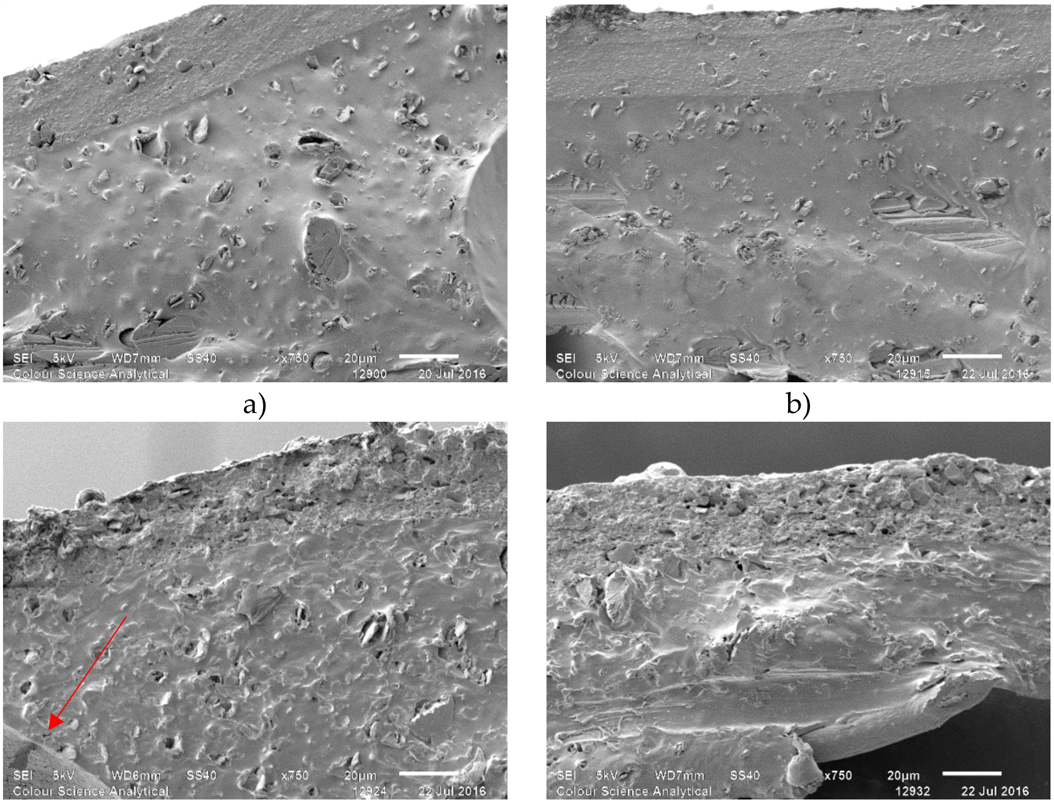


Figure 5-42: SEM image of leather fibres in TL samples at mag. 50x after H+RH ageing

Synthetic leather samples did not exhibit any sign of damage after UV ageing. Moreover, no evidence of degradation was identified on the fibrous layer after any ageing procedure. The coating bulk, though, started to present evidence of deterioration after the second ageing interval under mild heat conditions.

In Figure 5-43c it is possible to notice the appearance of small cracks, indicated by the red arrow, and an increase in the roughness of both the top and bottom layer of the coating. As a result, the definition of the limit between the two layers decreased. Similar issues were also encountered when observing the coating of H115 aged samples. However, in their case the roughness increase was already noticed after the first ageing interval, as can be seen comparing Figure 5-44a and Figure 5-43b. The distinct difference between the coating layers was already lost after 56 hours and after 168 hours the structure of the coating seemed highly compromised. However, it must be said that no clear difference was noticed when comparing the top surface before and after ageing.

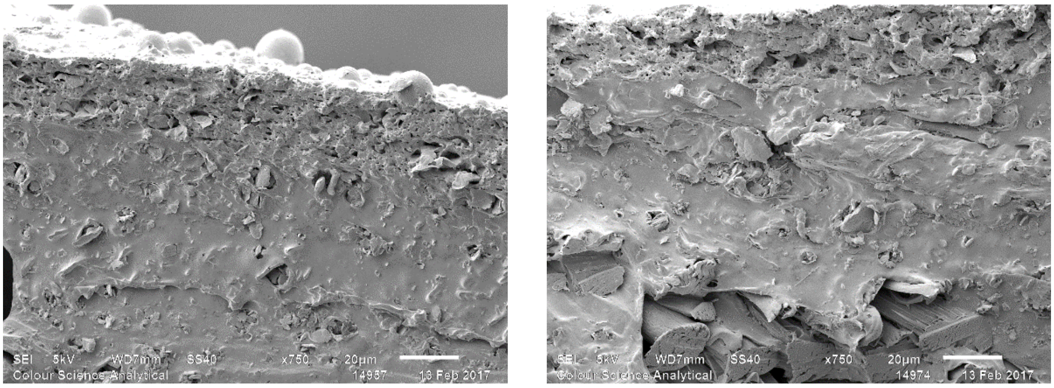


a) b)

c) d)

Figure 5-43: SEM images of SY samples at mag. 750x before (a) and after 56 hours (b), 112 hours (c) and 168 hours (d) of H70 ageing

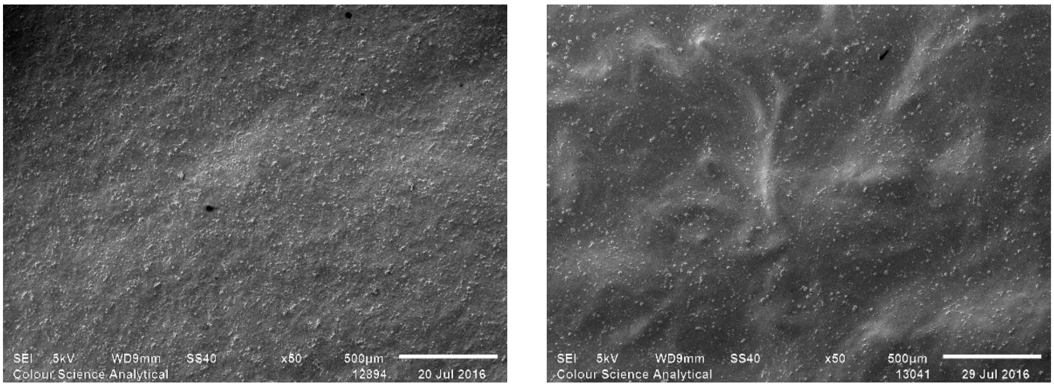
Previous studies conducted on PU coatings reported that when the binder in coating bulk is degraded pigments are more exposed, and in the long-term this leads to the formation of voids and cracks (Yang *et al.*, 2002). It is possible that the phenomenon noticed in SY was the first indicator of this degradation mechanism. In fact, while in the new coating the particles within the coating were closely surrounded by the polymer, after ageing the binder was less homogeneous and it did not surround the particles (Figure 5-44a).



a) b)

Figure 5-44: SEM images of SY samples at mag. 750x after 56 hours (a) and 168 hours (b) of H115 ageing

H150 ageing, as already seen, exhibited visible changes on the coating side after 56 hours of exposure. The increase in the roughness registered during image capture and 2D scanning seemed to contradict the SEM observations.



a) b)

Figure 5-45: SEM images of SY top coating at mag. 50x before (a) and after (b) H150 ageing

Figure 5-45 reports the top coating before and after ageing, and the latter illustrates a surface smoother than the former. Figure 5-45 depicts only a small portion of the coating (about 0.4mm) and it must be remembered that roughness perception depends on the scale that is used to measure it. Therefore, the evidence of a flatter surface was not in contrast with the previous results obtained for the roughness. By the naked eye the SY coating appeared glossier than before ageing and this initially seemed to contrast with the increased roughness that resulted from the appearance of the support fabric geometry (section 5.4.1.1). However, the smoothing of the surface in the microscale during the initial period was detected by the SEM technique and it explained the increased gloss and aligned the results with those reported in literature (Hu *et al.*, 2009). In general the smoother the surface the higher the gloss value. Meanwhile, the knitted fabric pattern of aramid fibres became visible by the naked eye and changed the roughness perception at the macroscopic level. Both phenomena could be explained if the coating went through a softening that relaxed the top surface and allowed the fibres to penetrate to a greater extent into the coating bottom layer. The polymeric coating then solidified once the samples returned to standard conditioning temperature, but the organisation of the structure was partially lost. Certain types of PU can start decomposing within the interval 150-200 °C (Chattopadhyay and Webster, 2009), therefore it is likely that softening of the PU coating was a first sign of this degradation mechanism.

Another interesting aspect of H150 aged samples was that, looking at the cross-section, the coating roughness was not significantly different from the one of samples after 168 hours of H70 and H115 ageing. This may indicate that similar phenomena occurred during the accelerated ageing procedures with a higher reaction rate in the case of H150.

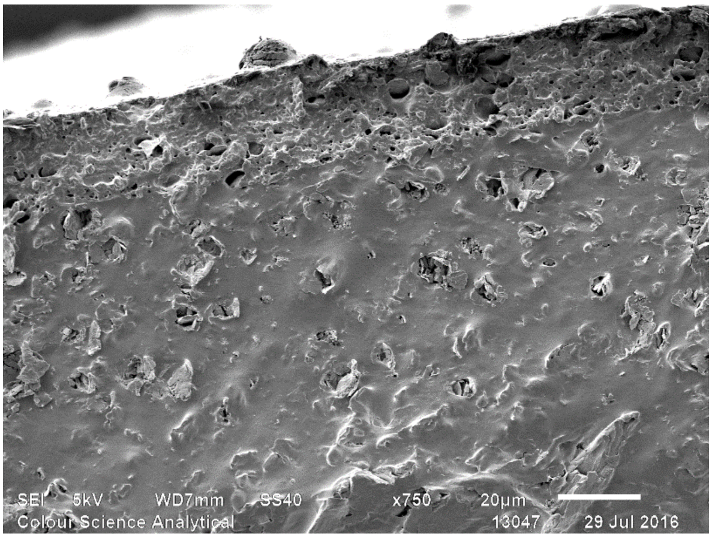
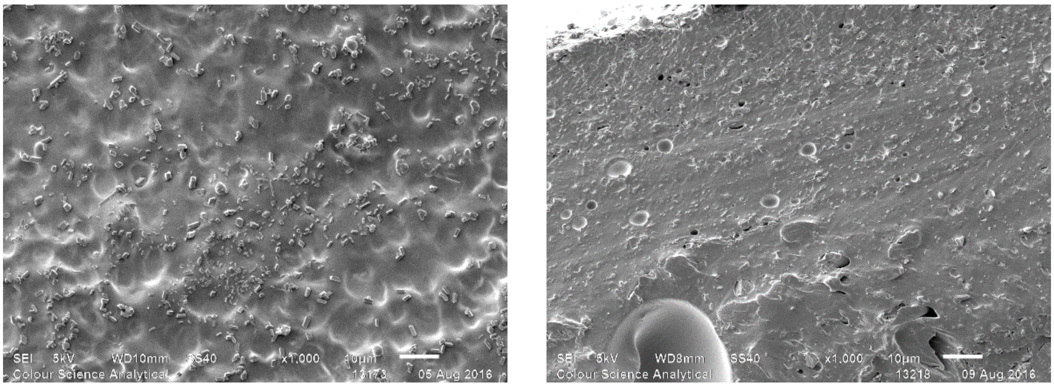


Figure 5-46: SEM image of SY cross-section at mag. 750x after H150 ageing

H150 ageing was the only procedure that produced obvious physical changes identifiable via SEM of the top coating. In fact, despite the effect of the other accelerated ageing on SY material was visible from the cross-sections, none of them caused significant changes of the coating that remained coherent. The same was also noticed in the case of H+RH exposure where SY was similar to samples after H115.

E-Leather samples presented different stability issues compared with TL and SY. On the one hand, changes in the fibrous layer were more difficult to detect because of the number of components that formed the HE face. On the other hand, the coating was made of a consistent polymeric layer that facilitated the detection of imperfections. Moreover, the two substrates (EL2 and EL3) demonstrated different degrees of sensitivity under the selected ageing conditions that were visible also during SEM observations.

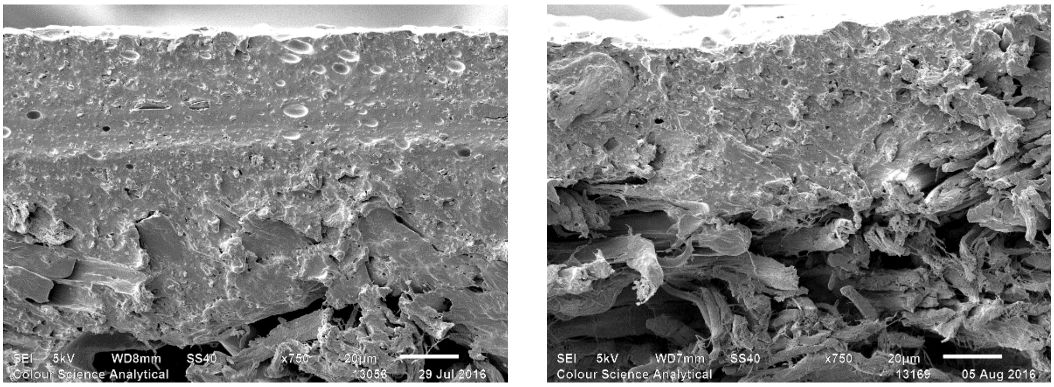
EL2 did not present signs of degradation after H70, H115 and UV ageing, indicating the high stability of the product under the selected conditions. The analysis of H150 aged samples, though, provided interesting results related with the behaviour of the coating. The presence of particles having size 2.63 ± 0.64 μm (Figure 5-47a) suggested that the pigments of the top surface started to be exposed. This phenomenon was initially attributed to the partial degradation of the polymeric coating that Yang *et al.* (2002) related with the PU oxidation. However, the coating bulk (Figure 5-47b) did not present significant differences with respect to unaged samples, as it was expected. Because of this reason EDX analysis was carried out to assess the composition of the particles (see section 5.4.3.1).



a) b)

Figure 5-47: SEM image of EL2 top coating at mag. 250x (a) and cross-section coating at 1000x (b) after 56 hours of H150 ageing

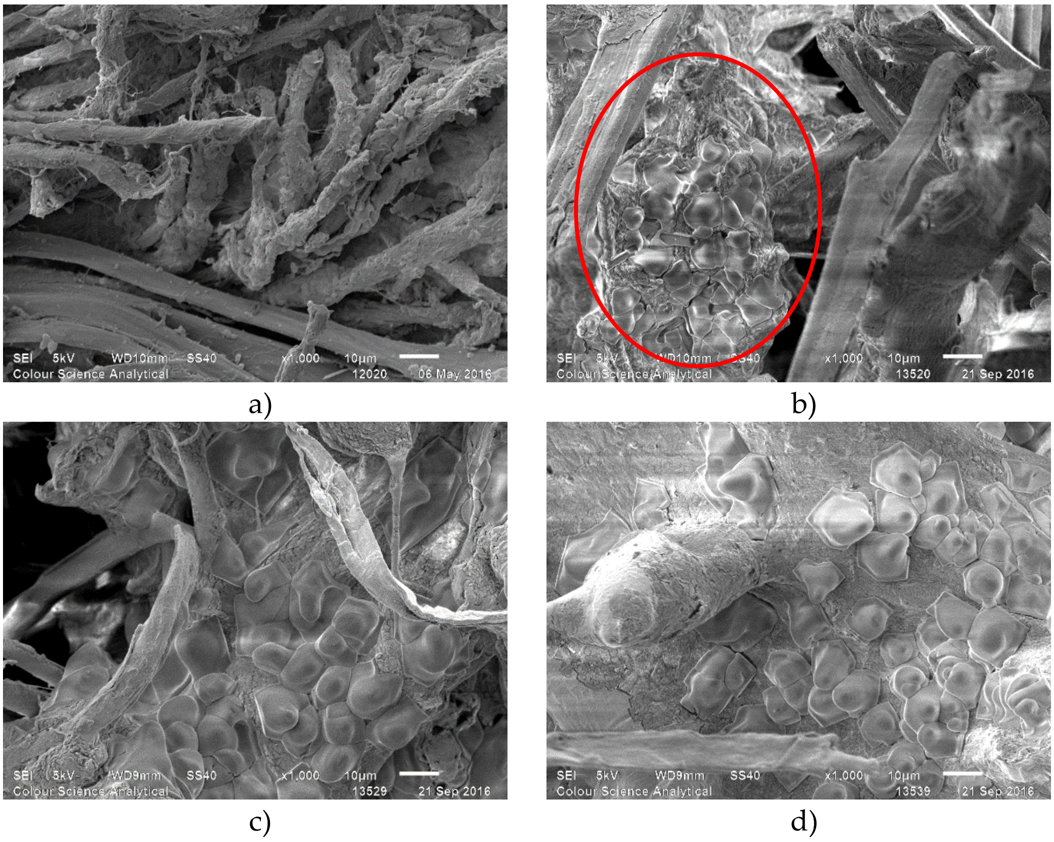
The other ageing condition that induced damage in the coating was H+RH, where the EL2 cross-section resulted significantly altered (Figure 5-48b). However, no evidence of particles was found on the top surface. Likewise, no evidence of clear damage was found in the fibrous layer, confirming that EL2 was more stable than TL and comparable to SY.



a) b)

Figure 5-48: SEM image of EL2 coating cross-sections before (a) and after (b) 168 hours of H+RH ageing at mag. 1000x

The SEM micrographs of EL3 presented evidence of degradation mainly on the fibrous layer. The PU coating seemed stable after H70, H115, H150 and UV, whilst it was less consistent after H+RH ageing, with the roughness gradually increasing after each interval. Nevertheless, the HE face exhibited a different morphology, with more compact structure and less voids, compared to the one of unaged samples after all the ageing procedures apart for UV ageing. The greater damage was caused by H+RH ageing (Figure 5-49).



a) b)

c) d)

Figure 5-49: SEM images of EL3 fibrous layer at mag. 1000x before (a) and after 56 hours (b), 112 hours (c) and 168 hours (d) of H+RH ageing. The red oval shape indicates the presence of a newly formed compound

The formation of new material between the fibre bundles was already identified after the first ageing interval. A hypothesis was formulated that the newly formed material was a side product of the brominated flame retardant. In fact, the presence of the material with this peculiar shape was not observed in EL2 samples and the only significant difference between EL2 and EL3 was the flame retardant. In addition, after EL3 treatment a number of solid residues similar to white-yellow crystals were found on the window of the weathering chamber. These deposits were analysed via EDX in order to confirm their composition (see section 5.4.3.1) and an image is reported in Figure 5-50. The formation of these deposits between the fibres may have led to a flexibility reduction of the EL3 samples, because they may have “glued” the fibres reducing the mobility of the whole material. Furthermore, a powder developed when the EL3 was handled.

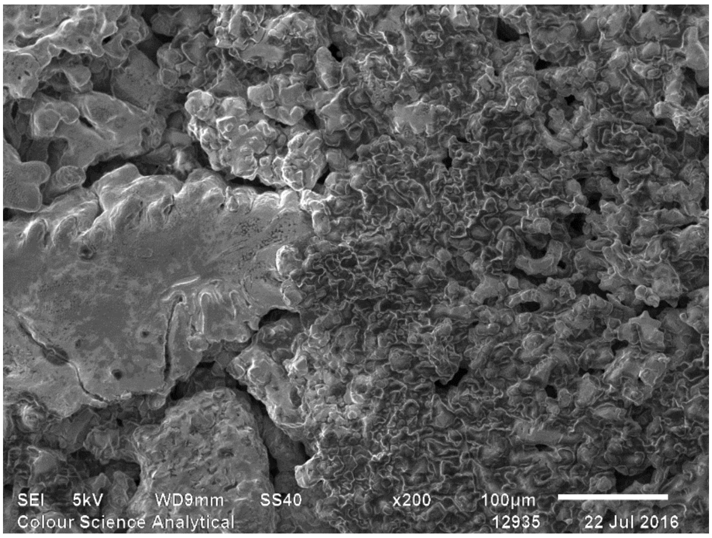


Figure 5-50: SEM image of deposit collected from the weathering chamber after H+RH ageing (mag. 200x)

The presence of similar deposits was also found into the oven used to conduct H115 and H150 procedure, indicating that both heat and the combination of heat and humidity were likely to cause the migration of the flame retardant. However, the presence of the newly formed material (deposits) was only identified after H+RH ageing, suggesting that humidity had an important role in their formation.

5.4.3 Chemical Analysis

Studies that document chemical and physical degradation behaviour of leather in museum context have mainly been focused on parchment and vegetable-tanned leather (Larsen *et al.*, 1994; Chahine, 2000; Larsen, 2008; Abdel-Maksoud, 2011). Despite these studies provide an important platform to conduct degradation studies on innovative leather materials, it is indispensable to assess to what extent the former are also representative for the latter. Moreover, research is mainly focused on evidences of degradation in the microscopic scale and less often on the impact and correlation they have with macroscopic behaviour.

Efforts in this direction have been made in the industrial sector with research that that aims at assessing the resistance of innovative leather products to environmental (Meyer *et al.*, 2006; Ollè *et al.*, 2012) and mechanical stresses (Milašienė and Bubnytė, 2007). For example, Ollè *et al.* described changes in chemical and physical properties after different accelerated ageing conditions and they stated that a decrease in shrinkage temperature and an increase in water soluble organic matter confirmed the drastic effect of high heat and relative humidity on the collagen molecule (Ollè *et al.*, 2011). They suggested that during exposure to tropical conditions the collagen molecule underwent cleavage of bonds previously formed with tanning agents and fatliquoring. In addition, they reported that wet-white leather went through a carbonisation process that made the physical tests impossible. This study partially responded to the need for further studies reported above, both regarding the relationship between chrome-free and chrome leather and the correlation between microscopic properties and macroscale variations. However, it only briefly mentioned the two main phenomenon that govern leather ageing: hydrolysis and oxidation.

The EC STEP leather project studied the effect of environmental factors on historic and naturally aged vegetable-tanned leathers (Larsen *et al.*, 1994) and identified the two reactions as the major mechanisms leading to the degradation of these leathers. The project not only allowed the measurement of chemical and physical damages in the investigated samples, but also investigated the accelerated ageing methods that would to better correlate with the simulated and natural ageing (Florian, 2006).

Larsen (2008) reported that hydrolytic breakdown, often in the form of acid hydrolysis, is common in polluted environments and causes the breakage of peptide chains in the collagen fibres. Heat, moisture and acid conditions are mainly responsible for this type of reaction (Thomson, 2005). In polluted environments acids dissolved in water dissociate and the hydronium ions originated by the dissociation of the acid react with the collagen amino acids causing acid hydrolysis (Florian, 2006). Oxidative breakdown, on the other hand, is related with factors such as light, heat and, of primary importance, free radicals (Florian, 2006; Larsen, 2008). These two degradation mechanisms, hydrolysis and oxidation, can occur alone or can take place together (Thomson, 2005) and can lead to powdering of vegetable-tanned leathers (Larsen, 2008). Unfortunately, extensive studies on chrome-tanned and wet-white leathers similar to the ones just described for vegetable-tanned leather have not been conducted.

Hydrolysis and oxidation is not only of primary importance in leather but also in PU coated fabrics. Design objects made of PU synthetic leather have become part of collection in recognised museums such as the German 'Die Neue Sammlung' in Munich (Die Neue Sammlung, 2017). Bechthold *et al.* reported on the detrimental effects of oxidation and hydrolysis on these substrates (Bechtold *et al.*, 2006). They recognised the most susceptible part of the PU macromolecule in the soft polyester (or polyether) polyol structural fragment. This is one of the limited sources of information regarding the degradation of PU coated fabrics, because most of the studies conducted on museum objects dealt with PU foams (van Oosten *et al.*, 2011; Pellizzi *et al.*, 2014; Lovett and Eastop, 2014). This difference cannot be ignored because, for example, hydrolysis of PU coating is accelerated by the presence of foam upholsteries as a consequence of their release of residual catalyst, e.g. organometallic compounds (Bechtold *et al.*, 2006). The large amount of objects manufactured using

PU coatings in the last 50 years should result in a greater interest towards these products.

Differently from the case of leather, where industry is partially responding to some of the unsolved questions regarding the degradation of innovative leather materials, the situation is more complex in the case of coated fabrics. Studies on the long-term stability of coated fabrics are scarce and mainly oriented towards identification of product's failure (Potočić Matković *et al.*, 2014). Interesting studies focused on degradation are the ones conducted on PU coatings for outdoor applications, where it has been reported that thermal and photo-oxidation can follow similar degradation pathways (Zhang, 2012).

Many routes can be followed to detect chemical degradation according to the type of information that one is looking for. EDX, ATR-FTIR, moisture content and pH analysis were used in this work with this purpose.

5.4.3.1 EDX

The use of EDX is generally associated with electron microscopy and in museum applications it is used for leather objects mainly to detect the presence of elements that can be ascribed to specific pigments (Chaplin *et al.*, 2010; Elnaggar *et al.*, 2017) or treatments carried out on the item (Rabin *et al.*, 2010). Its use to assess changes during degradation is less common and an attempt to evaluate its applicability was made for this thesis.

As mentioned in Chapter 4, the nature of the samples under investigation and the methodology applied did not allow any quantitative analysis. Stability, homogeneity and lack of voids are prerequisites indispensable to perform solid quantitative analyses and they would require inclusion in resin and polishing in order to be achieved. However, qualitative analysis can be conducted to evaluate if obvious differences between samples before and after degradation can be related with phenomena occurring within the specimen.

In this work the most interesting EDX results were related with the brominated flame retardants. In fact, most of the samples maintained the elemental compositions described during the chemical characterisation throughout the ageing procedures, but in some occasions other elements –bromine, in particular– appeared and possible reasons for their detections are described below.

TL exhibited spectra similar to the ones collected at 0 hours both on the coating and fibrous layer sides, but some differences were identified in the bromine content of the coating (Table 5-2).

Ageing Condition	C	O	Al	Si	Cl	Br	Ca	Cu	K
0 hr – H70	x	x	x	-	x	x	x	-	-
56 hr - H70	x	x	x	-	x	x	x	-	-
112 hr - H70	x	x	x	-	x	x	x	-	x
168 hr - H70	x	x	x	-	x	x	x	-	-
0 hr – H115	x	x	x	-	x	x	x	-	-
56 hr - H115	x	x	x	-	x	-	x	-	-
112 hr - H115	x	x	x	-	x	-	x	x	-
168 hr - H115	x	x	x	x	x	-	x	-	-
0 hr - H150	x	x	x	-	x	x	x	-	-
56 hr - H150	x	x	x	-	x	-	-	-	-
0 hr - H+RH	x	x	x	-	x	x	x	-	-
56 hr – H+RH	x	x	x	-	x	-	x	-	-
0 hr - UV	x	x	x	-	x	x	x	-	-
56 hr - UV	x	x	x	-	x	x	x	-	-
112 hr - UV	x	x	x	-	x	x	x	-	-
168 hr - UV	x	x	x	-	x	-	-	-	-

Table 5-2: Presence/absence of chemical elements in TL coating at different accelerated ageing stages. The bromine column was highlighted to emphasise the different behaviour of the element depending on the ageing technique used

Bromine was consistently detected in the coating at mild temperatures, and during the first two intervals of UV ageing. However, it was not detected after 168 hours of UV ageing, as well as after 56 hours of H115, H150 and H+RH ageing. This led to the hypothesis that part of the flame retardant in the coating might have migrated during the ageing procedures. This would be in agreement with recent studies conducted on upholstery textiles –such as polyester curtains– at increasing temperatures, which demonstrated that brominated flame retardants can volatilise at room temperature and heat increases their migration (Kajiwara and Takigami, 2013). Further investigations would be necessary to confirm the hypothesis of bromine migration in the case of leather samples.

Table 5-3 reports the results of investigations conducted on the fibrous layer of TL, and it is possible to notice that in some cases the presence of "light element" nitrogen (normally difficult to identify) was detected. Aluminium (from tanning agent) and bromine (from flame retardant) were also consistently present. In chapter 4 it was suggested that calcium might have not homogeneously distributed throughout the tanned hide. This was also confirmed during the ageing procedures because, in fact calcium was not consistently detected. However, this is related with the manufacturing process of the leather and not with changes due to the degradation procedure.

Ageing Condition	C	O	N	Na	Al	Si	Br	Ca
0 hr – H70	x	x	-	-	x	-	x	-
56 hr - H70	x	x	-	-	x	-	x	-
112 hr - H70	x	x	-	-	x	x	x	x
168 hr - H70	x	x	-	-	x	-	x	-
0 hr – H115	x	x	-	-	x	-	x	-
56 hr - H115	x	x	-	x	x	-	x	-
112 hr - H115	x	x	-	x	x	-	x	-
168 hr - H115	x	x	-	-	x	-	x	-
0 hr - H150	x	x	-	-	x	-	x	-
56 hr - H150	x	x	-	-	x	-	x	-
0 hr - H+RH	x	x	x	-	x	-	x	x
56 hr – H+RH	x	x	-	-	x	-	x	-
0 hr - UV	x	x	x	-	x	-	x	x
56 hr - UV	x	x	x	-	x	-	x	x
112 hr - UV	x	x	x	-	x	-	x	x
168 hr - UV	x	x	-	-	X	-	x	-

Table 5-3: Presence/absence of chemical elements in TL fibrous layer at different accelerated ageing stages. The bromine column was highlighted to emphasise the different behaviour of the element depending on the ageing technique used

EDX mapping was conducted on a sample of TL after H+RH ageing to evaluate the distribution of the elements (Figure 5-51). It was suggested during SEM observations in section 5.4.2 that the compactness of the samples and their hardening may have been the result of mechanisms of moisture and soluble compounds transport that concentrate substances on leather surface. This was reported in the literature (Thomson, 2005) and EDX mapping was conducted to confirm that the phenomenon took place also in the TL samples. As visible in Figure 5-51 only silicon and bromine were detected along with carbon and oxygen. Considering that silicon was already detected in the coating, it was not possible to confirm that its distribution was concentrated within a specific area of the sample. Carbon, though, was particularly concentrated in proximity of the top coating and this could indicate the accumulation of organic compounds. The second hypothesis formulated to explain the sample's hardening, related with the partial denaturation of collagen fibres and the formation of a collagenous glue, could not be discarded nor confirmed at this stage.

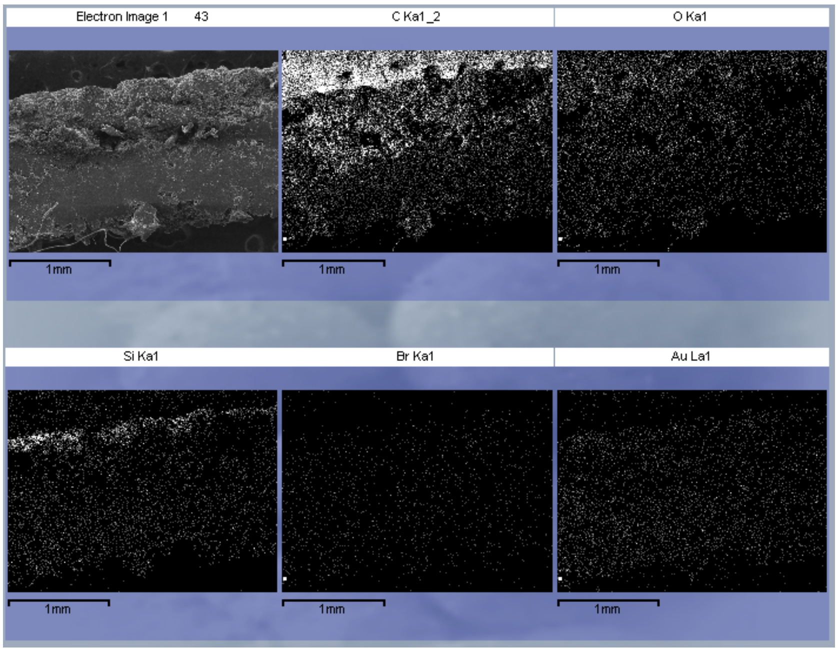


Figure 5-51: EDX mapping of TL cross-section at mag. 50x after 56 hours of H+RH ageing

SY and EL2 did not present significant variations in terms of elemental composition, therefore it was decided not to include the tables of their results. However, EDX mapping was conducted on EL2 samples after H150 ageing to assess the elemental composition of the particles found on the top of the coating after treatment.

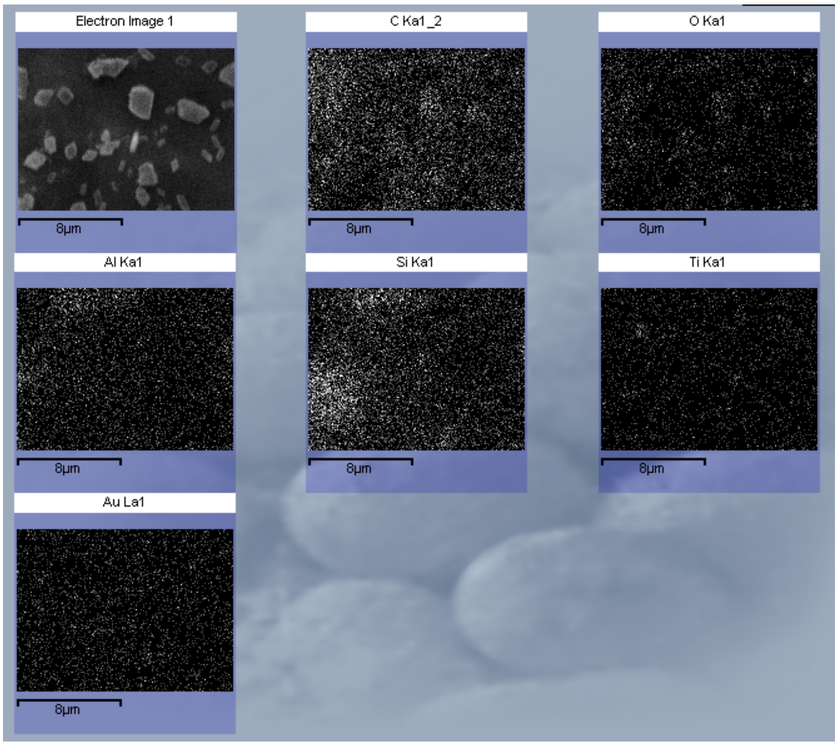


Figure 5-52: EDX mapping of EL2 coating at mag. 1000x after 56 hours of H150 ageing

During SEM observation these particles were thought to be pigments. Though, it was found that carbon and oxygen were the only elements of the particles. The manufacturer did not mention the use of pigments containing these elements (O'Keefe, 2015), therefore further investigations that focus on this issue are required to assess the exact composition and the reason why the particles were formed.

EL3 presented an unusual degradation behaviour on the coating side. The unaged material exhibited the presence of bromine exclusively in the fibrous layer but when exposed to temperatures above 70 °C and after 56 hours bromine was also detected on the coating side (Table 5-4). The only samples that did not show this behaviour were the ones exposed to UV ageing that, in addition, were subjected to 50 °C and 50% RH.

Ageing Condition	C	O	Na	Al	Si	Br	Ti	Fe
0 hr – H70	x	x	x	x	x	-	x	x
56 hr - H70	x	x	x	x	x	x	x	x
112 hr - H70	x	x	x	x	x	x	x	x
168 hr - H70	x	x	x	x	x	x	x	x
0 hr – H115	x	x	x	x	x	-	x	x
56 hr - H115	x	x	x	x	x	x	x	x
112 hr - H115	x	x	x	x	x	x	x	x
168 hr - H115	x	x	x	x	x	x	x	x
0 hr - H150	x	x	x	x	x	-	x	x
56 hr - H150	x	x	x	x	x	x	x	x
0 hr - H+RH	x	x	x	x	x	-	x	x
56 hr - H+RH	x	x	x	x	x	x	x	x
112 hr - H + RH	x	x	x	x	x	x	x	x
168 hr - H + RH	x	x	x	x	x	x	x	x
0 hr - UV	x	x	x	x	x	-	x	x
56 hr - UV	x	x	x	x	x	-	x	x
112 hr - UV	x	x	x	x	x	-	x	x
168 hr - UV	x	x	x	x	x	-	x	x

Table 5-4: Presence/absence of chemical elements in EL3 coating at different accelerated ageing stage. The bromine column was highlighted to emphasise the different behaviour of the element depending on the ageing technique used

This finding suggested that heat might have induced the migration of the brominated flame retardant from the fibrous layer towards the outer surface. Because the presence of newly formed material between EL3 fibres was only observed after H+RH ageing, it is possible that during the other ageing procedures the flame retardant migrated without depositing within the fibrous layer. This may indicate that dry heat did not allow the formation of deposits derived from the flame retardant as opposed to the wet heat condition.

The solid deposit collected from the oven after H+RH ageing of EL3 was analysed by means of EDX spectroscopy and the elemental mapping obtained (Figure 5-53).

Carbon, nitrogen, oxygen and bromine composed the deposit, and bromine and nitrogen seemed related to each other.

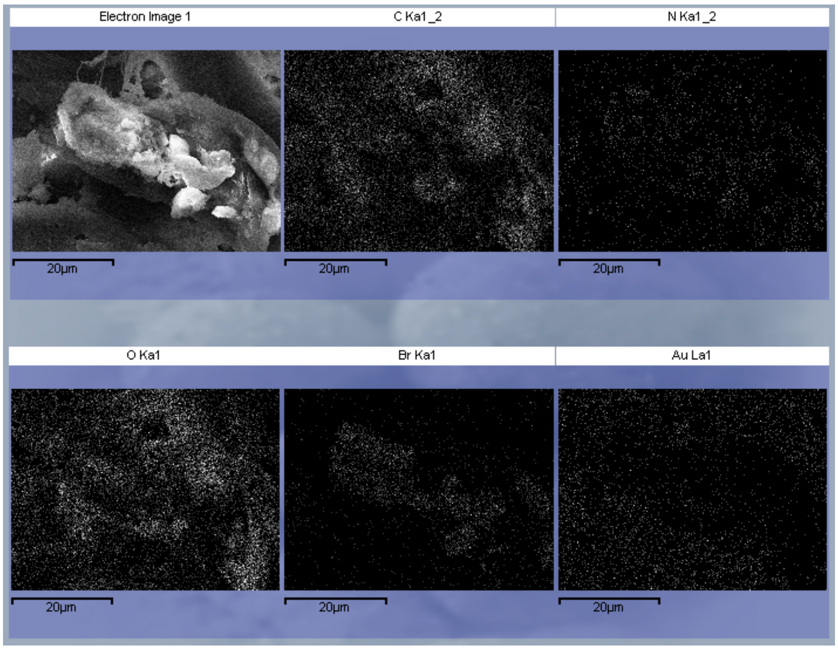


Figure 5-53: EDX mapping of oven deposit after H+RH ageing of EL3

The presence of nitrogen can be attributed to the fact that the bromine was bond to leather fibres, therefore it is possible that when bromine left the hydroentangled layer it also brought with it fragments of the collagen peptides. As a consequence, it would be advisable to study how the migration of the flame retardant affects the peptide chains of collagen and how it would affect them in the long term.

In this context, the use of EDX allowed to observe that bromine was not present in the TL samples coating after moderate, severe heat ageing and H+RH ageing. Moreover, the element was found in the EL3 coating after the first ageing procedure of all the accelerated ageing apart for the UV procedure. These findings suggested that the flame retardants used in the two materials may easily migrate from the substrates, as also highlighted by the deposits recovered from the oven window.

5.4.3.2 ATR-FTIR

FTIR has often been used both in leather (Ollè *et al.*, 2011) and PU substrates (Wilhelm and Gardette, 1997; Pellizzi *et al.*, 2014) to detect changes occurring as an effect of degradation by measuring changes in the peaks absorbance or their shift. The coatings of the investigated substrates were made of PU, hence the attention here was focused on the chemical reactions that could have led to degradation. PU can undergo two main degradation mechanisms, that is hydrolysis and oxidation. Hydrolysis is the prevalent mechanisms in the family of polyester PU while oxidation is dominant in polyether PU (Wilhelm and Gardette, 1997; Wilhelm and Gardette, 1998).

With respect to the different fibrous layers, particular attention was paid to the leather absorption peaks. Shao (2005) reported that the bands at about 1742 cm^{-1} increase and the band at 1244 cm^{-1} appears with heating, therefore it was expected to notice changes in the corresponding areas of the spectra after H70, H115 and H150 ageing.

Three measurements for each ageing interval were recorded in order to assess the effects of the selected accelerated ageing, and the average of the spectra compared with the unaged FTIR spectrum, in agreement with Pellizzi *et al.* (2014). Recordings were obtained on the coating and fibrous layer to allow the investigation of both the polymeric matrix of the former and the changes occurring within fibres of the latter. It was decided to report in this paragraph the summary of the measurements conducted on the samples before and after the final step of the ageing. This will establish whether or not the ageing had an impact on the material. A more detailed description of the change detected as a function of time was discussed in those cases where an effect was observed. The spectra of each ageing procedure at the different ageing times have been included in the Appendix.

Figure 5-54 reports the absorbance spectra of TL samples tested on the coating side. All TL samples after ageing had very similar absorbance spectra to the samples before ageing, indicating that most of the coatings were stable in the short term. This was particularly true for H70, H115 and H+RH procedures, where the spectra profiles resembled those of unaged TL.

After H150 ageing the absorptions between 2800 and 3000 cm^{-1} typical of CH_2 and CH_3 stretching increased while the shoulder at 963 cm^{-1} assigned to the stretching of C-C bonds decreased (see detail and red arrow in Figure 5-54). Moreover, the band at 1538 cm^{-1} referred to the bending of N-H started to decrease and became narrower (see Appendix). This suggested that part of the skeleton of the molecule was lost as a consequence of the breakage of the bonds between carbon atoms.

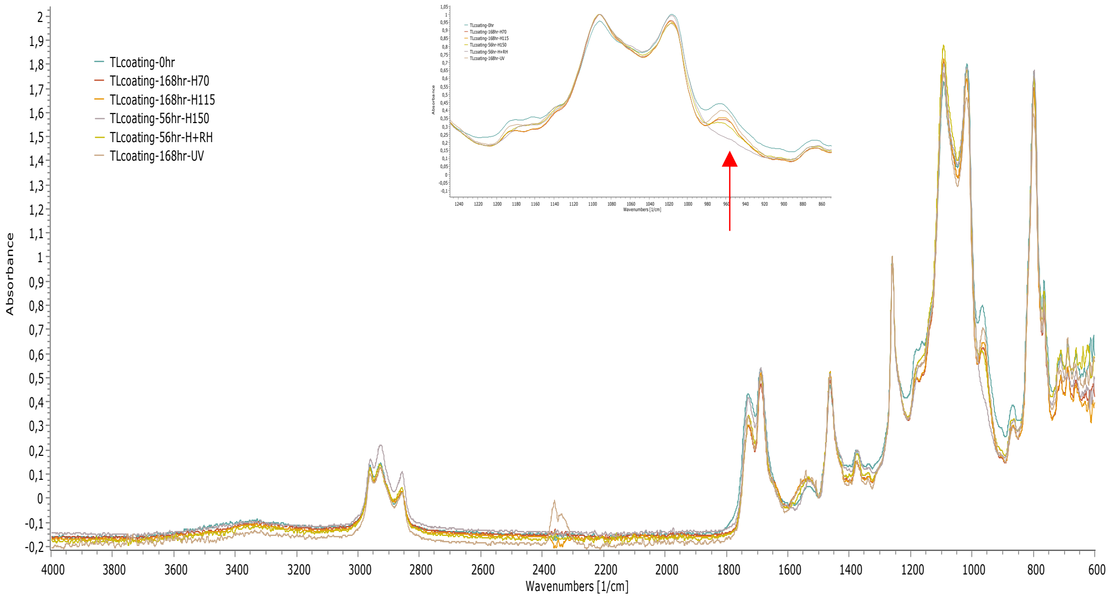


Figure 5-54: ATR-FTIR spectra showing absorbance peaks of TL coating before and after ageing. The detail of the region comprised between 1250 and 850 cm^{-1} is also reported

Also UV aged samples presented some sign of deterioration after 168 hours of ageing, with the decrease of the band at 1538 cm^{-1} assigned to the N-H bond of amide II. Previous research conducted on the influence of UV radiation on aliphatic PU pointed out that the decrease of amide II peak started after a limited amount of hours (about 30) and gradually lead to depolymerisation of the PU chain (Irusta and Fernandez-Berridi, 1999). Oxidation of the carbon atom adjacent to the N-H starts the mechanism that leads to hydroperoxy, then they form radicals and finally acetylurethane (Wilhelm and Gardette, 1998). It is likely that this phenomenon occurred both in H150 and UV samples and could represent a good indicator of degradation.

The analysis of the fibrous layer was challenging because of the high level of noise present in the spectrum (Figure 5-55) after degradation. This was caused by the imperfect contact between the sample and the area of analysis and was related to the higher stiffness of the sample. The greater noise was observed in H+RH aged samples that were extremely rigid. After H+RH ageing the bands of amide I at 1632 cm^{-1} and amide II at 1547 cm^{-1} decreased their intensity. Bicchieri *et al.* (2011) reported that in this region are comprised the absorptions of both helical and coil configuration of the collagen, but generally they are not visible together because the peaks are superimposed. The helical mode is characterised by peaks at higher wavenumbers (Bicchieri *et al.*, 2011) and it can be assumed that when leather is in good conditions this absorption is prevalent over the random mode.

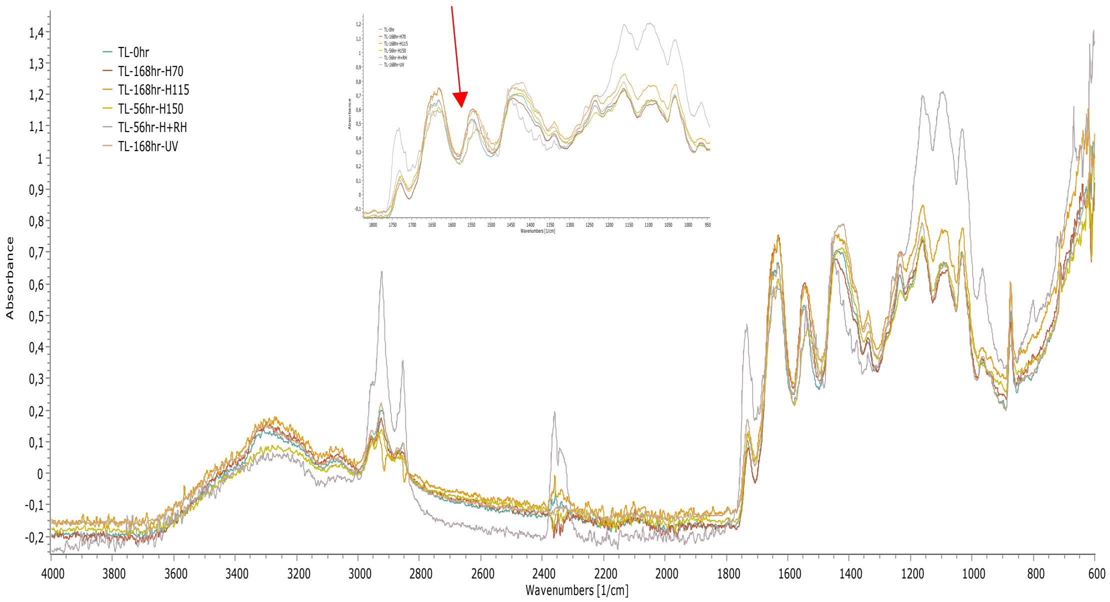


Figure 5-55: ATR-FTIR spectra showing absorbance peaks of TL fibrous layer before and after ageing. The detail of the region comprised between 1900 and 1000 cm^{-1} is also reported.

In TL samples after H+RH ageing the amide I peak shifted to the lower frequency and a shoulder was observed, also at lower frequencies. This was interpreted as a steep increase in the signal attributed to the random coil mode (arrow in Figure 5-55). The amide II also shifted towards lower wavenumbers compared to new samples indicating that lower energies were required to break the bond. Meanwhile, the signal of the carbonyl group at 1731 cm^{-1} increased, as also did the peaks comprised between 1200 and 1000 cm^{-1} and the ones relative to C-H (between 2850 and 3000 cm^{-1}). Finally, a broadening of the peak that denotes O-H bond was differentiated in the range above 3200 cm^{-1}. All together these observations suggested that there was a reduction in the level of organisation of the collagen molecule caused by the breakage of bonds in the helical structure and that more carboxyl groups became therefore available. This was in agreement with Covington (2009) that reported on this phenomenon in presence of wet heat.

Regarding the other ageing procedures no particular trend was found, apart for a similarity between the behaviour after H150 and the one after H+RH. Also in this case (H150) the peak at about 1540 cm^{-1} was shifted to the lower frequency, possibly indicating an increase of the random coil configuration to the expenses of the helical one. This finding could indicate that both dry heat at high temperature and wet heat have an effect on the collagen structure and within 56 hours these factors are able to induce a transition from the helical to the random coil mode.

Synthetic leather demonstrated a consistent remarkable appearance throughout the ageing procedures (see section 5.4.1) and the only obvious change was exhibited after H150 treatment.

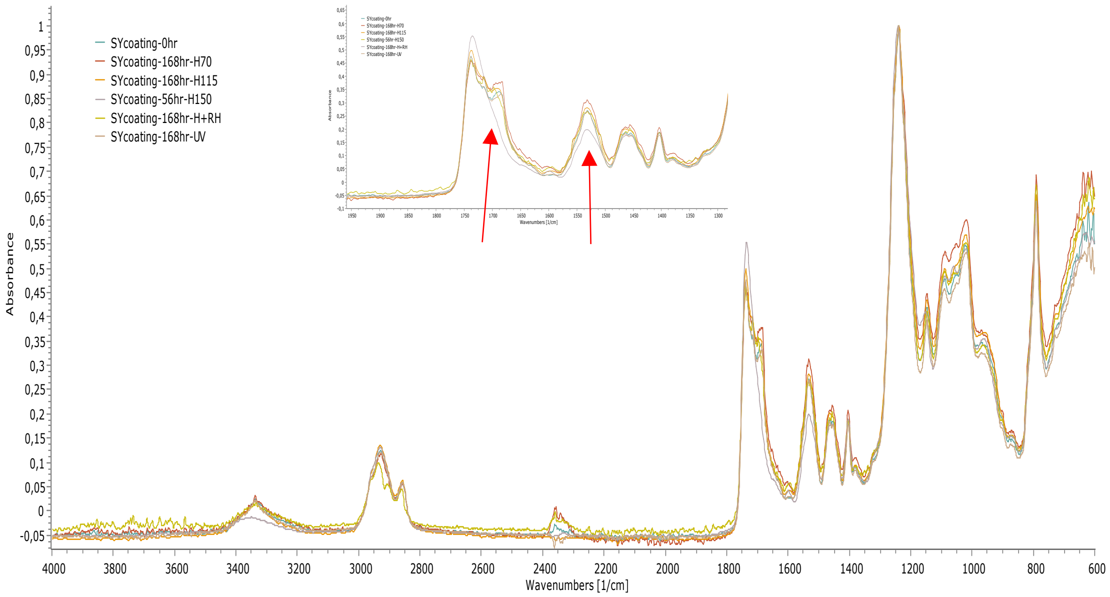


Figure 5-56: ATR-FTIR spectra showing absorbance peaks of SY coating before and after ageing. The detail of the region comprised between 2000 and 1300 cm^{-1} is also reported.

By observing the results of the ageing procedures it is clearly visible that H150 aged samples were those that exhibited the most prominent change. The red arrows in Figure 5-56 indicate two interesting peaks: the one of C=O bond (1738 cm^{-1}) and the one of secondary amide (1531 cm^{-1}). The former increased, became narrower and the smaller peak of the urethane group at 1683 cm^{-1} disappeared (left red arrow in detail in Figure 5-56), while the latter decreased in intensity. In addition, the absorptions of the N-H at 3339 cm^{-1} decreased, became broader and shifted towards higher wavenumbers. Likewise, the C-H absorptions also tended to decrease. Research conducted in this area suggested that oxidation of methylene groups in the region 2950 – 2850 cm^{-1} may induce the creation of hydroperoxides in the polyurethane chain (Wilhelm and Gardette, 1997). This initial mechanism leads to the formation of other compounds, such as acetylurethane, that increase the absorption at about 1750 cm^{-1} and finally lead to the scission of the polymer (Wilhelm and Gardette, 1997). These reactions are supposed to take place when the polymer is subject to UV irradiation or, in alternative, when heated. It was thus suggested that a similar phenomenon took place in the case of H150 ageing and, to a lesser extent, in H115 ageing (see Appendix).

UV ageing of the materials did not produce comparable spectral degradation behaviour. This was probably due to the fact that the conditions used for the procedure and the length of the experiment were not long enough to produce detectable spectral changes. The increase of the peaks in the region 1200 – 1000 cm^{-1} was possibly due to minor differences in the absorptions of the samples.

H+RH ageing did not affect the coating to a great extent, even if it was initially considered the most potentially harmful treatment on the basis of the know sensitivity of PU to the hydrolysis process (van Oosten *et al.*, 2011; Lovett and Eastop, 2014). Minor changes in absorbance were detected in the secondary amide (1531 cm^{-1}) and C-O-C (1089 and 1018 cm^{-1}) regions (see Appendix). It was not possible to establish whether these peaks were linked to degradation processes, though it is highly possible.

In investigating the fibrous layer of SY samples the same difficulties encountered during the examination of TL were found. Also here the difficulty of achieving a good contact between the substrate and the instrument analysis area influenced the quality of the spectra. The summary of the spectra before and after ageing is reported in Figure 5-57.

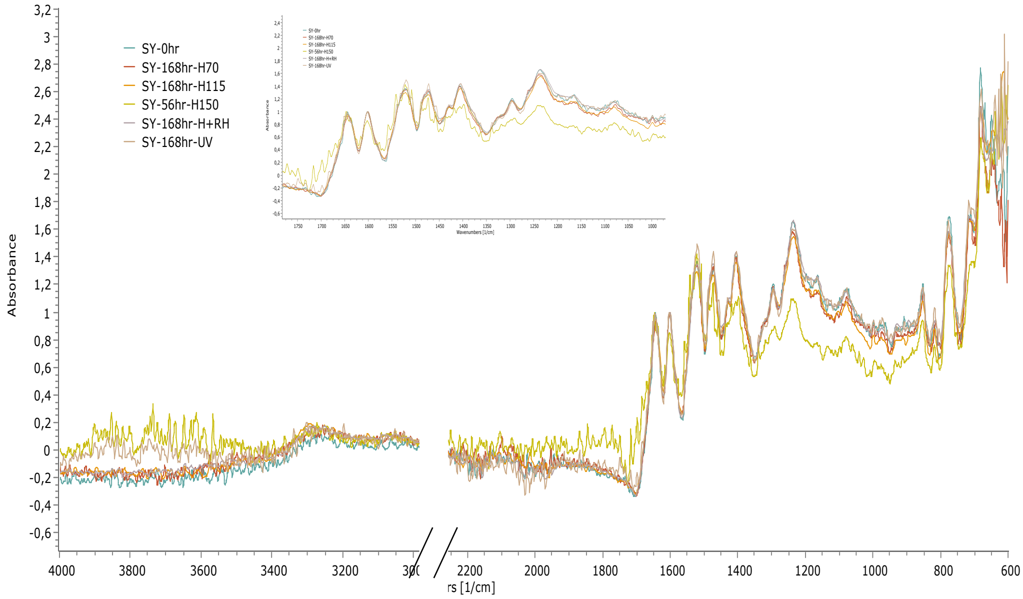


Figure 5-57: ATR-FTIR spectra showing absorbance peaks of SY fibrous layer before and after ageing. The detail of the region comprised between 1700 and 1000 cm^{-1} is also reported.

The detection of differences in the absorbance peaks of SY fibrous layer was not easy. If a qualitative analysis of the functional groups was possible in Chapter 4 and allowed the identification of the fibres, in this case the investigation would have required a higher level of detail. The bulky fabric and the amount of hollow spaces resulting from the fibre's distribution complicated the detection of well-defined peaks. The only clear difference that was evident from the comparison of the spectra regarded the H150 aged samples that in the region between 1350 and 850 cm^{-1} showed a significant decrease of intensity. These signals were potentially related to the same samples that exhibited obvious yellowing after treatment, therefore it would be possible that ongoing phenomena within the aramid fibres were responsible for the colour variation. However, no new peaks and no major difference in the other absorptions were identified when comparing unaged and aged samples.

With regard to EL2, one of the most interesting findings concerned the effect of H115 and H+RH on the coating (Figure 5-58). If TL samples did not present any specific variation associated with the two ageing procedures, in EL2 the effect of those procedures was particularly clear in the region of the C-H bond.

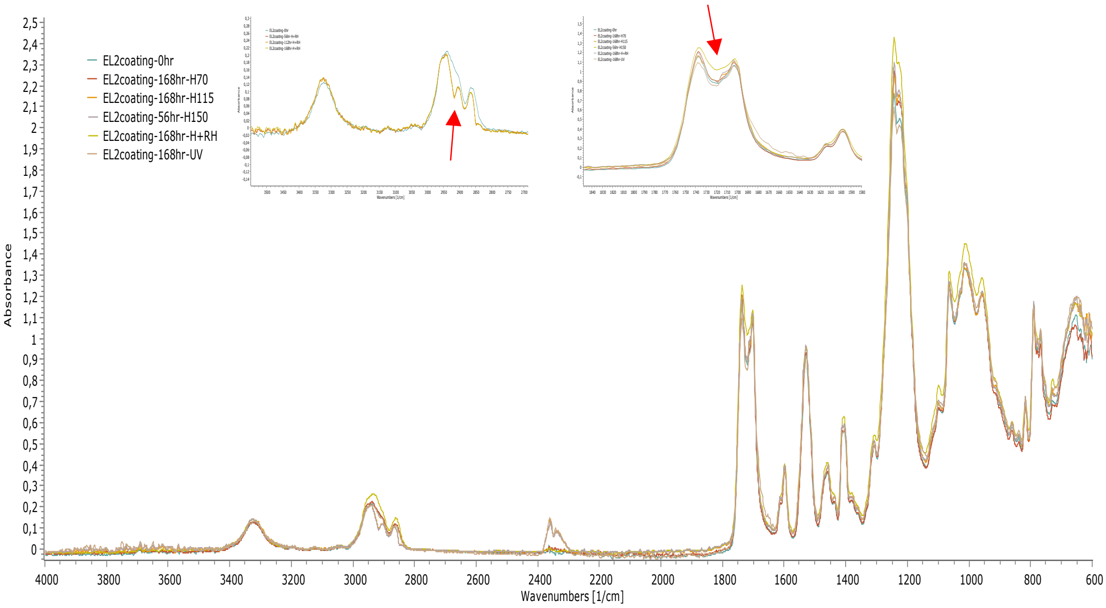


Figure 5-58: ATR-FTIR spectra showing absorbance peaks of EL2 coating before and after ageing. The details of the region comprised between 3500 and 2700 cm^{-1} (left) and between 1900 and 1600 cm^{-1} (right) are also reported.

The two absorptions of the methyl and methylene groups, defined in unaged samples by peaks at about 2900 cm^{-1}, became three immediately after the first ageing interval (only after H115 and H+RH ageing). A new peak appeared just above 2900 cm^{-1} between the other two, as indicated by the red arrow in the left detail in Figure 5-58. Meanwhile, the total contribution of this absorption slightly decreased whilst the absorptions of amine and hydroxyl groups (between 3450 and 3200 cm^{-1}) increased. Evidence of the formation of a new absorption was found in previous studies focused on the hydrolytic degradation of PU foams (Pellizzi *et al.*, 2014). In that context, however, the peak in the CH_2, CH_3 region was not assigned to a specific group. One possibility is that changes in the abundance and symmetry of the C-H groups occurred in EL2 coating, and this may destabilise the macromolecule. It should be noticed that the same phenomenon was observed in the case of SY coating after H115 but the change did not seem to be associated with other peaks. Also SY samples subjected to H150 procedure exhibited a mild decrease of the same vibrations, without the formation of the third peak, that were associated with other variations in peaks absorbance (Figure 5-56). This behaviour was attributed to the formation of radicals that, in the long-term, lead to depolymerisation (Wilhelm and Gardette, 1997). This difference represents an interesting aspect and could reflect different degradation mechanisms taking place in the polymers of the two materials.

H115 and H+RH ageing affected also the carbonyl domain by inducing the formation of a peak at 1714 cm^{-1}, indicated by the red arrow in the right detail in Figure 5-58. The wavenumber is associated with the carbonyl of carboxylic acids. This behaviour of the coating was also noticed in UV aged samples and could indicate that a partial decarboxylation started within the polymer.

The fibrous layer of EL2 (Figure 5-59) presented the same difficulties already pointed out for TL and SY, with a greater noise after prolonged ageing times that complicated the spectra interpretation. This can be clearly noticed looking at the CO_2 absorption at about 2350cm^{-1}.

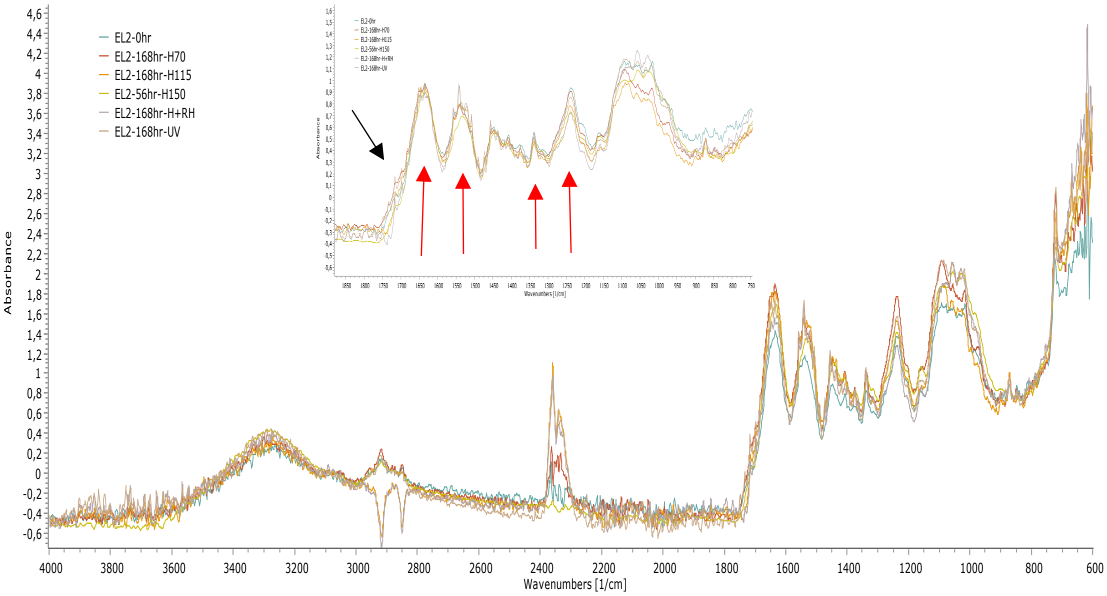


Figure 5-59: ATR-FTIR spectra showing absorbance peaks of EL2 fibrous layer before and after ageing. The red arrows indicate the amide peaks and the black arrow indicates the collagen-chromium complex.

Most of the changes were identified in the amide (I, II and III) bands and in the N-H and C-O absorptions, indicating that the collagen went through mild modifications of the structure (red arrows in Figure 5-59). The region between 1150 and 1000 cm^{-1} decreased in intensity during and after H70 ageing in conjunction with the amide III at about 1340 cm^{-1}. A greater reduction of the same peaks was observed during H115 ageing, together with a decrease of the amide I peak (1650 cm^{-1}). The peak at 1720 cm^{-1} of the chrome complex increased (black arrow in Figure 5-59). This absorption was also observed in all the other samples after ageing. These results seemed to suggest that the number of collagen-chromium complexes increased, possibly as a result of the interaction between amino units and chromium compounds (Nashy *et al.*, 2012).

The spectra before and after H150 ageing showed that the absorption at about 1540 cm^{-1} attributed to the amide II was shifted to the lower frequency (1530 cm^{-1}) suggesting a prevalence of the random coil configuration to the expenses of the helical one (see Appendix). This evidence may indicate that the short fibres used to produce E-Leather® may be prone to degradation under the selected conditions even if the raw material was chrome-tanned.

As far as EL3 is concerned, H150, H+RH and UV procedures affected the material in a similar way to what was observed in the case of EL2. However, a number of differences were also noticed between the two and can be noticed when comparing Figure 5-60 with Figure 5-58.

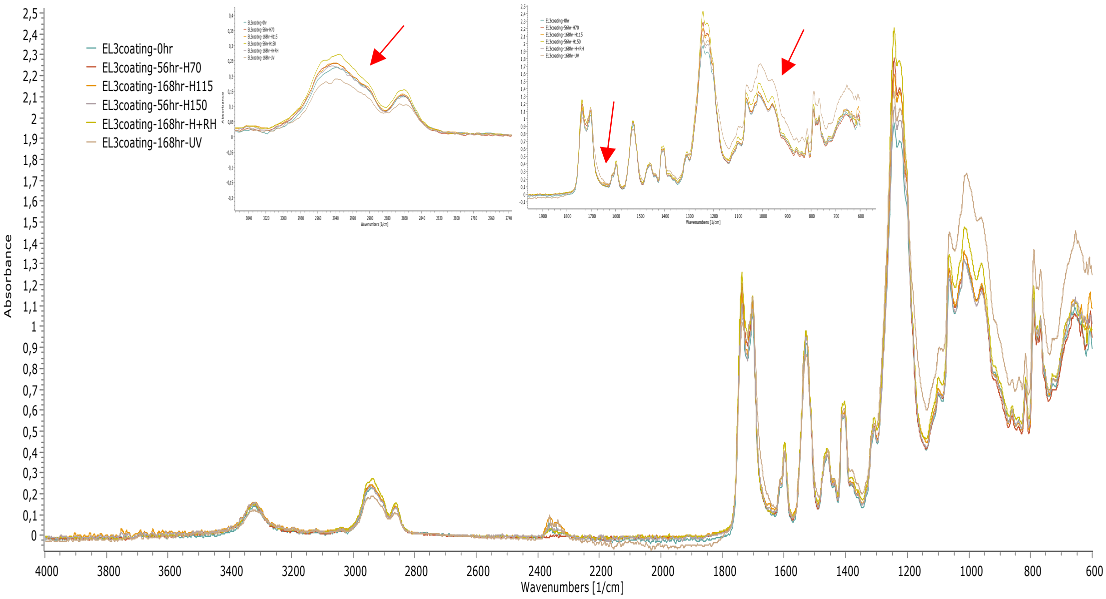


Figure 5-60: ATR-FTIR spectra showing absorbance peaks of EL3 coating before and after ageing. The details of the region comprised between 3100 and 2700 cm^{-1} (left) and between 1900 and 600 cm^{-1} (right) are also reported.

The absorptions of the methyl and methylene groups at about 2900 cm^{-1} did not change as much as in EL2 after any of the ageing procedures and the formation of a third peak was only noticed after H150 and UV. This peak was not observed at 2900 cm^{-1} but at 2935 cm^{-1} (left detail in Figure 5-60), where the asymmetric methylene absorptions are confined, possibly because different PU coating/environment mechanisms where induced. In addition, the intensity of the absorption slightly decreased after UV ageing whilst it increased after H150 ageing.

On the one side, apart for these variations the spectrum of H150 aged samples did not differ from the one before ageing and only the absorption of C-O tended to increase. On the other side, after UV irradiation the formation of a peak at 1714 cm^{-1} was noted and attributed to carboxylic acid formation. A broadening of the ester peak (1738 cm^{-1}) with formation of a shoulder at 1660 cm^{-1}, visible in the right detail in Figure 5-60, was also noticed and a decrease of the ester absorption occurred gradually and proportionally with the increase of the peak at 1714 cm^{-1}. These results may be in agreement with the hypothesis of a hydrolysis of the polyol fraction (Pellizzi *et al.*, 2014), however other bands associated with the ester group (1103, 1065 and 1013 cm^{-1}) did not decrease as it was expected. On the contrary, the band of C-O-C asymmetric stretching increased following a pattern that was not found in literature. These evidenced may indicate that only the initial stages of the degradation took place when the samples were analysed, therefore other areas of the macromolecule were still undamaged.

The H115 and H+RH ageing FTIR spectra exhibited the formation of the peak at 1714 cm^{-1} and another at 1650 cm^{-1}, together with an increase of the C-O of ester bond absorbance. The intensity of C-H peaks was slightly reduced as also were those at 1103, 1065 and 1013 cm^{-1}. These observations replicated to some extent the results obtained for SY and EL2 with the difference that there was no formation of a third peak within the C-H domain.

It is interesting to note that no evidence was found of new bromine compounds formed in the coating surface as a consequence of the accelerated ageing. Confirmation of the bromine presence within the coating of EL3 came from the EDX analysis, though FTIR did not provide further evidence of the bromine compounds on the coating surface. A possible explanation is that as soon as bromine reaches the surface it is able to volatilise in the surrounding atmosphere, as suggested by previous studies (Chattopadhyay and Webster, 2009; Kajiwara and Takigami, 2013).

The EL3 fibrous layer presented the most complex and inhomogeneous spectra of all the materials analysed (Figure 5-61). As already noticed in Chapter 4, the difficulty of identifying the typical leather peaks was likely to be connected with the presence of synthetic fibres that interacted with the collagenous matrix. The same difficulty was encountered during the observation of the accelerated ageing results, though a number of considerations could be done.

H70 and UV aged samples were the only ones that exhibited the same profile of the spectra before ageing and minimal differences in the absorbance values. This confirmed that EL3 was not affected by those treatments. Greater differences in absorbance were noticed after H115 ageing, with consistent decreases of the N-H and O-H stretching vibration at about 3100 and 3017 cm^{-1}. The spectral peak of the collagen and chrome-complex at 1720 cm^{-1} (black arrow in Figure 5-61) increased and became more defined by increasing the ageing time (see Appendix). This rise in absorption was also observed in the other samples after ageing, as in EL2. The vibrations within 1150 and 1000 cm^{-1} decreased in intensity as also did the amide III bands at 1340 and 1241 cm^{-1}. In addition, the band at about 1390 cm^{-1} also went through significant modifications and this may be connected with changes between the bonds originally formed between collagen fibres, flame retardant and melting fibres (made of PP/PE).

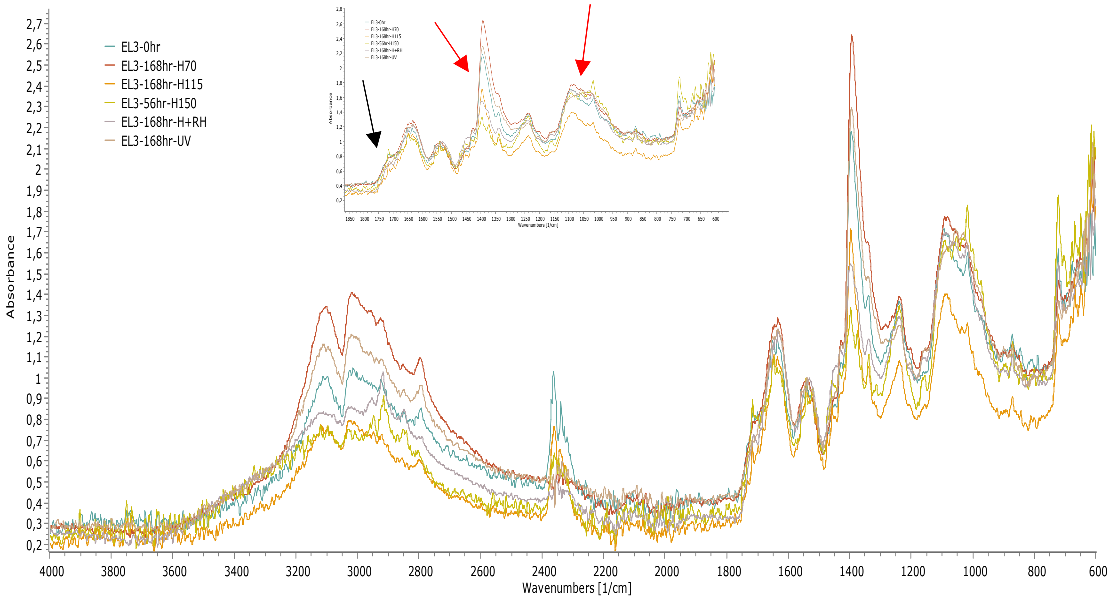


Figure 5-61: ATR-FTIR spectra showing absorbance peaks of EL3 fibrous layer before and after ageing. The detail of the region comprised between 1800 and 600 cm^{-1} is also reported.

In observing the effects of H150 and H+RH exposure a change in the relative intensities of the peaks at about 1390 and 1090 cm^{-1} was found (red arrows in Figure 5-61). Before both the procedures the former absorption was the most intense feature of the spectrum, while after ageing it decreased vigorously at the expenses of other peaks. After H150 ageing the peak at 1090 cm^{-1} became the strongest spectral signal, whilst after H+RH ageing the signal at 1016cm^{-1} was the strongest. During the latter, also the vibration at 1090 cm^{-1} decreased compared to its initial absorbance, though it was stronger than the amide III peak. Moreover, a decrease and broadening of the absorbance was noticed in the broad absorption above 3000 cm^{-1} that comprises O-H and N-H signals in the case of H+RH. It is possible that the interaction between collagen and melting fibres or, more likely, between collagen and flame retardant were responsible for these changes. For the reasons described in Chapter 4, the attribution of the signals was not confirmed by any literature source. However, most of the macro- and microscopic changes identified in the previous sections also occurred within H+RH ageing. It was thus postulated that a correlation between this spectral region and the formation of new material should exist.

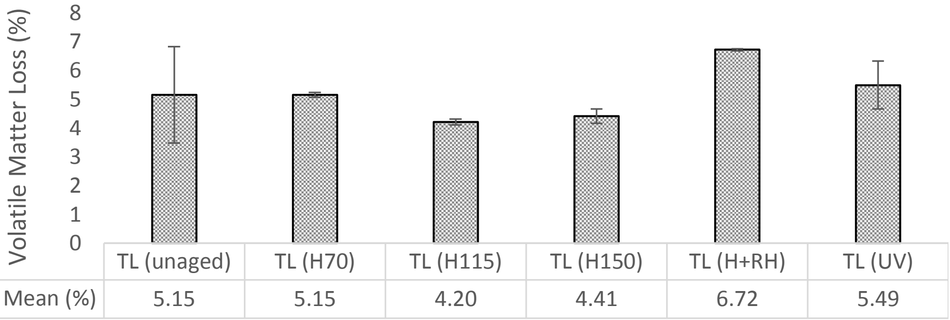
The ATR-FTIR results provided further evidence of the detrimental effects of the H150 ageing procedure on both the coated and fibrous layer of all the samples. Despite the coatings did not degrade in a dramatic way, the early signs of their degradation became already obvious after the first ageing interval. The other ageing procedures also affected the coatings to some extent, with the EL3 samples less stable than the other substrates. The fibrous layers of the TL, EL2 and EL3 materials were less stable to ageing as a consequence of the presence of collagen fibres. Their molecular structure was modified during the ageing procedures, as testified by the decrease and shift in the amide I, II and III absorptions.

The lack of publications on the interaction between chrome tanned and chrome-free leather and brominated flame retardants has limited the understanding of the phenomena that govern the leather-based substrates. However, new hypothesis have been formulated that will need to be validated by further studies. Additional studies will also be required in order to understand how the various components of the composite leather fibre, in particular chrome-tanned fibres and flame retardant, interact with each other during ageing. In order to achieve this goal, other analytical methods should be included, e.g. nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) and chromatography.

5.4.3.3 Moisture Content

The manifold roles of water in leather, and particularly its ability to stabilise the collagen molecule, has been discussed in Chapter 2. In that context, the importance of functional groups, structure of the material and properties such as capillarity was also explained and the importance of moisture during preservation underlined. The limited amount of literature suggests that research, so far, did not focus on measuring the humidity content during or after accelerated ageing. An evaluation of the volatile matter loss was therefore carried out in order to evaluate whether dry and wet heat affected the ability of collagen to absorb and desorb water.

Samples of leather and related materials were tested before and after treatment in order to assess the effect of each accelerated ageing on the substrate and the results were compared with those found in literature for unaged substrates (Sudha *et al.*, 2009; Higham, 2011). Figure 5-62 reports the percentage values of volatile matter loss (VML) by TL samples before and after the ageing procedures.



	TL (unaged)	TL (H70)	TL (H115)	TL (H150)	TL (H+RH)	TL (UV)
Mean (%)	5.15	5.15	4.20	4.41	6.72	5.49

Figure 5-62: Volatile matter loss (%) measured on unaged and aged TL samples

The values of moisture content measured on unaged leather samples were about 5%, a value that is normally associated with deteriorated leathers. Thomson (2011), in fact, reported that new leathers contain 14% moisture and that old ones contain less than 10%. However, Sudha *et al.* (2009) studied samples of sheep nappa containing 11% moisture, that is not widely above the 10% of historical samples. It is likely that, to some extent, the method used to conduct the measurement during this work affected the result, because the rate of evaporation is dependent on the surface area exposed to the surrounding environment. Therefore, a certain degree of error can be expected by avoiding to cut the samples, in particular in the case of a compact material as leather.

H70 ageing did not affect the moisture content of the samples, indicating that after the procedure the collagen was still able to absorb and desorb moisture. Reductions of the volatile matter loss were noticed after H115 (VML 4.20%) and H150 (VML 4.41%) ageing. During the former procedure the temperature was lower, thus the result may seem in contrast with the measurement. However, H115 ageing was carried out for a longer period (168 hours against 56 hours of H150) and the change in temperature and humidity after each interval may have contributed to increase the damage. Florian (2006) explained that both the energy transferred to the collagen through dry heat and the fluctuations in the absorption/desorption due to relative humidity cycles may reduce moisture regain. These factors can induce the triple helices separation and the increase in number of N-terminal amino acids. A study focused on these amino acids residues would be useful to confirm whether these mechanisms determined the reduction.

H+RH and UV ageing, which were carried out in presence of different relative humidities, behaved differently. UV aged samples had a slight increase in the VML but it was not significantly different from the values before ageing. H+RH ageing resulted in the moisture content to rise to 6.72%, an increase that could seem unexpected considering what reported above regarding the moisture regain.

However, studies conducted on archaeological leathers subject to wet conditions have demonstrated that in heavily degraded leathers the water that acts as a helix stabiliser can lose its function (Chahine, 2000). As a result, type I and type II water may leave the collagen and more polar sites become available for type III (free water). Therefore absorption of water may still occurs, but because free water forms with collagen bonds that are weaker (Wright and Humphrey, 2002) the molecule can easily collapse causing leather to shrink and become hard (Chahine, 2000). These phenomena may have occurred during the H+RH ageing, a hypothesis that is in agreement with the shift towards the random coil detected via ATR-FTIR.

Unaged synthetic leather samples (Figure 5-63) presented lower values of moisture content (1.46%) when compared to TL (5.15%) in agreement with previous studies (Sudha *et al.*, 2009). If the values of H70, H115, H150 and UV aged samples were slightly below the measured values before ageing –notice the standard error associated with the measurement–, the values of SY after H+RH signalled an increase of the moisture content (1.57%).

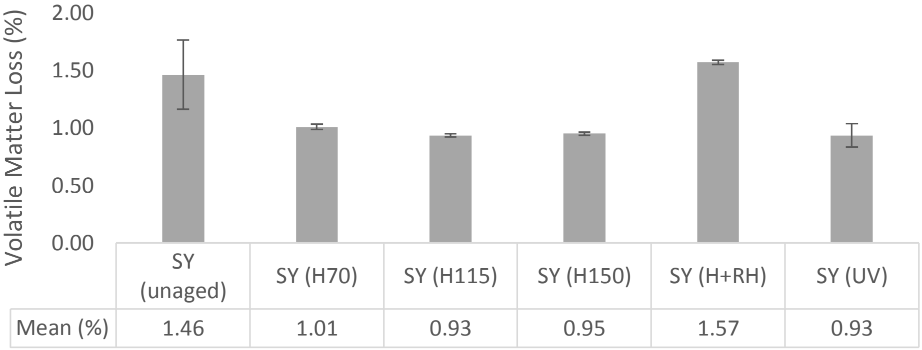


Figure 5-63: Volatile matter loss (%) measured on unaged and aged SY samples

Aramid fibres have high thermal stability (Perepelkin *et al.*, 2003) and it is improbable that this short term treatment had a significant effect on the fibres properties. However, aramids are sensitive to hydrolysis, also as a consequence of the hydrophilicity of the amide linkage (Derombise *et al.*, 2009). Therefore it was not surprising that H+RH increased the volatile matter loss, even if the fibres did not experience clear degradation. The variation of temperature and humidity may have been responsible for stresses that determined the higher degree of looseness noticed after the treatment. Likewise, their combined action may have increased the amount of moisture present within the fabric. Also in this case, though, due to the high stability of the fibres in the short term, it was expected that the fibres would maintain their mechanical properties (see section 5.4.4).

The results of the volatile matter loss from EL2 samples, Figure 5-64, showed the percentage values measured on unaged samples are slightly lower (VML 4.57%) than those measured on TL samples (VML 5.15%), probably as a consequence of the presence in E-Leather® substrates of synthetic fibres and fabric core.

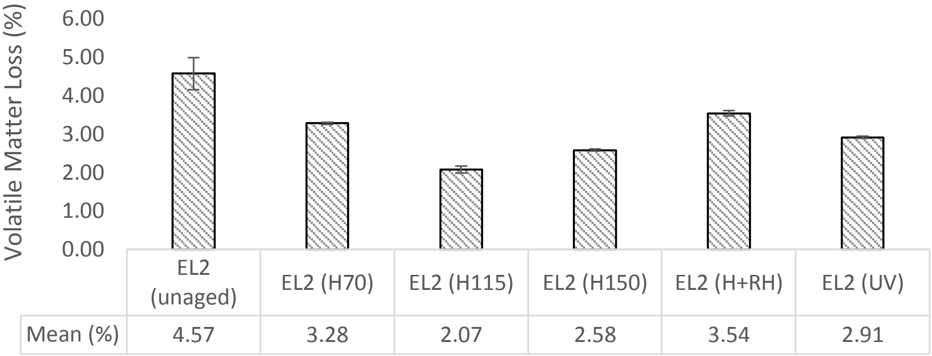


Figure 5-64: Volatile matter loss (%) measured on unaged and aged EL2 samples

All the ageing procedures produced a decrease of the moisture content that suggested that both temperature and humidity had an effect on the SL2 to a differing extent. H70 aged samples reduced their moisture content to 3.28% from the initial value 4.57%, indicating that heat affected the substrate even when mild temperatures were used. The worst damage was caused by moderate dry heat during H115 procedure (2.07%) while the combined effect of high temperature and relative humidity seemed to have a lower impact compared to the other procedures. This was attributed to the high stability of chrome-tanned leather to tropical climate and was supported by previous research (Meyer *et al.*, 2006; Ollè *et al.*, 2011).

It is interesting to note that also in TL the least moisture content was measured after H115 ageing, even if there the decrease of volatile matter loss was of about 1% unit. This difference in the volatile matter loss may indicate the higher resistance of chrome-free leather to dry heat with respect to chrome-tanned leather, in agreement with Meyer *et al.* (2006). In EL2 the high energy transfer in presence of heat that may have destabilised the protein molecule, and the 56 hours cycles may have deteriorated the protein side chains of collagen fibres. Moreover, it must be noticed that the leather fibres in E-Leather® are shorter and less compact than those in any kind of natural leather. Hence, it is likely that different mechanisms of water transport regulate this type of substrate that is characterised by properties half way between nonwovens and leather.

EL3 (Figure 5-65) exhibited moisture content lower than EL2 and TL and the values decreased markedly after all the ageing procedures carried out. H115 was the procedure that resulted in the lowest value (VML 1.45%), followed by H150 (VML 2.20%) and H70 (VML 2.27%). UV ageing decreased the volatile matter loss of 1% unit, while H+RH presented the value closest to those of unaged samples (VML

2.83%). These results followed the exact same trend described by the ones of EL2, suggesting that similar mechanisms regulate the two substrates.

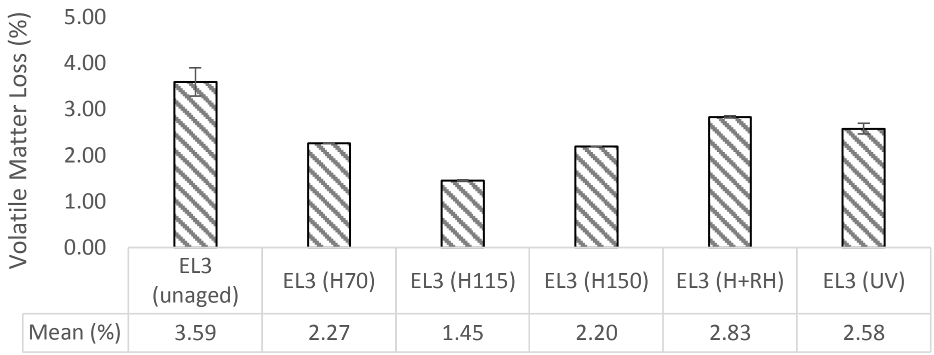


Figure 5-65: Volatile matter loss (%) measured on unaged and aged EL3 samples

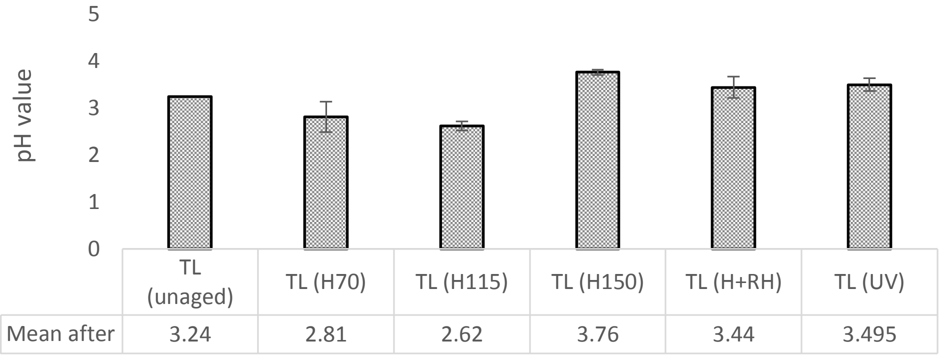
The considerations made for EL2 are valid also in the case of EL3. In the latter material it was expected that H+RH procedure would have had a low moisture content, because the samples were stiff after the ageing. Nonetheless this analysis emphasised that low moisture level was not responsible for the phenomenon. Therefore, the bromine crystals detected during SEM-EDX (see § 5.4.3.1) were suggested as the most likely cause of the change in the sample's rigidity.

The moisture content analysis highlighted that the four substrates contained different amounts of water within their structure. The SY material, made of synthetic fibres and a dense PU coating, exhibited low moisture content both before and after ageing with the highest VML value after the H+RH treatment. This same treatment also increased the moisture content of the TL samples, that containing leather fibres was more hydrophilic. The EL2 and EL3 materials also contained leather fibres, but in different arrangements compared to leather. They presented the highest moisture content before ageing while VML values decreased after the ageing procedures. All the three leather-based substrates exhibited the lowest moisture content value after 168 hours of the H115 exposure.

5.4.3.4 pH

The analysis of pH conducted on leather and related materials before and after accelerated ageing could provide insights on the shift of the materials towards more acidic or basic values. In vegetable-tanned leathers the increased acidity of a leather extract solution is an indication of degradation. This is related with the rise in acidic amino acid residues that form as a consequence of collagen hydrolytic and oxidative breakdown (Florian, 2006; Larsen, 2008).

In this work two samples of the whole substrate (coating plus fibrous layer) were used to assess pH variations. The resulting extract was tested and the mean of the two measurements calculated.



	TL (unaged)	TL (H70)	TL (H115)	TL (H150)	TL (H+RH)	TL (UV)
Mean after	3.24	2.81	2.62	3.76	3.44	3.495

Figure 5-66: pH values measured on unaged and aged TL samples

Figure 5-66 reports the pH values of TL samples before and after accelerated ageing. Unaged samples had a pH value of 3.24, which was above the limit that indicates the degradation. Leathers that exhibit pH values below 3.00 are considered unstable and they are more likely to undergo hydrolytic breakdown (van Soest *et al.*, 1984; Vest, 1999; Larsen, 2008). Values below the limit were measured in samples after H70 and H115 ageing (2.81 and 2.62). The remaining procedures increased the pH value to 3.76 after H150, 3.44 after H+RH and 3.49 after UV.

The partial degradation of collagen and the increased number of acidic amino acid residues has the effect of lowering the pH value, that describes what happened after the H70 and H115 exposures. The result of the H150, H+RH and UV procedures may seem surprising because the first two procedures greatly affected the samples and a lower pH value was expected. However this increase may be interpreted as an indicator of the presence of ammonia caused by the oxidative breakdown. Florian (2006) reported that oils are among the responsible for oxidative breakdown in vegetable-tanned leathers, hence it is possible that fatliquoring agents facilitated the collagen oxidation leading to ammonia formation. In addition, TL was produced to be used for aircraft seats, hence its composition is likely to be different from the one of the typical leather objects found in museum collections. As a result, the pH values measured on the substrate were not only influenced by the collagen but also by the flame retardant, coating, dyes and fatliquoring decomposition.

The pH values of coated fabrics are normally higher than those of leathers (Sudha *et al.*, 2009). The SY samples, made of PU coating and aramid fabric support, were expected to be stable after accelerated ageing. Based on the information identified in the previous paragraphs, the worst effects were expected after H150 ageing. However, a different pattern was observed and it is evident in Figure 5-67.

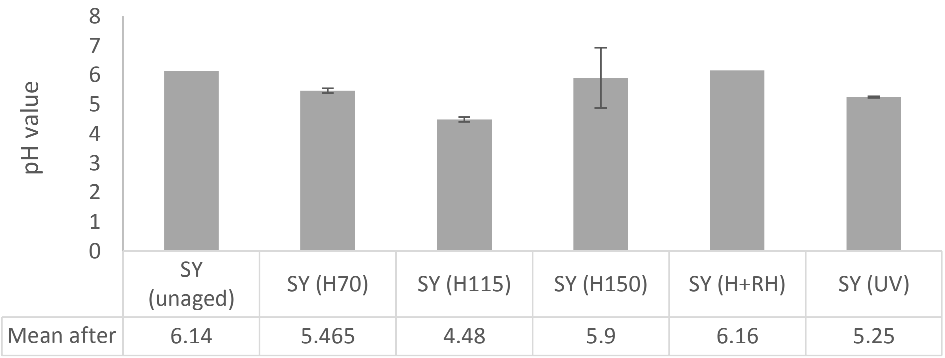


Figure 5-67: pH values measured on unaged and aged SY samples

The initial pH value was higher than the TL material, but lower than the one reported in previous studies on unaged synthetic leather materials (Sudha *et al.*, 2009). This was probably due to the presence of the flame retardant. Following the degradative exposures the pH decreased for all the procedures apart for H+RH ageing, diminishing from 6.14 to 5.46 (H70), 4.48 (H115), 5.90 (H150) and 5.25 (UV). This result indicated that the combination of high temperature and humidity left the material pH conditions almost unchanged possibly due to alternative degradative pathways. In contrast heat ageing and UV treatment both affected the samples.

The only study found in literature where pH tests were conducted on PU museum items was focused on PU foams (Lovett and Eastop, 2014). Aqueous solutions exposed in the same confined environment of PU foam samples developed an acidic pH after accelerated ageing in presence of high humidity and this was attributed to the release of acidic molecules from the foam. In the experiments conducted for this thesis water was used to bring in solution residues weakly bonded to the substrate that were solubilised or mechanically detached during stirring. As a consequence, the pH may have been influenced from the residues left on the coating or from the compounds within the coating. As already seen in the case of TL, flame retardants could be responsible for the pH value reductions.

The results of pH analysis on EL2 are presented in Figure 5-68. The pH value was lower compared to SY samples, due to the presence of leather in the supporting fabric, and higher compared to TL samples. One reason for the pH higher than the one of TL may be found in the different type of tanning method used for the two substrates. Covington (2009) reported that chrome tanned leather has a range of stability between pH 3 and 11. Below pH 3 the chromium complex can be solubilised as Cr(III) ion, while above 11 the complex can hydrolyse and solubilisation occur (Covington, 2009).

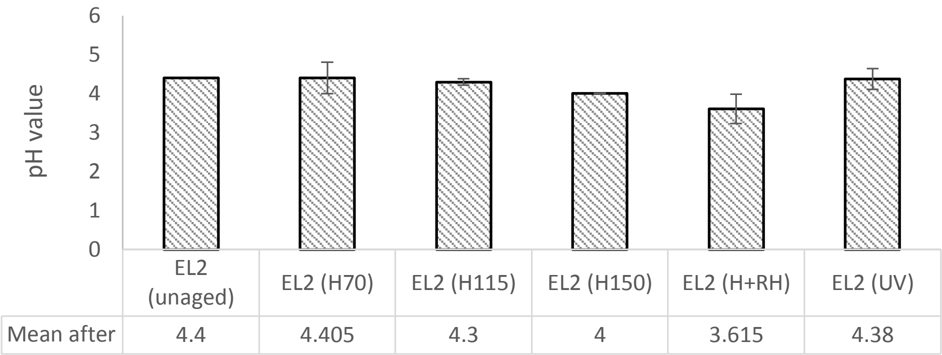


Figure 5-68: pH values measured on unaged and aged EL2 samples

After accelerated ageing the H70, H115 and UV aged samples all kept their pH values similar to their initial pH. H150 ageing reduced the pH to 4.00, while H+RH lowered the value to 3.6. These results are likely to be related to changes in the collagenous matrix, because no further changes were noticed within the coating. Moreover, EL2 represented the only substrate that did not contain flame retardants and therefore it was possible to exclude their contribution to the analysis. Indeed, E-Leather® was constructed from many components such as fatliquoring agents, dyes, woven core and synthetic fibres that may have contributed to alter the pH.

Assuming that the contribution of the other factors was negligible, a pH reduction suggested that acidification may be the result of partial collagen breakdown. Larsen (2008) reported that hydrolysis and oxidation may both be involved in the deterioration leading, respectively, to cleavage of the peptide chain and to changes of the collagen side chains. The results of his study referred to vegetable-tanned leather, though, and it would be useful to assess if the same pattern was valid in the case of chrome-tanned samples. Ion-exchange HPLC (High Performance Liquid Chromatography) analysis would be useful to determine the ratio of acidic and basic amino acids and assess whether pattern similarities can be found between vegetable- and chrome-tanned leather.

EL3 (Figure 5-69) exhibited a behaviour that replicated the pattern exhibited by TL. Also in this case there was a decrease of the pH values after H70 (2.94) and H115 (2.48) exposures, even if the extent of the decrease was less evident than in TL. Likewise, limited increases of pH were noticed after H150 (3.19), H+RH and UV (both 3.06) exposures. Pearson’s correlation was calculated in order to investigate the correlation between the values of TL and EL3 and it was found that the results were highly correlated ($r = 0.86$, $p < 0.05$). This suggests that similar pathways of degradation may characterise chrome-free and chrome-tanned leather, though more specific studies should be conducted to confirm this hypothesis.

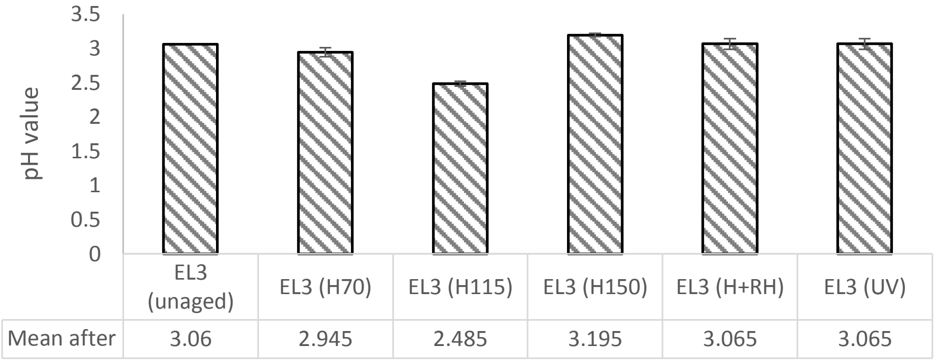


Figure 5-69: pH values measured on unaged and aged EL3 samples

Although the H150 and H+RH aged samples visibly changed, their pH values remained almost static. Though, it is worth noticing that an interesting phenomenon took place after stirring EL3 samples after H150 and H+RH ageing. Finely cut leather was stirred in water and the resulting solution used for the pH analysis. It was noticed that the colour of the solution was different from the one obtained after the other ageing procedures. The solution was therefore transferred into a small glass container and stored for further investigations. After two days the formation of a number of semi-spherical particles were detected at the bottom of the container (see Figure 5-70).

Figure 5-70: Formation of semi-spherical agglomerates after EL3 stirring

Attempts to test these agglomerates were made, but the appropriate method was not found because the agglomerates tended to lose their shape once removed from the solution. It was hypothesised that the agglomerates may be the result of the partial degradation of the collagen matrix, which led to the cleavage of the collagen side-chains. In fact, the final stage of parchment deterioration consists in gelatinisation of the collagenous matrix (Hansen *et al.*, 1991; Kennedy and Wess, 2003; Larsen *et al.*, 2005) but the formation of gelatine as a result of chrome-tanned leather is less documented. In future chromatographic studies on the extracts after stirring may be useful to ascertain the presence of collagenous residues, thus confirming the partial decomposition of EL3 matrix after the ageing treatment.

The pH analysis of the four substrates emphasised that EL2 seemed the most stable product. The H115 ageing produced the greatest reductions in the pH values of the TL, SY and EL3 materials possibly as a consequence of the flame retardants decomposition. In the case of collagen-based substrates, however, this phenomenon was mainly attributed to the fibrous layer and in particular to the increase in the acidic amino acids of the leather-based materials. In addition, the TL and EL3 samples exhibited increases of the pH after the H150 and H+RH procedures that were attributed to the ammonia formation as a consequence of the collagen breakdown.

5.4.4 Mechanical Tests

As already observed for chemical analyses, a range of physical tests have not been conducted on wet-white and chrome-tanned leathers in museum artefacts. Physical tests often require large samples and multiple repetitions (Feller, 1994), and frequently they result in sample impairment or destruction. Moreover, Feller mentioned that changes in the chemical properties normally precede those in the physical ones and therefore chemical tests are used more frequently (Feller, 1994). It is not surprising, therefore, that also in the case of vegetable-tanned leather and parchment the publications on physical changes due to ageing are lacking. Similar considerations can be made in the case of coated fabrics that, as reported above, have only been studied to a minimum extent.

Generally, publications that deal with both chemical and physical properties have been conducted in the industrial sector with the aim to suggest possible relationships between the two types of properties to respond to unsolved questions regarding the sample's lifetime and degradation (Ollè *et al.*, 2011; Schröpfer and Meyer, 2012). The same can be said in the case of PU coated fabrics (Potočić Matković *et al.*, 2014).

In this study tensile tests along with bending, compressibility and friction analysis were conducted in order to study their relationship with change in appearance and chemical analysis.

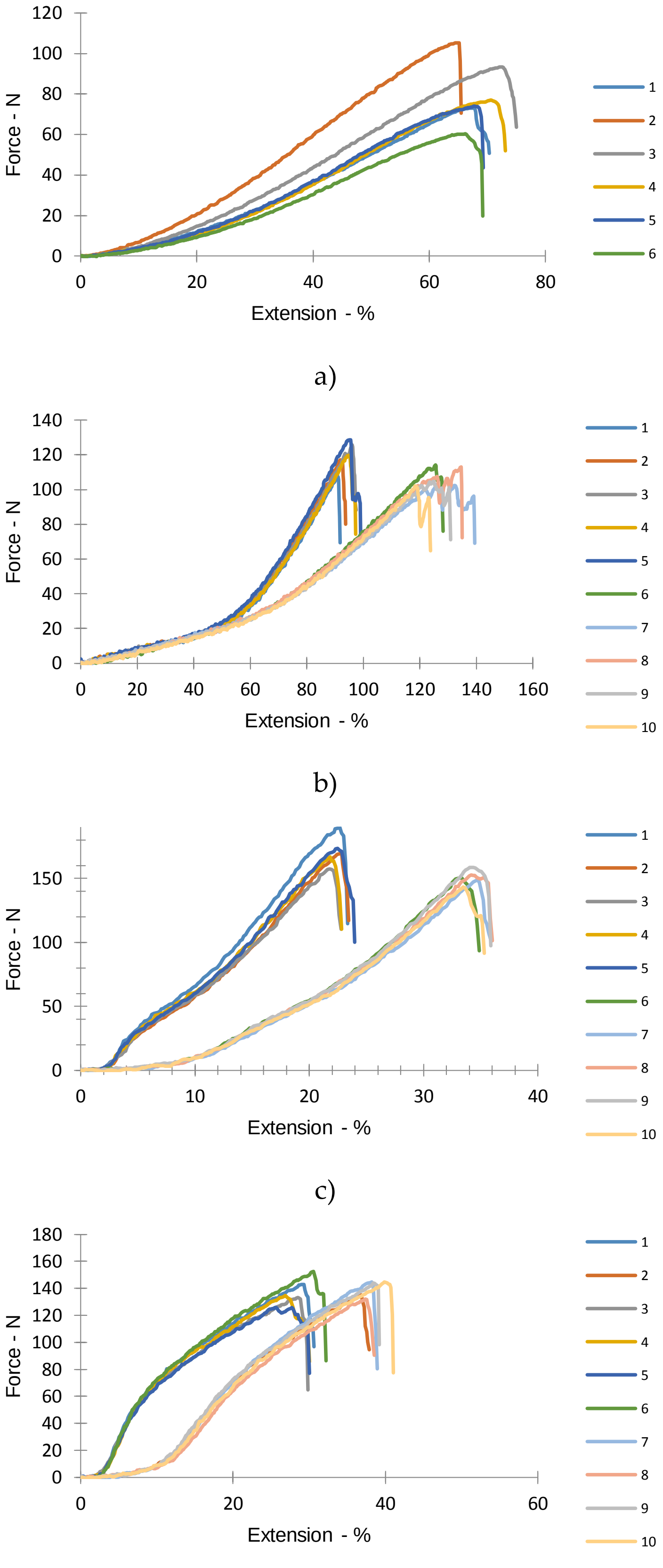
5.4.4.1 Tensile Tests

Research concerning the tensile properties of leather has been conducted to assess the resistance of the substrate to the application of stresses that are typical of the material in use (Mutlu *et al.*, 2014). Various authors have reported on the difference in tensile properties according to the sampling position (Mutlu *et al.*, 2014), tanning method (Li *et al.*, 2009), animal age (Wang and Attenburrow, 1993) and manufacturing treatments the leather experienced. Also, efforts have been made in order to investigate the differential behaviour of leather and synthetic substitutes in order to assess whether synthetic manmade substrates can effectively substitute their natural counterpart (Sudha *et al.*, 2009). Among all the literature studies only two have focused their attention on the effect of ageing procedures on chrome-free (Li *et al.*, 2016) and chrome-tanned leather (Işik and Karavana, 2012), while one dealt with the influence of fatigue cycles on tensile strength (Milašienė and Bubnytė, 2007). However, no evidence was found of papers that compare physical properties of leather and synthetic leather after ageing cycles and it was decided to begin to fill this gap.

Force/extension curves were recoded for a minimum of three and a maximum of five samples in both machine (MD) and cross-machine direction (CD), respectively parallel and perpendicular to the backbone (for TL). In the case of SY, EL2 and EL3 the longitudinal direction indicated the machine direction (or warp/wale). Values of tensile strength, elongation at break and force at break were determined after 168 hours of exposure under the specified conditions.

Figure 5-71 presents the deformation curves of unaged materials, where the differential properties of the four materials is obvious. EL2 was the material with the highest strength and the least elongation, followed by EL3, then SY characterised by the highest elongation and high strength and finally TL. It is also worth noting that while TL and SY, tended to break in two parts when the operating limit was reached (30 % decrease in force) this was not the case when EL2 and EL3 were tested. Despite the SY samples often being split in two parts, on a number of occasions their supporting fabrics were kept together by a few fibres. E-Leather® samples were clearly compromised and could not return to the original shape when breakage was detected. The samples were kept together by the coating whilst the fibrous layer was compromised but they were not visibly broken or split in two parts, thus it is possible that the break detection was related to the internal fabric core rather than to the whole hydroentangled layer.

The shape of the TL curves was similar in the two directions, with a section slightly deviated from linearity between the initial application of the tension and the 40 % of the elongation values. The linearity of the curve was related with the elastic behaviour of the sample, therefore TL showed a rather consistent elasticity until when it reached the maximum force (90.64 ± 16.26 in parallel and 70.44 ± 8.80 in perpendicular direction). The importance of the sampling position in leather is crucial, as discussed in Chapter 4, because the thickness and entanglement of collagen fibres affects the physical properties. This variability was also evident when examining the force/extension curves reported in Figure 5-71a.



a)

b)

c)

d)

Figure 5-71: Tensile strength curves of unaged TL (a), SY (b), EL2 (c), EL3 (d). Samples 1 to 3 of TL, were parallel to the backbone, and 1 to 5 of SY, EL2 and EL3, represent machine direction; samples 1 to 3 of TL, were perpendicular to the backbone, and 1 to 5 of SY, EL2 and EL3, represent cross-direction

The break detection occurred within a wide interval of values despite the samples were all collected following the official standard procedure. It would be expected that the wide standard deviation of TL samples (Table 5-5) could affect to some extent the detection of the effects due to ageing procedures. However, Li *et al.* (2016) successfully detected reductions in tensile strength after ageing.

Apart for TL, all the materials exhibited greater elongation values in the perpendicular direction and, likewise, the distribution of the results was much less spread. SY, in Figure 5-71b, exhibited values easily distinguishable in the two directions (wale and course) with a narrow distribution of the results. This narrow distribution was due to the fact that the sample was made of a fabric support characterised by a regular construction and consistent properties. The different behaviour in the two directions underlined the greater strength of the samples along the wale and the high elongation of the course. SY presented greater extension after the application of the same force when compared to TL, and only above the 50 % of the original length the samples showed a steep increase in force values that denoted the elastic region. Also EL2 and EL3 showed different behaviours along the two directions, but when compared with SY it became evident that the standard deviations of the samples were greater (Table 5-5), providing the evidence that the physical properties of E-Leather® were not as consistent as in artificial leather. This lower consistency was attributed to the hydroentangled supporting fabric.

	Max Force (N)	SD	Elongation (%)	SD	Stress (N/mm^2)
TL-0 hr-Parallel	90.64	16.26	68.17	3.85	7.55
TL-0 hr-Perpendicular	70.44	8.80	68.08	2.20	5.87
SY-0 hr-Parallel	123.15	5.54	90.71	0.86	9.85
SY-0 hr-Perpendicular	107.31	1.71	128.26	3.97	8.58
EL2-0 hr-Parallel	171.57	12.00	22.31	0.49	16.34
EL2-0 hr-Perpendicular	150.77	5.62	33.96	0.56	14.36
EL3-0 hr-Parallel	142.95	7.48	28.87	0.81	15.37
EL3-0 hr-Perpendicular	133.67	11.89	36.56	1.98	14.37

Table 5-5: Max Force, extension and tensile strength of unaged TL, SY, EL2 and EL3 samples in parallel and perpendicular directions

EL2 presented higher maximum force (171.57 ± 12.00, MD and 150.77 ± 5.62, CD) and lower elongation (22.31 ± 0.49, MD and 33.96 ± 0.56, CD) than EL3 (142.95 ± 7.48, MD and 133.67 ± 11.89, CD; 28.87 ± 0.81, MD and 36.56 ± 1.98, CD), probably as a consequence of the greater thickness of the hydroentangled face. The stiffness of the samples was reflected in the high force values required to stretch the sample of some percentage points.

With respect to the effect of the ageing procedures, for clarity it was decided to present and discuss separately the results obtained for each material. The results of t-tests conducted on TL samples before and after ageing demonstrated that H70, H115 and UV ageing did not result in significant variations of the maximum force, while it shifted from 90.63 ± 16.26 N to 33.92 ± 1.78 N after H150 ageing (Figure 5-72).

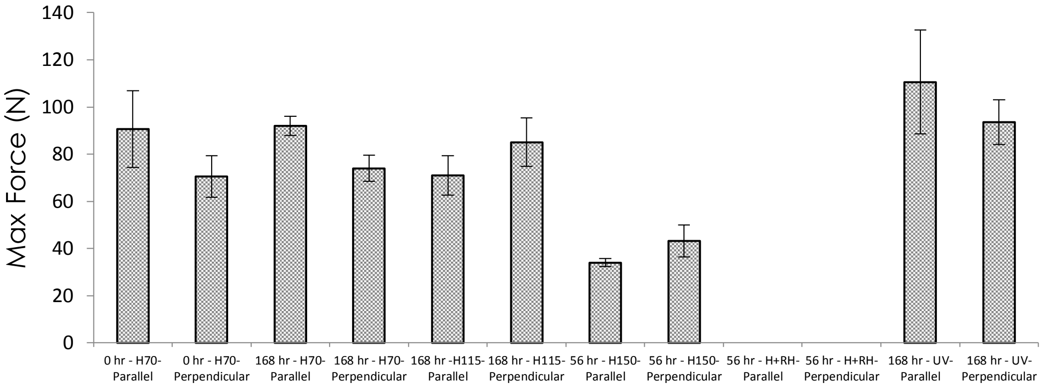


Figure 5-72: Maximum force histogram of TL samples, before and after ageing, in both parallel and perpendicular directions

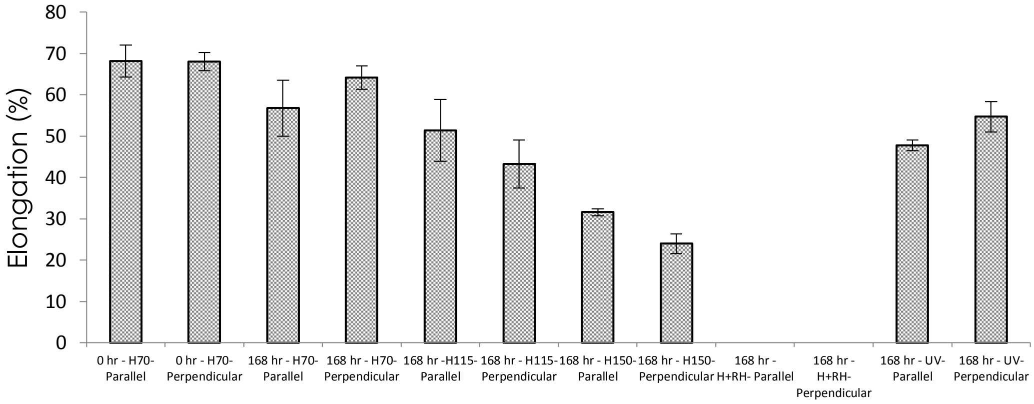


Figure 5-73: Elongation histogram of TL samples, before and after ageing, in both parallel and perpendicular directions

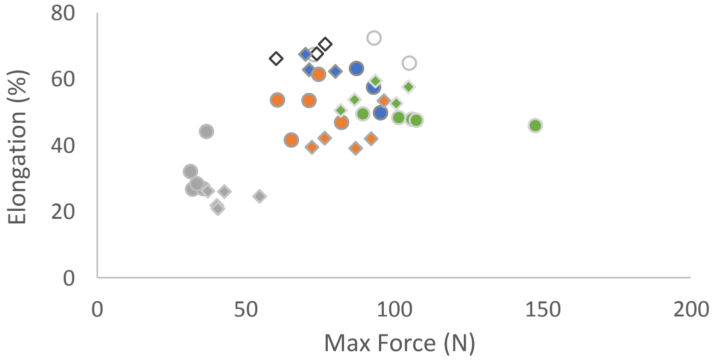


Figure 5-74: Maximum force/elongation scatterplot presenting the results of TL samples, before and after ageing, in both parallel (circular markers) and perpendicular (rhombus markers) directions. Markers with no fill: unaged samples; blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; green markers: UV

However, it is interesting to notice that after H115 exposure the maximum force value in the perpendicular direction was greater than the initial value. This was attributed to the anisotropy of leather and to the fact that leather fibres shrank consolidating the structure of the material along preferential directions.Elongation values of all the samples (Figure 5-73), apart for those subject to H70 ageing, varied as a consequence of the ageing procedures and resulted in a significant reduction of the percentage elongation (p-values < 0.05).

These results indicate that moderate and severe heat had a great influence on the elongation of chrome-free leather but not on the tensile strength. The difficulty in testing the leather samples subject to the combined effect of heat and relative humidity did not allow a comparison of these results with the literature data. Nevertheless the drastic shrinkage of those samples and the marked reduction in the samples' flexibility would have produced a graph with a steep increase of the force corresponding to very small elongation values, close to 0. TL was alum tanned, and its stability was highly compromised by the treatment with heat and humidity. Shrinkage of the collagen fibres may have been an important factor in determining the macroscopically visible contraction of leather after heat and heat plus humidity treatments. In addition the shrinkage of the collagen fibres may have been the cause of the reduction in the elongation values noticed in TL after heating.

The maximum recommended elongation value for the garment industry is 60 % (Işik and Karavana, 2012), and values above or below are desired depending on the application of the leather. Lower values should be better in the case of leather used for seat covers, because higher values would result in easily deformable substrates. In the case of TL the initial values were around 70 %, but these values moved towards smaller figures after the ageing procedures (Figure 5-73). It is likely that all the substrates but the ones after H150 ageing would be able to withstand tear even after ageing and, in addition, they would be less prone to deformation. Therefore, the exposure to those ageing factors would affect the material's appearance but not its usability.

The SY material was demonstrated to be stable to ageing in many occasions within this research, therefore its behaviour when subject to mechanical stress was considered of primary importance. Figure 5-75, Figure 5-76 and Figure 5-77, respectively, present the histograms of the different ageing procedures on maximum force and elongation after ageing, and the scatterplot of the values recorded for each sample.

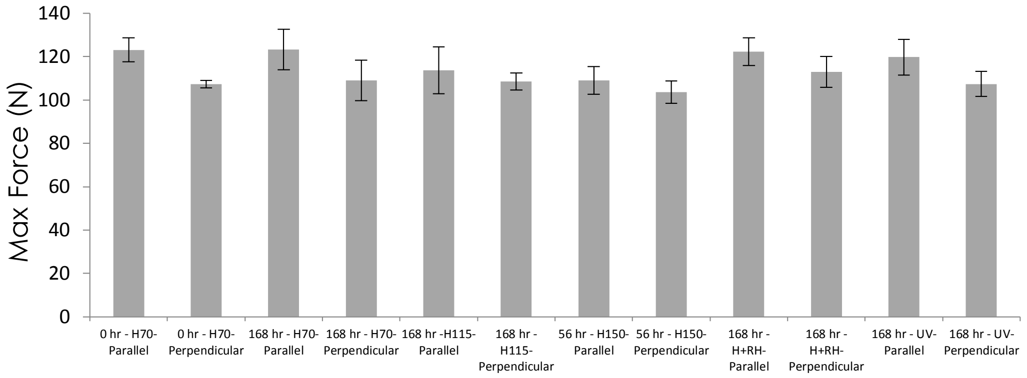


Figure 5-75: Maximum force histogram of SY samples, before and after ageing, in both parallel (wale) and perpendicular (course) directions

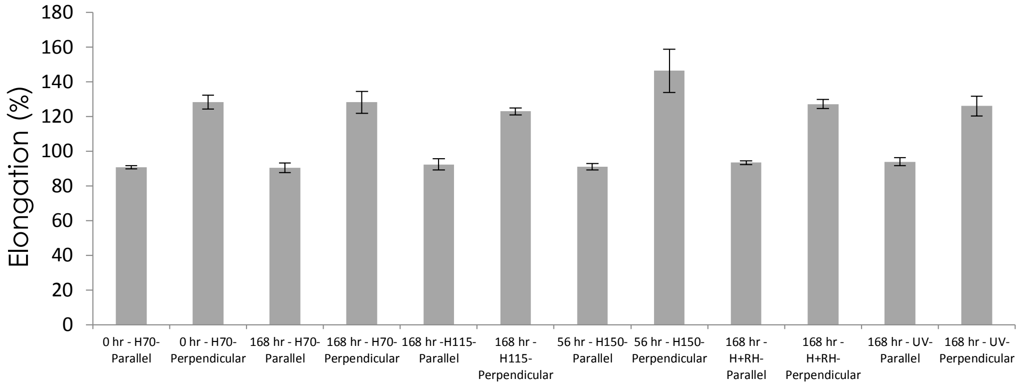


Figure 5-76: Elongation histogram of SY samples, before and after ageing, in both parallel (wale) and perpendicular (course) directions

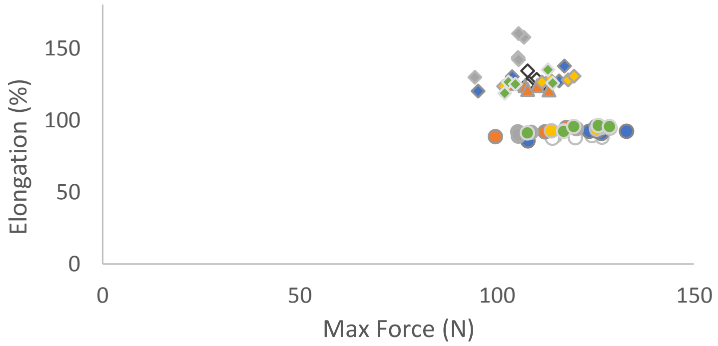


Figure 5-77: Maximum force/elongation scatterplot reporting the results of SY samples, before and after ageing, in both wale (circular markers) and course (rhombus markers) directions. Markers with no fill: unaged samples; blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH; green markers: UV

The mean stress before and after ageing did not change significantly after any of the procedures. T-tests were conducted on maximum force and elongation for parallel and perpendicular directions and they provided supplementary evidence of the substrate stability under the selected conditions. H150 was the only ageing able to induce a significant change in the maximum force value (p-value = 0.02) but only along the wale direction.

However, evidence of changes in the material was provided by the variations in the elongation of the coated fabric. H115, H+RH and UV ageing imparted increases in the extension of the samples in the wale direction, whilst both wale and course elongation increased after H150 ageing. This increase was attributed to the changes that occurred within the coating structure that were described in § 5.4.2. It is known that coating processes change the mechanical properties of fabrics, but in the case of knitted materials the textile core is the main responsible for those variations (Potočić Matković and Skenderi, 2013). Therefore, it would be expected that properties variations were determined by changes in the supporting fabric. However in SY, the relative stability of the fabric was assessed. In contrast the coating was not equally stable, in particular after H150, hence it was concluded that the ageing treatments, by altering the coating, may have increased the fabric stretchability.

The work carried out during this thesis has confirmed that SY, which represents one type of highly engineered leather substitute, was able to maintain its tensile properties almost unvaried after ageing. This difference in the tensile properties when compared to TL is central in the museum context, because it represents one evidence that the presence of the same ageing factor in the storage location or during exhibition may easily affect the mechanical properties of the two materials in different ways.

On considering EL2 and EL3, the results of the tensile tests indicated that the samples exhibited different behaviour during ageing compared to the TL and SY materials. It has been already noticed that the first two materials had higher dimensional stability than TL, though changes in appearance and handle (to the touch) lead to the hypothesis that E-Leather® substrates, and EL3 in particular, may have gone through processes able to modify their mechanical properties.

Figure 5-78 and Figure 5-79 illustrate the values of maximum force and extension of unaged and aged samples in both the machine direction and transverse direction. T-tests conducted to measure the statistical significance of variations in EL2 provided the evidence that maximum force in the MD was consistent after every ageing procedure, but in the CD the H115, H+RH and UV ageing caused slightly significant changes (p-value = 0.04, 0.03 and 0.02, respectively). The elongation in both MD and CD was affected to a higher extent by H115 and H150 ageing, increasing of some percentage points, but it was unchanged after the other procedures.

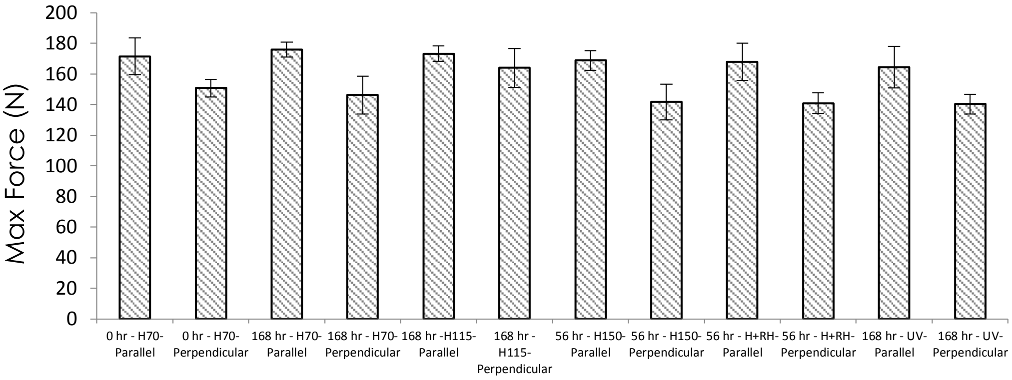


Figure 5-78: Maximum force histogram of EL2 samples, before and after ageing, in both parallel (MD) and perpendicular (CD) directions

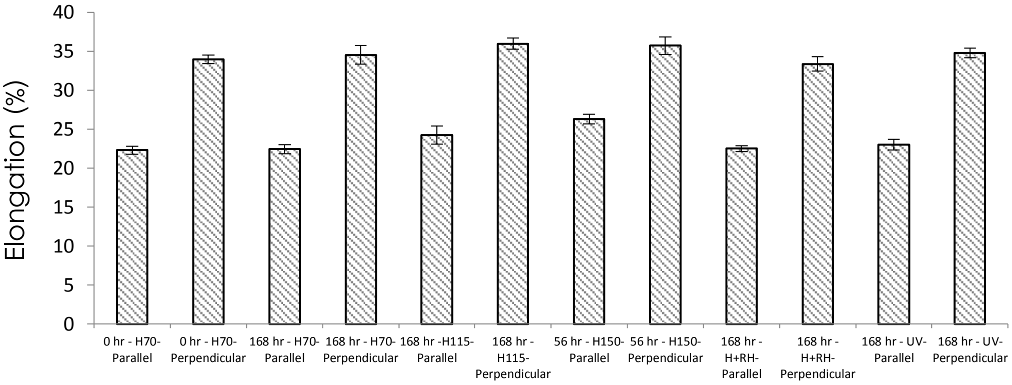


Figure 5-79: Elongation histogram of EL2 samples, before and after ageing, in both parallel (MD) and perpendicular (CD) directions

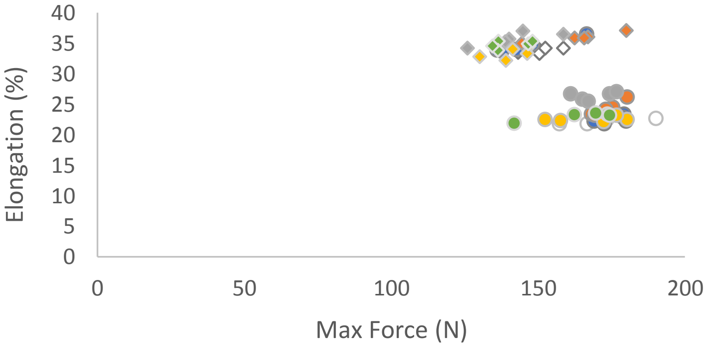


Figure 5-80: Maximum force/elongation scatterplot reporting the results of EL2 samples, before and after ageing, in both MD (circular markers) and CD (rhombus markers) directions. Markers with no fill: unaged samples; blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH; green markers: UV

The results indicated that the EL2 samples were able to preserve their tensile properties after most of the procedures. In those cases where significant changes were observed, two phenomena were identified as possible responsible: the coating softening and the reduction in the moisture content. The measurement of the moisture content, in section 5.4.3.4, indicated that the H115 and H150 procedures reduced vigorously the water within the samples. This would suggest that an inverse relationship between this parameter and the elongation, which was considered unlikely. For this reason the coating was thought to be the main responsible for the elongation and tensile strength change.

The plot representing the distribution of the results obtained for all the samples is reported in Figure 5-80. It is possible to notice that the values were comparably less and more dispersed than the ones of TL and SY also after the ageing procedures. This indicated that the mechanical properties of the samples were affected in the same way both before and after ageing, thus no drastic variation in the homogeneity of the properties occurred after the procedures were carried out.

The results of the same tests conducted on EL3 are reported in Figure 5-81, Figure 5-82 and Figure 5-83, respectively. The maximum force and extension values and the results distribution seemed in line with the data trends reported for EL2. This was an interesting result because a marked change in tensile strength and elongation was expected as a consequence of the problems pointed out in the previous paragraphs. However, no significant difference was observed. The only procedure that affected the maximum force, in the MD and CD was H115, but the reason for this change was not identified. The same ageing also caused a significant increase of the elongation values along the CD (from 36.56 ± 1.98 to 41.40 ± 1.03), while H150 ageing affected the MD (from 28.87 ± 0.81 to 31.31 ± 0.65).

Following H+RH ageing, visual observations and roughness investigations indicated that, while the coating appeared to be adversely affected, this damage did not seem to impact on the mechanical properties of the composite. It could be argued that the leather fibres used in the composite may contribute only to a minimum extent in providing strength to the finished material. It is in fact known that the leather fibre sheets are rather weak before going through the hydroentanglement process (Bevan, 2005) and this is one of the reasons why a fabric core was included during E-Leather® manufacturing. As a consequence, changes that may have affected the collagenous fibre components may have had a lower impact on the overall strength of the composite, with the fabric core and the coating being mainly responsible for the overall strength and elongation of the substrate.

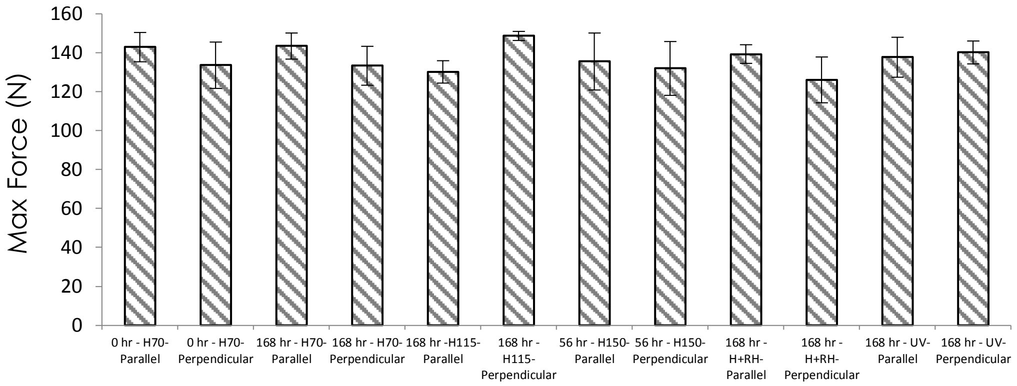


Figure 5-81: Maximum force histogram of EL3 samples, before and after ageing, in both parallel (MD) and perpendicular (CD) directions

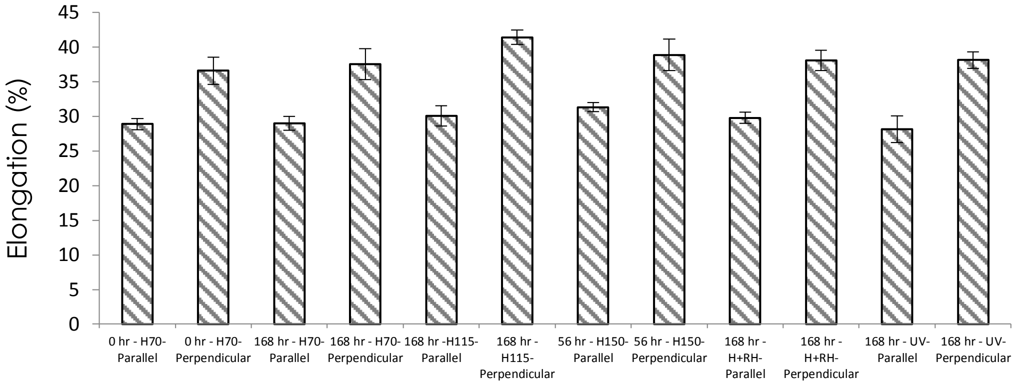


Figure 5-82: Elongation histogram of EL3 samples, before and after ageing, in both parallel (MD) and perpendicular (CD) directions

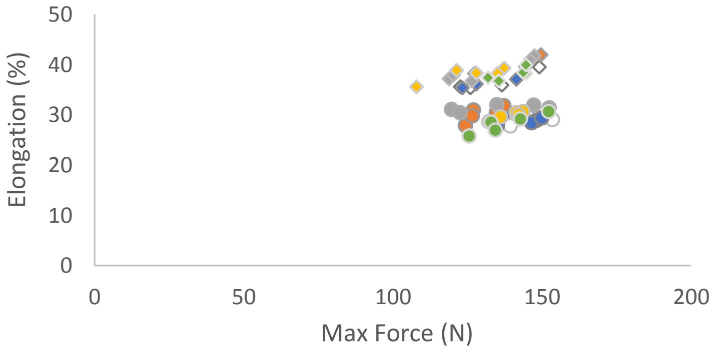


Figure 5-83: Maximum force/elongation scatterplot reporting the results of EL3 samples, before and after ageing, in both MD (circular markers) and CD (rhombus markers) directions. Markers with no fill: unaged samples; blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH; green markers: UV

It could seem somewhat surprising that the presence of the chrome-tanned fibres had so little influence on the tensile properties of the composite because several authors demonstrated that leather fibre content influences the physical properties of composites (Madera-Santana *et al.*, 1998; El-Sabbagh and Mohamed, 2011). However, leather fibres used for this application have smaller dimensions, density and entanglement than the comparable fibres in natural leather. In addition, E-Leather® minimised the fibre's impact on the final material by including the fabric core. The fabric core in EL3 is made of aramid fibres, therefore it is likely that its resistance to accelerated ageing was greater than the one of leather fibres. The relationship between these components of the fabric constitutes an important issue for future research.

5.4.4.2 Kawabata Evaluation System for Fabrics (KES-F)

The use of the KES graphic output to discriminate leather, synthetic leather and composite substrates was discussed in Chapter 4. In this paragraph the use of the numerical output of the instrument to detect changes due to the ageing procedures will be presented.

Flexibility, compressibility and smoothness have been recognised as key parameters that define the suitability of fabrics and leather for applications in the clothing and upholstery industries and KES has been effectively used to measure these parameters (Roh *et al.*, 2013). Moreover, the ability of materials to return to their initial shape after the application of a stress, defined as resilience or recovery, is central when materials are in use and it changes as a consequence of their water content (Liu *et al.*, 2007). Therefore, resilience can change as a consequence of the ageing leather has been subject to.

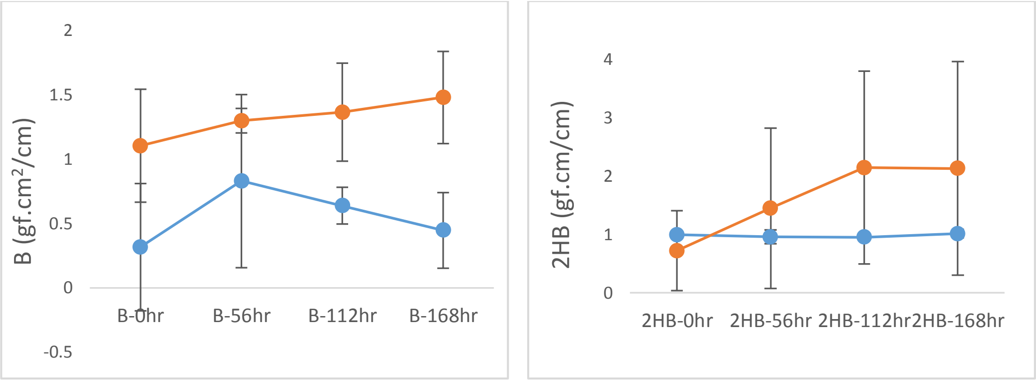
The use of KES to identify changes in the physical properties after ageing has only been reported in one case on cultural heritage items and limited to the compression tester device (Sato *et al.*, 2011). Sato *et al.* (2011) carried out tests on silk samples, both new and taken from Japanese ceremonial dolls of the Edo period, in order to investigate the relationship between chemical and mechanical damage. Initially the authors correlated the compression results of new samples after accelerated ageing with data obtained from tensile test and showed that a positive correlation existed between the two. Then they tested the original Edo period samples and noticed that the results were similar to the ones of the new silk after 28-42 days of accelerated ageing, confirming the suitability of KES-FB3 to identify the silk's state of conservation. The study did not involve leather samples, therefore it was interesting to assess the suitability of KES in this context.

One of the main difficulties encountered during KES analyses on the samples in this research stemmed from the significant change of sample's properties after ageing. TL and EL3 were particularly affected by these changes, as already described in the previous paragraphs, and this determined the impossibility of conducting the bending and friction tests on all the substrates. Nonetheless, in some cases the fact of not being able to conduct the test also provided information on the condition of the samples after ageing.

5.4.4.2.1 Bending Tests (KES-FB2)

The bending properties of TL, SY, EL2 and EL3 were measured with the KES-FB2 tester. A total of six measurements were recorded, three in the parallel and three in the perpendicular direction. These six measurements were used to calculate mean values and standard deviations of the samples without distinguishing between parallel and perpendicular direction.. Bending rigidity and hysteresis, respectively described by B (gf.cm^2/cm) and 2HB (gf.cm/cm), were used to evaluate the change in the properties as a function of the exposure to the ageing factors. The substrates subjected to UV ageing required a specific sample size in order to be placed in the ageing chamber. For this reason, the UV aged samples were not tested via the KES-FB2 device because the size necessary to place the samples in the UV machine exceeded the dimension required for the KES-FB2 test. As a consequence, if samples were resized they would have not been able to fit in the machine and the test would have been interrupted.

The results of the ageing procedures on TL samples are reported in Figure 5-84 and it is possible to notice that only two ageing procedures were successfully completed.



a) b)

Figure 5-84: Values of TL bending rigidity, B, and hysteresis, 2HB, respectively in (a) and (b), represented with related standard deviations, at different ageing times. Blue markers: H70 ageing; orange markers: H115 ageing

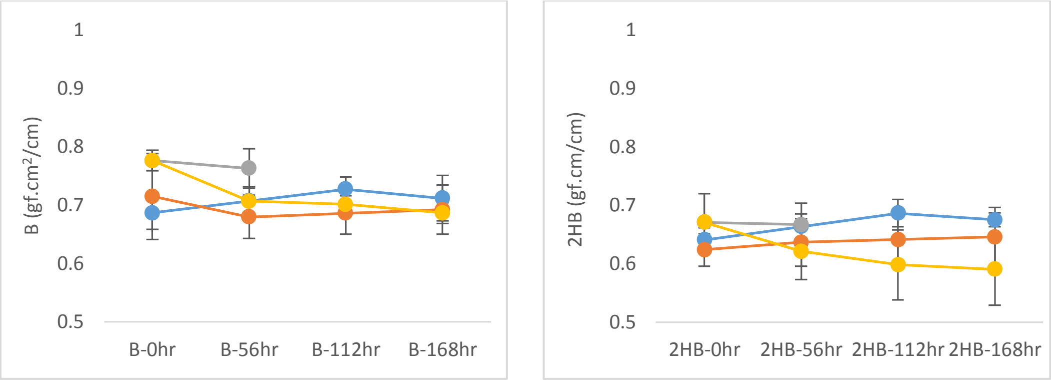
ANOVA single-factor analysis was conducted to evaluate the significance of the changes in B and 2HB throughout the ageing. It was found that the variations were not statistically significant, probably as a consequence of the great variance encountered within each group of samples (see error bars indicating the standard deviation). However, it is interesting to notice that after the first ageing interval of H70 ageing the values of B increased from 0.317 to 0.82 gf.cm^2/cm, meaning that the material became stiffer. The values started to decrease after the first interval, whilst they continued to increase in the case of H115 ageing. 2HB did not change during H70 ageing, but it increased steadily until 112 hours during the H115 exposure procedure.

The different behaviour after the two ageing methods suggests that H70 mainly affected the samples during the initial step but then it was not equally affected in the following stages, while H115 triggered changes that continued growing throughout the procedure. The latter treatment may have changed the structure in a permanent manner and, as a consequence, the sample's bending rigidity may have moved towards higher values. This was also confirmed by the 2HB values, because the greater the values the lower the ability of the samples to recover after the application of the stress (Von Hoven, 2002). Therefore, H115 ageing increased the 2HB figures lowering the ability of the sample to return to their initial state.

The measurement of B value was possible on unaged samples before H150 ageing, but when conducted after H150 ageing it provided results that were out of scale because the limit of the measurement was exceeded. This confirmed that the bending rigidity after the procedure was too high to be calculated from the instrument. Therefore the three heat ageing procedures were evaluated and produced results that confirmed the relationship between bending rigidity and heat.

As already said, the KES is a system able to detect minimal changes not only in fabrics but also in yarns. Therefore it was not surprising that very large changes in the properties of the samples could not be measured. Nevertheless, the fact that H70 and H115 ageing procedures gave measurable B and 2HB values constituted an encouraging result. In fact, the use of the KES-FB2 tester is limited in the field of leather testing, often as a consequence of the sample's thickness (Roh *et al.*, 2013). This work allowed to assess the applicability of the device in detecting changes in the substrate and proved that the variations of the bending properties can be used to follow the progress of the ageing.

The bending results of the SY ageing presented a few differences when compared to the TL data. Examination of Figure 5-85 highlights that the standard deviation associated with each measurement was significantly less than in the TL samples. ANOVA analysis confirmed that H70, H115 and H150 procedures did not affect the bending properties of the samples.

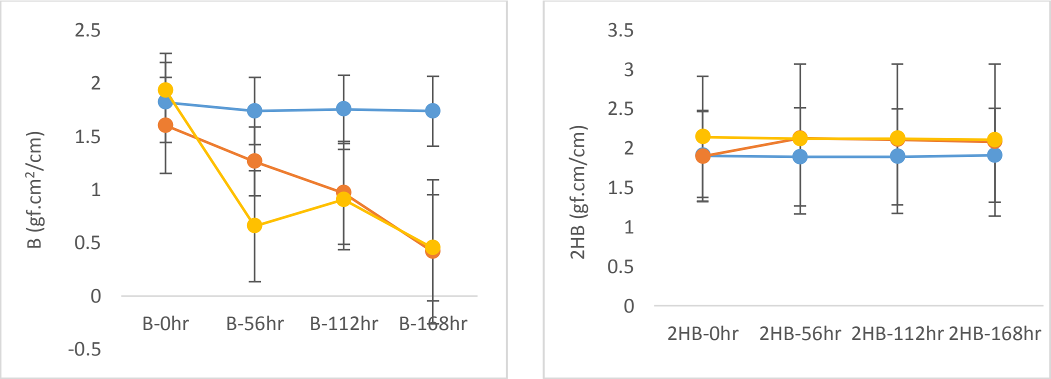


a) b)

Figure 5-85: Values of SY bending rigidity, B, and hysteresis, 2HB, respectively in (a) and (b), represented with related standard deviations, at different ageing times. Blue markers: H70 ageing; orange markers: H115 ageing; grey markers: H150 ageing; yellow markers: H+RH ageing

In contrast H+RH ageing significantly reduced the bending rigidity (p-value = 4.38 x 10^{-7}) and, likewise, the hysteresis values decreased even if the significance of the variation was still above the limit (p-value = 0.07). These findings suggested that high levels of humidity significantly influenced the behaviour of the samples, lowering its rigidity and enhancing recovery. As already stated, aramid fibres are normally stable to ageing and their affinity to water might have increased the flexibility of the material. In addition, it is likely that the changes were a consequence of variations occurring within the coating. This would also be in agreement with the hypothesis that the increased elongation of SY was mainly determined by changes within the coating (see § 5.4.4.1).

EL2 and EL3 samples presented standard deviation values similar to those measured for TL and clearly more scattered than those of SY. The graph in Figure 5-86 illustrates that, as in TL, the measurement was not possible after H150.



a) b)

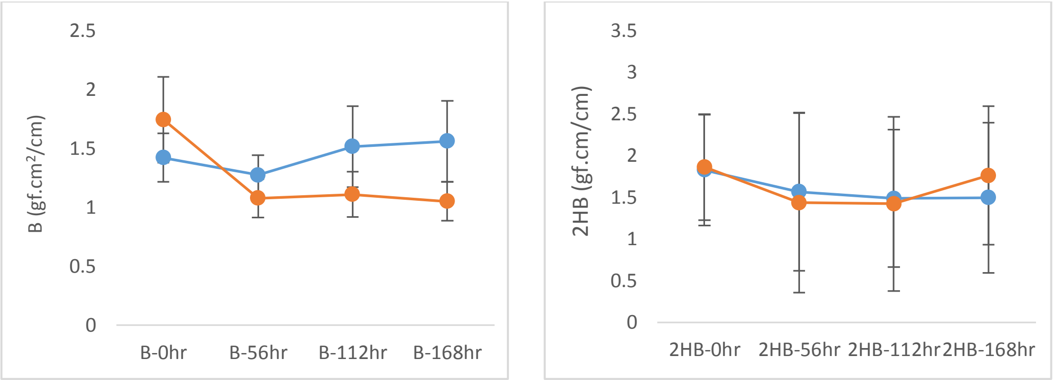
Figure 5-86: Values of EL2 bending rigidity, B, and hysteresis, 2HB, respectively in (a) and (b), represented with related standard deviations, at different ageing times. Blue markers: H70 ageing; orange markers: H115 ageing; yellow markers: H+RH ageing

The 2HB hysteresis values for the samples were essentially unchanged indicating that the fibre hysteresis within the samples remained almost unaffected by the different accelerated ageing processes. However, there were clear signs of reduction of the bending rigidity values during H115 and H+RH procedures, while H70 only had a minor effect on the substrate. ANOVA analysis confirmed the significance of these results by providing values above the significance level (p-value < 0.05). This result was unexpected, because the stiffness of the samples to the touch seemed to have increased, in particular after the treatment with high temperature and humidity.

A careful analysis of the results obtained for the two directions of the composite (parallel and perpendicular) pointed out that the MD values were the ones most affected by the ageing. During both ageing procedures, the bending rigidity measured along the MD equalled 0 after a certain ageing interval –that is 112 hours in the case of H115 test and 56 hours in the case of H+RH. As a consequence, the measurement was not conducted effectively in the MD throughout the ageing, possibly as a result of the changes induced in the composite. Confirmation of the limited usability of the results in the MD came also from the graphic output of the measurement.

In addition, it was noticed that the graphic output of the instrument consisted in curves less extended on the positive side, meaning that the maximum force that could be calculated from the instrument was reached before completing the whole curvature cycle. The positive side of the curvature, according to the way in which the samples were positioned, corresponded to the side where the coating was compressed and the fibrous layer stretched. This suggested that one of the two components of the material, or both of them to a different extent, presented a different behaviour compared with the initial one. It is possible to state that after ageing the difference in the bending rigidity in the two directions became substantial and that B remained measurable only along the CD.

The EL3 data collection presented the same difficulties observed for the TL samples, where the great rigidity of the sample resulted in the inability to perform the analysis after H150 and H+HR ageing processes (Figure 5-87). Also in this case, the stiffness of the samples was the element that did not allow the test to be performed.



a) b)

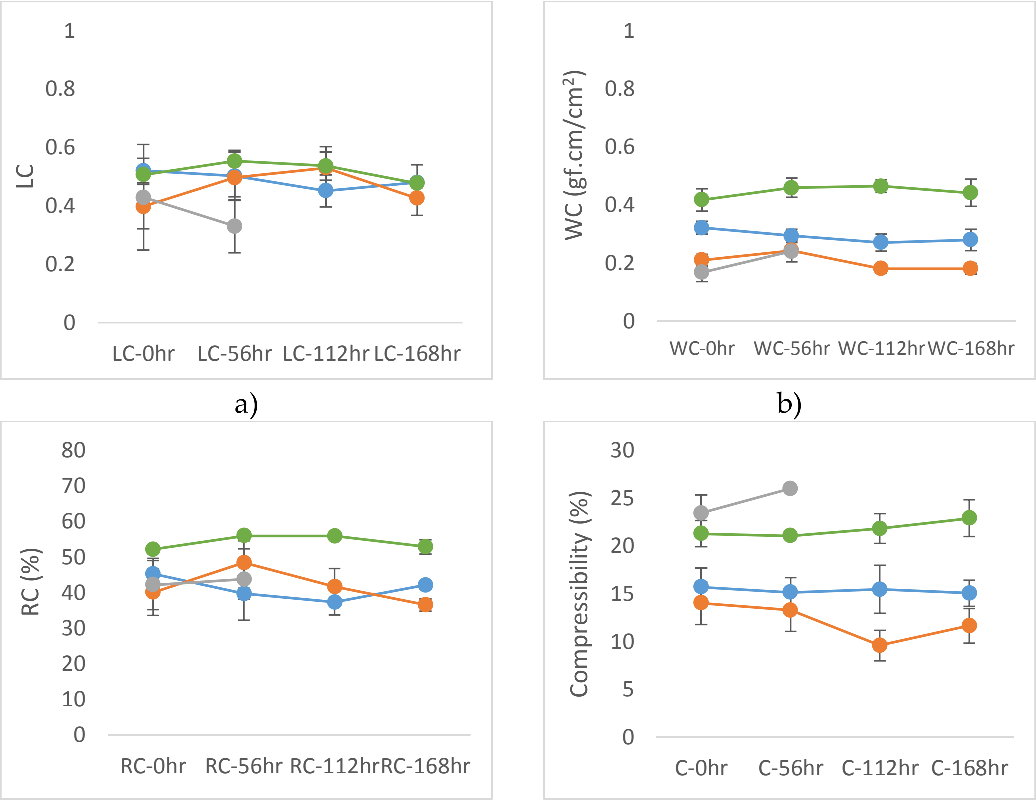
Figure 5-87: Values of TL bending rigidity, B, and hysteresis, 2HB, respectively in (a) and (b), represented with related standard deviations, at different ageing times. Blue markers: H70 ageing; orange markers: H115 ageing

ANOVA analysis on H70 and H115 demonstrated that changes of B values were highly significant only in the case of H115 ageing ($p\text{-value} < 0.05$). The bending rigidity diminished during the first interval of the H115 procedure and then stabilised around 1.1 gf.cm^2/cm. Similarly the hysteresis values tended to diminish after the first two intervals. These evidences seemed to suggest that considerable changes in the bending properties occurred mainly within the first exposure period.

5.4.4.2.2 Compression Tests (KES-FB3)

Compressional properties were measured with the KES-FB3 tester using three repetitions per each material. The influence of ageing on compressional energy, resilience and linearity of compression, respectively described by WC (gf.cm/cm^2), RC (%) and LC were calculated. In addition, compressibility can be obtained as a percentage value that considers the initial and final thickness of the tested sample (Urbanija and Geršak, 2004).

The graphs in Figure 5-88 show the results of the compression test on TL samples at different ageing times. It is possible to notice that also in this case the variability of the results was high both before and after the beginning of the procedures as noticed during the bending analysis. Despite the difficult perception of regular patterns, these results provided information on the linearity of the relationship between stress and strain (LC), the amount of energy necessary to compress the sample (WC) and to what extent the material returned to its original position (RC).



a) b)

c) d)

Figure 5-88: Linearity of compression, LC (a), compressional energy, WC (b), resilience, RC (c) and compressibility (d) values of TL at different ageing times. Blue: H70 ageing; orange: H115 ageing; grey: H150 ageing; green: UV

ANOVA analysis was conducted in order to identify whether the specific degradation factor (or factors) used for each procedure impacted significantly on the properties. H70 and UV ageing were expected not to have a significant impact on the compressional properties and this was in fact confirmed. However, both H115 and H150 were expected to show some degree of difference but in the case of H150 this did not happen.

WC was statistically different during H115 ageing (p-value < 0.05) and it showed that the energy required to compress the samples increased within the first interval and then started to decrease, indicating a possible stiffening of the surface. This could not be confirmed from the other values because they were within the level of significance (p-values > 0.05). Though, it must be remembered that statistical analyses and ANOVA in particular, take into consideration the variance within groups of samples. Therefore if there is great variance within a group it is more difficult to identify changes of the selected parameters. Bearing this in mind, one can notice that WC exhibited the lowest spread of data points while LC, RC and compressibility had higher variances. Also the recovery of TL samples started to decline after the first interval, and likewise the compressibility decreased after the same amount of time.

These trends suggested that the material became more rigid, reducing both the ability to recover and the compressibility.

The results of H150 ageing showed that the relationship between compression force and deformation decreased while WC increased, again indicating a general stiffening of the samples. These observations were in agreement with the expected results, but RC and compressibility had an opposite trend. This was explained by the fact that, after extreme heat was applied, the samples appeared to be convex, and hence the device measured values slightly higher than the actual ones (see Figure 5-89).

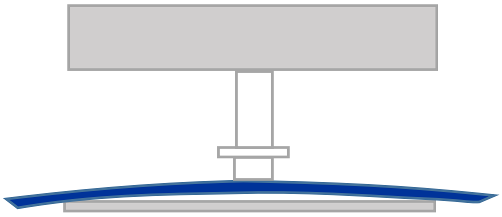
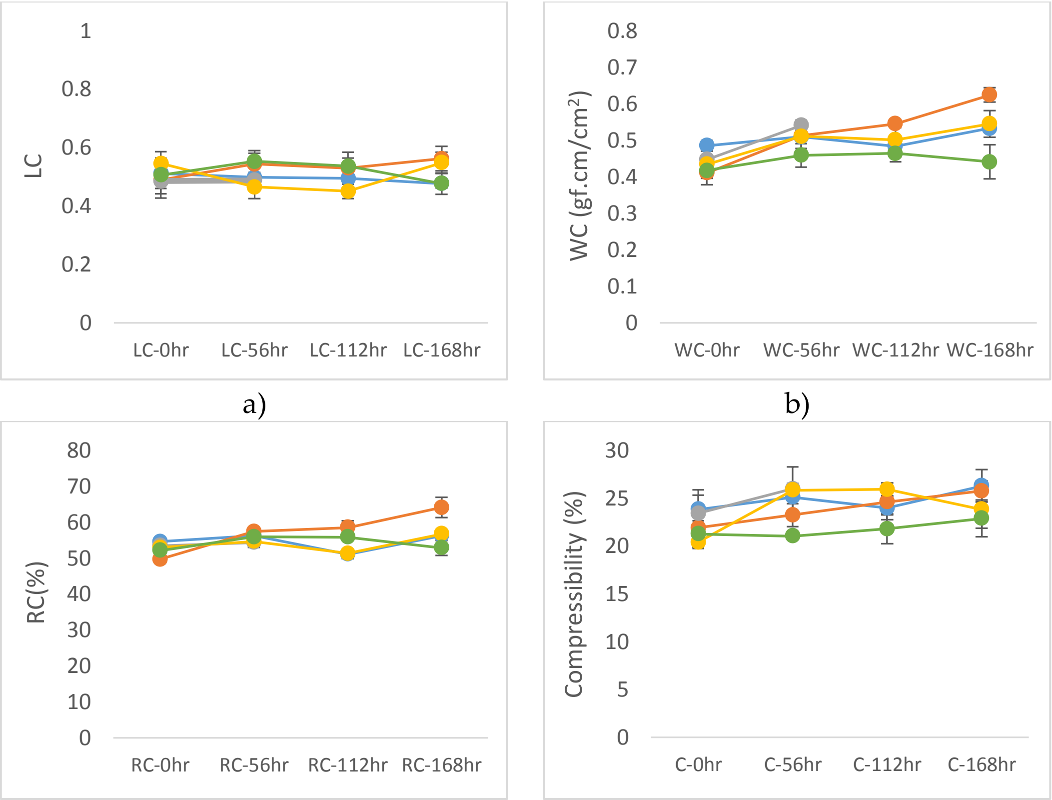


Figure 5-89: Schematic frontal view of convex TL sample positioned under the KES-FB3 plunger

The importance of the variance of the results became even more evident when SY samples were analysed. In fact, the variance was lower than in TL and this translated in more easily detectable changes. The H70, H115 and H+RH treatments produced significant differences in WC and RC values (p-values < 0.05), but only in the case of H115 the results tended to increase in a constant manner while they were discontinuous during the other two procedures. After 168 hours of ageing SY samples were more compressible and they had both higher recoveries and linearity of compression. This may be related with the variations that took place in the coating and that are associated to the resistance and rigidity of the material.

For the H+RH ageing the bending test showed significant decreases in B and 2HB. Significant variations in WC and RC, but also in LC and compressibility were identified for the same ageing during compression tests. While the impact of this type of ageing on the substrate was therefore confirmed by the apparent increased WC and RC values, it is not clear why the linearity of compression and compressibility reached a peak after 56 hours, followed by a plateau and then by a marked increase/decrease. All these changes were attributed to rearrangements of the coating structure that after the first ageing stage returned towards initial values.



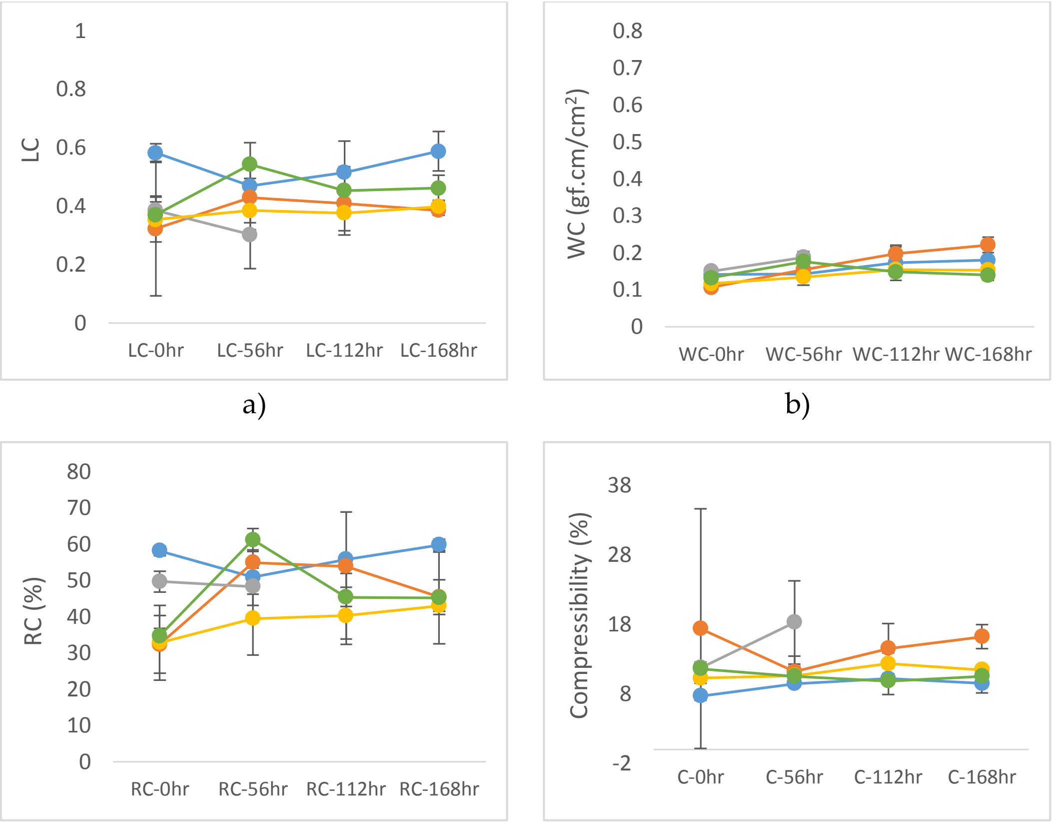
a) b)

c) d)

Figure 5-90: Linearity of compression, LC (a), compressional energy, WC (b), resilience, RC (c) and compressibility (d) values of SY at different ageing times. Blue: H70 ageing; orange: H115 ageing; grey: H150 ageing; yellow: H+RH ageing; green: UV

H150 ageing only influenced the WC parameter, indicating that more energy was required to compress the sample. This result was not expected because it indicated that the samples were stiffer than before the procedure. It is likely that before going through softening the polymeric coating was able to transmit the energy from the top coating to the bottom coating, softer, and finally to the fibres. Once softening occurred, the total thickness of the coating layer decreased bringing it in closer contact with the fibres. The reduction of the intermediate layer would be thus responsible for the increased compressional energy. The initial and final thickness values, T_0 and T_m, which are routinely collected by the KES-FB3 instrument to measure samples compressibility were observed. It was noted that the value of T_0 before ageing was lower than that of T_0 after the H150 ageing, passing from 1.58 to 1.7 mm. This indicated that the total thickness of SY unexpectedly increased after ageing and therefore it was not possible to confirm whether there was a reduction of the coating.

Similarly to the case of TL, EL2 showed a great variability during compression tests as visible from the error bars associated with each measurement (Figure 5-91). Because of this great variability in the results the ANOVA analysis could not be effectively conducted on all the samples.



a) b)

c) d)

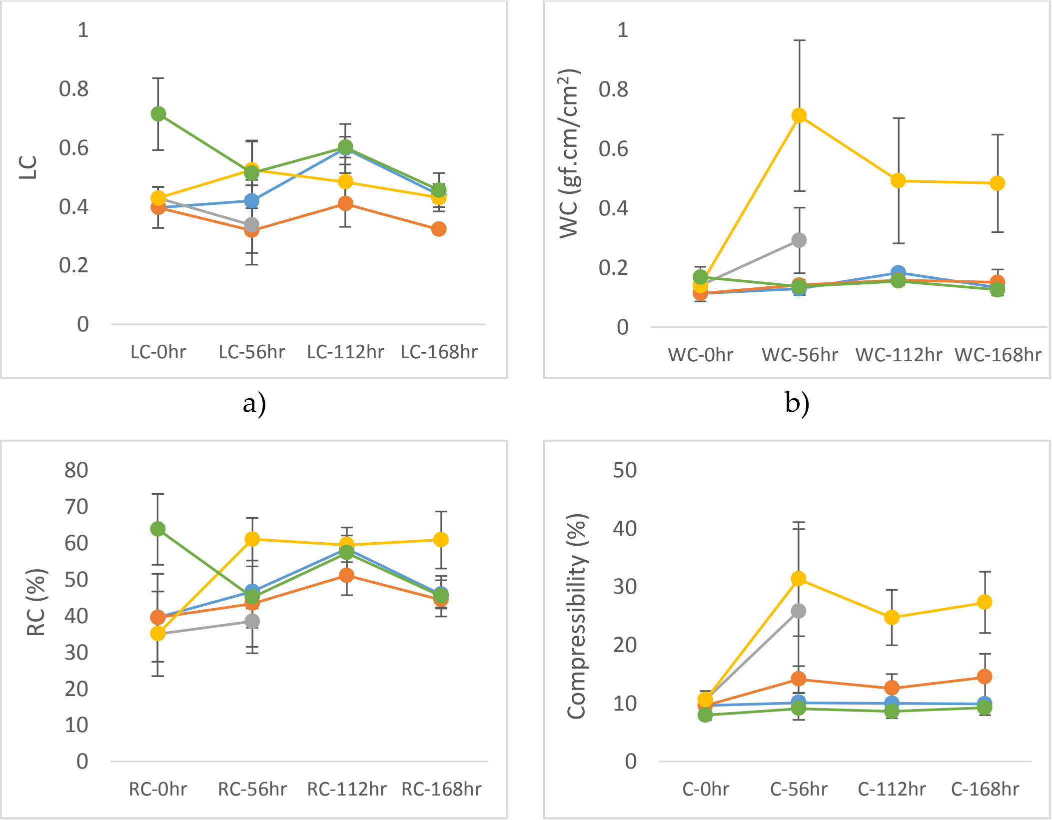
Figure 5-91: Linearity of compression, LC (a), compressional energy, WC (b), resilience, RC (c) and compressibility (d) values of EL2 at different ageing times. Blue: H70 ageing; orange: H115 ageing; grey: H150 ageing; yellow: H+RH ageing; green: UV

Linearity of compression did not change significantly during any of the procedures probably as a consequence of the spread of the results before the treatment. This high variance also affected other parameters and in particular compressibility at 0 hours of the H115 samples. In TL samples the wide results distribution was related to the intrinsic inhomogeneity and compactness of leather fibres, whilst in E-Leather® it was attributed to the presence of areas of the composite where the leather fibres had different degrees of entanglement. The two less aggressive procedures, H70 and UV, impacted on the material in a minimum way. During the former compressibility increased from 7.68 % to 9.49 %, whilst during the latter RC had a peak after 56 hours (61.12 %) but then it stabilised at around 45.30 %. These variations were attributed to sample inhomogeneity.

During H115 exposure WC and RC also changed significantly indicating that the samples were less compressible. WC increased from 0.106 to 0.221 gf.cm/cm^2 and RC from 32.27 % to 45.38 %. A rise in WC values (p-value = 0.05) was also noted during H+RH exposure, where the values had a consistent increase from 0.11 to 0.15 gf.cm/cm^2, but the other compression parameters did not vary significantly.

Also during H150 ageing the values of WC and compressibility increased while the ones of RC and LC decreased, though only WC was statistically significant (p-value = 0.02). This confirmed that the samples became stiffer and that the rougher surface increased the compressibility of the samples, though limiting the ability to recover.

The difference in behaviour between EL2 and EL3 was again confirmed by the results of KES-FB3. Figure 5-92 reports the results of compressional tests on EL3. The most interesting result was related with the effect of H+RH ageing because, the results clearly indicated a change in the compressional properties and this distinctly differed from the other degradation environments.



a) b)

c) d)

Figure 5-92: Linearity of compression, LC (a), compressional energy, WC (b), resilience, RC (c) and compressibility (d) values of EL3 at different ageing times. Blue: H70 ageing; orange: H115 ageing; grey: H150 ageing; yellow: H+RH ageing; green: UV

The energy required to compress the samples increased from 0.139 to 0.710 gf.cm/cm^2 between 0 and 56 hours and then the values decreased to around 0.49 gf.cm/cm^2. Compressibility followed a similar trend, with a peak at 56 hours and decrease in the following intervals. RC reached the maximum point after the first interval and then it remained around the same values (60 %) until the end of the ageing. The data pointed out that the energy required for the compression and the compressibility rose markedly only during the first interval, but then they returned to lower values yet higher than the initial ones. These results were in agreement with previous observations.

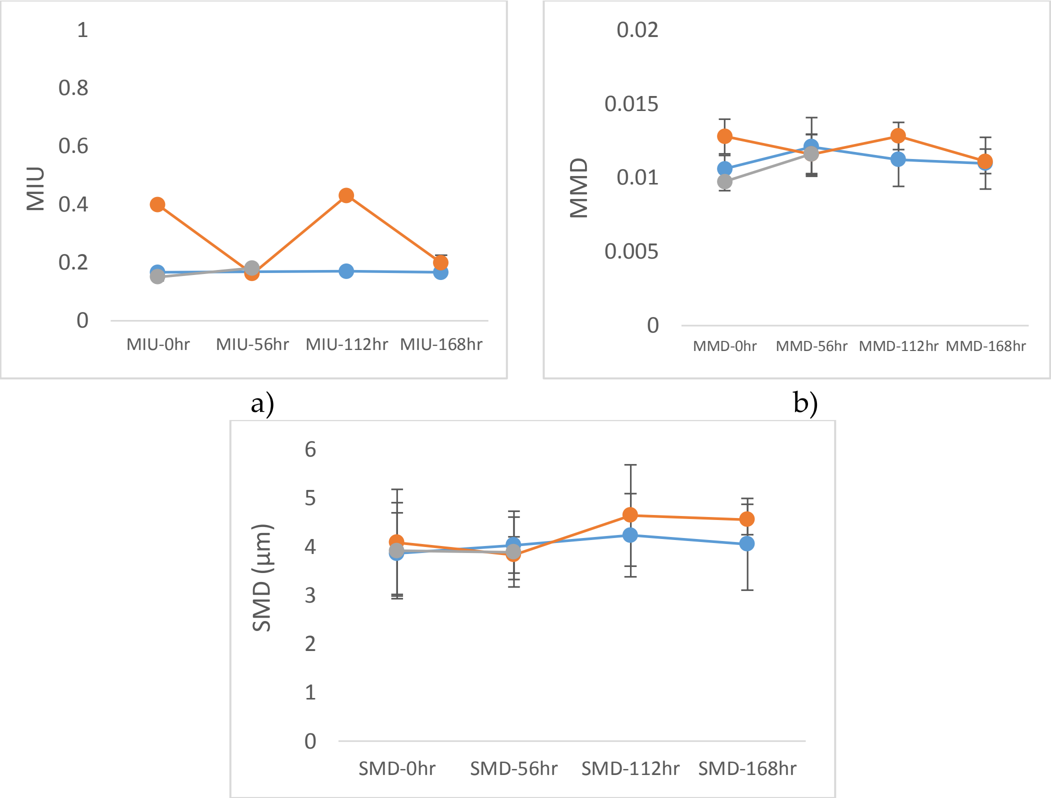
Also the other ageing procedures had an impact on the properties, though it is important to report that the statistical significance of the variations was sometimes difficult to assess, as in other substrates. For example, H150 ageing did not seem to affect the material in any way because the data did not present statistical significance. However it was possible to notice that WC and compressibility had a steep increase, similar but to a lesser extent than that during H+RH ageing, probably related with the stiffening of the fibrous layer. As for H150 ageing, also in the case of H115 the statistical significance was low but the pattern of the values was similar. Nonetheless, while LC and compressibility varied in inconsistent manner, WC and RC tended to increase following the same pattern of H+RH. This indicated that degradation procedures conducted using different ageing factors affected the compressional properties in a similar manner.

5.4.4.2.3 Surface Tests (KES-FB4)

Attempts to use the KES-FB4 device were conducted on leather and related materials in order to investigate the usability of the machine as a non-destructive method to characterise the properties of the substrates. On the one hand, previous research conducted in the area of leather has pointed out that, because of the roughness of the substrate, this instrument is not suitable for this purpose (Von Hoven, 2002). On the other hand, recent studies have successfully applied the KES-FB4 to achieve this goal by testing PU-coated fabrics (Roh *et al.*, 2013)

Surface properties were measured with the KES-FB4 tester and, as for the KES-FB2 tester, six measurements (three in each direction) were recorded. In this study the effect of ageing on the friction coefficient (MIU), its mean deviation (MMD) and surface geometrical roughness (SMD, µm) were evaluated.

The results obtained for TL samples during three ageing procedures are reported in Figure 5-93. As in other cases, the analysis was not possible on all the samples because of their condition after ageing (H+RH ageing) or for the samples size (UV ageing).



a) b)

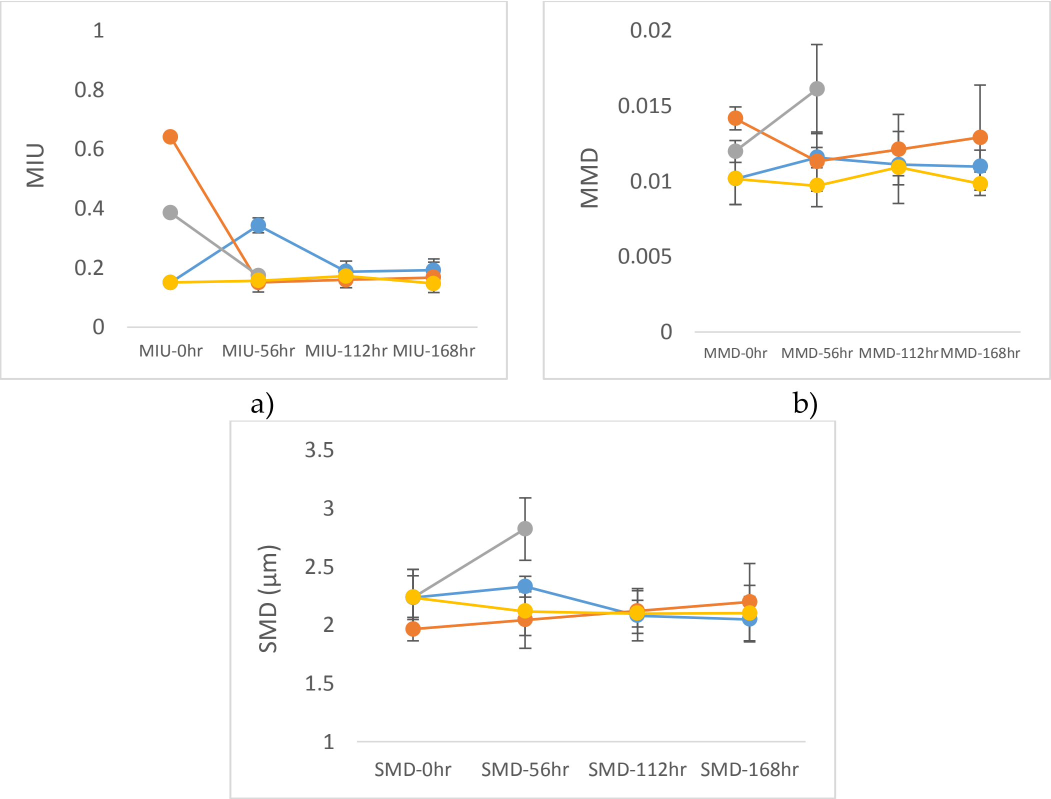
c)

Figure 5-93: Friction coefficient, MIU (a), mean deviation of MIU, MMD (b) and geometrical roughness, SMD (c) values of TL at different ageing times. Blue: H70 ageing; orange: H115 ageing; grey: H150 ageing

H70 did not present any significant variation during ageing, while both MIU and MMD increased during H150 ageing. SMD did not exhibit statistically significant changes and this result was surprising because, as indicated earlier, the image capture and processing and 2D scanning all suggested the values decreased after H150 ageing as a consequence of the flattening of the coating. One possible explanation for this result is that the measurements conducted with the KES-FB4 did not detect effectively the variation as a consequence of the size of the contactor (6.00 mm x 0.8 mm). This weakness of the devise was pointed out in previous papers where the different surface roughness methods were compared, and KES-FB4 demonstrated to be less precise than optical methods and the Multipurpose Fabric Tester (Mooneghi *et al.*, 2014).

The H115 test had a clear impact on the friction parameters (MIU and MMD p-values < 0.05) of the samples analysed. The test seemed to suggest that the friction changed in a discontinuous way throughout the procedure. It is known that a relationship exists between friction and roughness and that a number of characteristics, such as amplitude and spacing of the surface profile, may affect them in a different way (Mao *et al.*, 2016). This relationship was confirmed, because the roughness varied following a similar pattern to the one of friction, but with lower values and with more dispersed results that determined a reduction of the significance level (p-value > 0.05).

Observing the results obtained for SY it was noticed that the MIU values changed to some extent during every ageing procedure (p-values < 0.05). H+RH ageing presented constantly increasing results, but all the other ageing procedures indicated that changes occurred within the first interval. After 56 hours they returned around values below 0.18, suggesting that the friction was reduced as an effect of the ageing. The mean variation of the friction did not change accordingly, hence the friction was not homogeneous among the different intervals.



a) b)

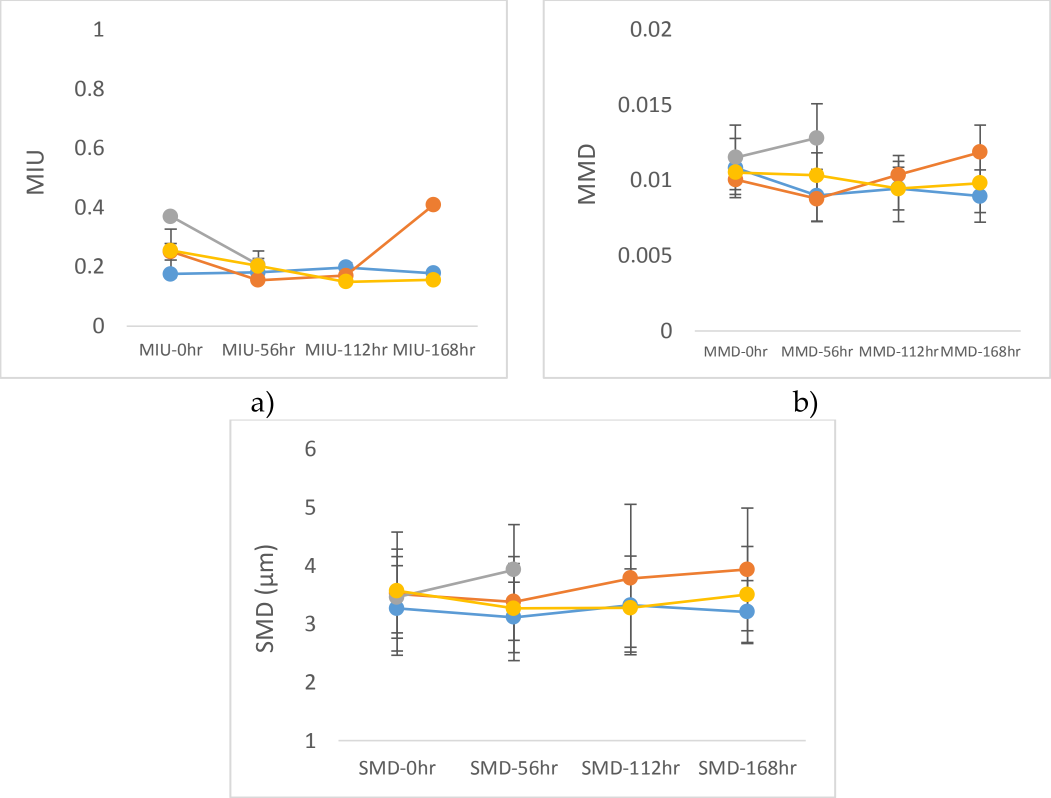
c)

Figure 5-94: Friction coefficient, MIU (a), mean deviation of MIU, MMD (b) and geometrical roughness, SMD (c) values of SY at different ageing times. Blue: H70 ageing; orange: H115 ageing; grey: H150 ageing; yellow: H+RH ageing

The geometrical roughness seemed to be significantly affected only in the case of H150 ageing, which referred to those samples where the support fabric became visible through the top coating (see Figure 5-10). The results confirmed that surface properties were greatly influenced by the high temperature ageing (moderate and severe) and less by the combination of high temperature and relative humidity.

EL2 exhibited changes in the friction coefficient during all the procedures, with the most significant effects in the case of H115 and H150 ageing (p-value < 0.05).

However, if the friction was increased by H115, it seemed to decrease after the H150 procedure.



a) b)

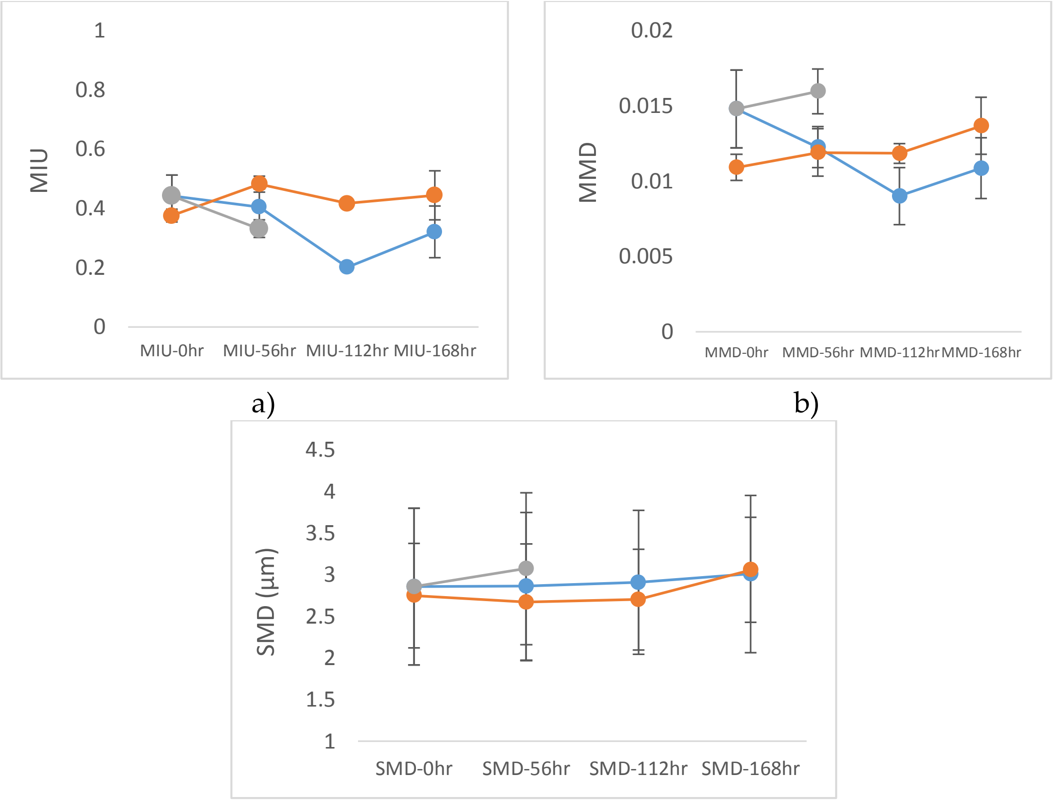
c)

Figure 5-95: Friction coefficient, MIU (a), mean deviation of MIU, MMD (b) and geometrical roughness, SMD (c) values of EL2 at different ageing times. Blue: H70 ageing; orange: H115 ageing; grey: H150 ageing; yellow: H+RH ageing

2D scanning detected variations in the roughness of H115 and H150 aged samples, hence it was expected to find the same pattern in this occasion. ANOVA analysis, though, did not recognise the variations during these procedures as statistically significant (p-value < 0.05), probably also in this case as a consequence of the wide distribution of the results. Leaving aside the variance analysis spread, it is possible to recognise that SMD and MMD values increased as a consequence of heat ageing (H150). This was in agreement with the roughness observations conducted in the previous paragraphs of this work.

EL3 was the most interesting material to be tested via KES-FB4 because during image capture and processing and 2D scanning the surface resulted highly damaged. By means of those techniques it was possible to identify the significance of the roughness variation and similar results were expected with KES. However, also in this case the stiffness of some of the samples did not allow the measurement. H+RH aged samples, that presented the greatest damage, were so stiff that their analysis was not allowed.

Examining Figure 5-96 it is possible to notice that H70 procedure seemed to have a greater effect on the friction than H115. Moreover, H150 ageing did not show great variations compared with the other two procedures. This limited change of the friction and roughness during the two most aggressive ageing was considered the evidence that the device did not provide accurate data.



a) b)

c)

Figure 5-96: Friction coefficient, MIU (a), mean deviation of MIU, MMD (b) and geometrical roughness, SMD (c) values of EL3 at different ageing times. Blue: H70 ageing; orange: H115 ageing; grey: H150 ageing

The results of the KES-FB4 analysis were interpreted in the light of the limitations highlighted in the literature. The results of the surface friction and roughness, particularly for the TL, EL2 and EL3 samples, confirmed that the analysis of leather and leather imitates is not always reliable. The high sensitivity of the instrument, together with the roughness of the substrate make the results spread and reduce the statistical significance. Apart for the samples subjected to the H150 procedure, SMD values were far to be representative of the actual roughness of the samples, and the data of the different ageing procedures at the different ageing stages did not provide meaningful results. Therefore, although SMD provided a value measurable in µm, its applicability in this context was limited.

5.4.4.3 Fastness to Dry Rubbing

Fastness to crocking is often used to assess dye fastness of textiles and colour fastness of leather objects (Smith, 1994; British Standards Institution, 1992). In this study six samples (three per each direction) were tested to measure the effect of rubbing on the selected coated substrates. Due to the limited space available in the ageing chambers, it was decided to restrict the test to dry rubbing. If fact, this procedure can be virtually related to dry cleaning procedures, such as brushing, that may take place in museum environments in particular when objects are sensitive to solvents (Higham, 2011).

A standard grey scale, ranging from 5 (no difference) to 1 (great difference), was used to assess the staining of the abradant fabric used to rub the sample. This provided an indication of the colour that was transferred from the sample to the fabric. As described within the standard, the use of intermediate units is allowed, e.g. 4/5 when the staining is comprised between 4 and 5 units.

Leather samples were, among all the samples tested in this work, the ones with the poorest colourfastness. In Table 5-6 it is apparent that the degree of colour transferred to the abradant was between 5 and 4 after just 10 rubbing cycles both in the case of unaged samples and of samples subject to H70 and UV ageing, while it was 4 after H115. Overall only elevated temperature test, H115, adversely affected the performance worse than the control.

	10cy	**20cy**	**100cy**	**250cy**	**500cy**
0 hr	4/5	4	3/4	3	3
168 hr - Heat	4/5	4	3/4	3	3
168 hr - H115	4	3	2/3	2	2
168 hr - Heat + RH	ND	ND	ND	ND	ND
168 hr - UV + 45° C	4/5	4	3/4	3/4	3

Table 5-6: Degree for staining transferred from unaged and aged TL to abradant fabrics during rubbing

SY was demonstrated to be more resistant than TL, as visible when comparing Table 5-7 with Table 5-6. Unaged samples did not show any evidence of colour transfer until 100 cycles, when the staining decreased to 4/5 units and then stabilised at that value. The samples performances were affected to a greater extent by the H+RH procedure. After the ageing procedures all the samples stained the abradant to the same extent (4/5 units) until when 250 cycles were reached. At that point H+RH ageing increased the colour transfer (4 units).

	10cy	20cy	100cy	250cy	500cy
0 hr	5	5	4/5	4/5	4/5
168 hr - Heat	4/5	4/5	4/5	4/5	4/5
168 hr - H115	4/5	4/5	4/5	4/5	4/5
168 hr - Heat + RH	4/5	4/5	4/5	4	4
168 hr - UV + 45° C	4/5	4/5	4/5	4/5	4

Table 5-7: Degree for staining transferred from unaged and aged SY to abradant fabrics during rubbing

EL2 exhibited remarkable resistance to colour transfer that is noticeable when looking at Table 5-8. All the samples showed that the abradant fabric was not stained after any of the rubbing cycles. Similarly, any of the ageing procedures affected the fastness to rubbing that was consistently of 5 units.

	10cy	20cy	100cy	250cy	500cy
0 hr	5	5	5	5	5
168 hr - Heat	5	5	5	5	5
168 hr - H115	5	5	5	5	5
168 hr - Heat + RH	5	5	5	5	5
0 hr - UV + 45° C	5	5	5	5	5

Table 5-8: Degree for staining transferred from unaged and aged EL2 to abradant fabrics during rubbing

EL3 was less resistant than EL2 to rubbing, and samples subjected to H115 ageing stained the abradant after only 10 rubbing cycles (4/5 units). Staining also occurred after 500 cycles on H+RH aged samples, indicating that both moderate heat and the combined effect of heat and humidity affected the colourfastness.

	10cy	20cy	100cy	250cy	500cy
0 hr	5	5	5	5	5
168 hr - Heat	5	5	5	5	5
168 hr - H115	4/5	4/5	4/5	4/5	4/5
168 hr - Heat + RH	5	5	5	5	4/5
168 hr - UV + 45° C	5	5	5	5	5

Table 5-9: Degree for staining transferred from unaged and aged EL3 to abradant fabrics during rubbing

These results highlighted that EL2 coating was the most resistant substrate among the tested ones, followed by EL3. SY coating was less resistant than E-Leather® samples and the data suggested that some level of staining occurred in all the samples both before and after ageing. This indicated that rubbing affected the coating to some extent even when SY was not subject to ageing, hence changes within the coating or its surface did not occurred only as a consequence of the ageing procedures.

It was observed that leather presented lower colourfastness than manmade substrates despite the presence of a superficial coating. However, the colourfastness values were in agreement with those reported in previous studies (Ollè *et al.*, 2011; Örk *et al.*, 2014). This evidence indicated that, despite polymeric coatings are applied to increase the resistance of the substrate to abrasion, rubbing and other stresses, it is not always possible to maintain the same level of protection. For this reason, extreme care should be taken when aged samples are subjected to dry cleaning treatments, in particular when leather samples are considered and after exposure to moderate heat.

5.5 Discussion of Degradation Results

5.5.1 Chrome-Free Leather (TL)

Accelerated ageing conducted with mild heat (H70) left the TL material almost unchanged. The method used for image capture and processing detected variations of the substrate after the second exposure interval, with these variations likely to be related to the structural rearrangement of the material as a consequence of the heating. The more detailed 2D scanning detected changes that were not statistically significant and need further work to validate the preliminary observation. The pH of the aged material decreased, although the ATR-FTIR spectra did not present significant variations. Also ageing of the material imparted greater stiffening, as shown by the increased bending rigidity, while the recovery and most of the remaining mechanical properties were unvaried.

H115 ageing exhibited a drop in the roughness parameter during 2D scanning, while no change was apparent with photographic data collection and image processing method. SEM highlighted a reduction in the coating thickness and an increase in the compactness of the leather fibres. They may indicate a slight shrinkage of the material and, as a result, an increase in the tension of the coating that flattened. Colour changes occurred both on the coating and fibrous layer and they were attributed to changes in the colorant structure. In fact, ATR-FTIR analysis of the coating did not indicate any signs of degradation of the macromolecule backbone that may indicate oxidation of polymers (Shashoua, 2008). The same analysis conducted on the fibrous layer showed a slight reduction of some of the amide peaks. Moreover, the moisture content after this treatment was the lowest of all the ageing procedures, as also the pH, and this was attributed to the greater number of cycles that may have weakened the collagen molecule. If the tensile test results did not detect particular differences compared with the unaged samples, both bending and compressional analysis suggested that the samples became more rigid.

The effect of severe heat (H150) was clearly detected both by image capture and processing and 2D scanning. A reduction of the coating roughness was measured and was associated with a thickness reduction, observed via SEM. The analytical tools also characterised the yellowing of the surface. These results were compared with those of ATR-FTIR, which indicated the disappearance of the stretching of C-C bonds. This suggested that the coating surface went through degradation and part of the polymer backbone was lost. On the fibrous layer side, the amide I and amide II peaks decreased while the C=O band increased, testifying that heat deteriorated the collagen structure. In addition, the shift of the peaks was attributed to the change from the helical to the random arrangement. The moisture content decreased, as expected when the collagen molecule is compromised (Florian, 2006), though the pH increased. One explanation could be that ammonia formed after the collagen oxidative breakdown and increased the pH value. The tensile test emphasised the great impact of this degradation method on the material, decreasing both the maximum force at break and the elongation value. In addition, the bending test was not utilised in the testing portfolio because the high stiffness of some of the samples meant it was not possible to measure them on the KES-F system. The increased stiffness was also confirmed by the compression test (higher work for compression).

The H+RH procedure was the most damaging for TL samples and this became evident immediately after the initial exposure to the test. The samples looked already compromised within the first hour from the introduction of the specimens in the weathering chamber. The shrinkage was evident to the naked eye, but instead of resulting in a rougher surface the opposite trend was noticed. Both image processing and 2D scanning detected decreases in the roughness, however SEM observations highlighted that in the microscopic scale the surface was rougher. The colour coordinates were the most distant damage indicators from the unaged specimens, which highlighted the darkening of samples particularly on the reverse side. Moreover, a blue oily substance was released from the fibrous substrate. The high hygroscopicity of leather is well known, as also are the shrinkage and dilatation effects that come together with it (Thomson, 2005). Splitting, tearing and hardening are the most common consequences of heat/humidity fluctuations in the leather surroundings and they are associated with darkening of the leather colour (Thomson, 2005; Axelsson *et al.*, 2016). All these phenomena took place, and they were attributed to the denaturation of the collagen molecule because of the well-known relationship with the shrinkage of the fibres (Wright and Humphrey, 2002).

FTIR analysis showed that Amide I and II bands decreased also in this damaging environment while the C=O stretching vibration increased in intensity. The position of the bands led to the hypothesis that the random mode of the collagen vibrations was prevalent over the helical mode. The moisture content increased with damage and was ascribed to effect of the great degradation of collagen, which produced more polar sites (Bicchieri *et al.*, 2011). The pH of the aged materials also increased, as in the case of H150 ageing, again probably because of deamination processes within the collagen molecule. Because of the great rigidity of the specimens following ageing, the aged samples began to feel more similar to moulded polymer than leather, and it was subsequently impossible to conduct physical investigations on these samples.

UV ageing had its main deleterious impact on the coating as a result of the spectral irradiation. The samples seemed smoother after ageing, as detected by image processing as a consequence of the way the samples are placed in the UV chamber, while the trend was not consistent with all the samples characterised by 2D scanning. The colour gradually shifted towards the green, possibly as a consequence of changes to the colorants and coating chemical structure, and ATR-FTIR confirmed that oxidation occurred within the coating during the ageing processes (Wilhelm and Gardette, 1997; Irusta and Fernandez-Berridi, 1999). However, light irradiation did not appear to have an effect on the material's tensile or compressional properties.

It is also interesting to remember that the samples subjected to H115, H150 and H+RH exposure showed a reduction in the surface bromine content after 56 hours, suggesting that the flame retardant was volatilising from the surface regions of the coated materials.

5.5.2 Synthetic Leather (SY)

The behaviour of SY material was very different from the natural leather. The coating exhibited the greatest change, while the aramid fibres of the supporting fabric remained almost unchanged throughout the ageing procedures. This confirmed the resistance to high temperatures and hydrolysis of aramids (Bourbigot and Flambard, 2002; Perepelkin *et al.*, 2003). UV radiation did not induce any significant change apart for a slight shift of the coating colour towards the green, while the other processes affected all the samples to some extent.

H70 ageing reduced the roughness values detected via image capture and processing. A different trend closer to the perceived roughness was observed via 2D scanning. The bulk of the coating seemed less homogeneous after the second ageing exposure, probably as a result of partial degradation of the binder surrounding pigments and additives (Yang *et al.*, 2002). However, this did not result in obvious changes of the top coating. The colour coordinates did not change and, likewise, the samples demonstrated similar mechanical properties to those of unaged samples.

An analogous pattern was observed after treatment with moderate heat (H115). An increase in the roughness, not identified via image capture and processing, was detected through 2D scanning. In this case the SEM technique also detected a reduction in the homogeneity of the bulk coating. ATR-FTIR spectral analysis showed the appearance of a new peak in the C-H domain within the same intervals where the change in homogeneity were observed. The mechanical elongation along the warp direction increased compared with the value before ageing, as did the compressional recovery and the work for compression, as measured by KES-F analysis. However, the bending rigidity of the material was unaffected by the treatment, demonstrating that the limited changes to the coating had negligible effects on the mechanical properties of the whole material that was similarly unaffected.

SY was mainly degraded by the action of severe heat (H150) and the part of the substrate subject to the greatest damage was again the coating. Although the aramid fibres guaranteed stability within the fibrous layer, a shift of their chromatic coordinates towards yellow and red was registered after the treatment. The coating roughness value increased and the geometry of the supporting fabric became visible to the naked eye through the top coating. SEM observations seemed to contradict these results because the surface appeared smoother. On the one hand, this reduction of the roughness at the microscopic level resulted in a glossier surface, explaining the different macroscopic appearance of SY. On the other hand, the detection of a rougher surface via 2D scanning was considered as a result of the high temperature, which may have induced the coating softening allowing a greater penetration of the aramid fibres. The partial degradation of the PU coating was confirmed by ATR-FTIR analysis. The maximum force at break decreased after this treatment, and the work at compression increased. This suggested that H150 ageing impacted to some extent on the mechanical properties.

The H+RH procedure did not change the roughness values of the samples as characterised by both the image processing and capture and 2D scanning. The only parameters that varied after this ageing process were moisture content and bending rigidity, which increased and decreased, respectively. It is possible that these two parameters were connected and that the higher water content allowed the samples to become more flexible and deform more easily.

5.5.3 E-Leather® without Flame Retardant (EL2)

The EL2 material was demonstrated to be resistant to the application of the selected ageing procedures and the image capture and processing did not detect changes after H70 ageing. A slight flattening was measured particularly after the first interval via

2D scanning. These findings suggested that, as in TL, the supporting fabric may have been subject to minimal stress in the first interval that introduced tension on the coating side. After that stage the material relaxed/settled, but part of the collagen structure had probably lost its protein organisation, as demonstrated by the ATR-FTIR results. The change in colour that was evident after ageing occurred mainly on the fibrous layer side, where the ΔE after 168 hours was 1.69, indicating that changes took place also in presence of mild heat. The moisture content decreased compared to unaged samples, though it did not affect the mechanical properties.

H115 ageing had a greater effect on the substrate, starting with the increase in the roughness (2D scanning) and the change in the colour on both the coated and fibrous layers, with the latter being particularly obvious. SEM characterisation did not reveal clear signs of changes on the top coating, whilst ATR-FTIR detected the same variation in the C-H domain that was noticed in SY after H115 ageing. The fibrous layer presented the same absorbance changes that were noticed after H70 ageing, e.g. in the region between 1150 and 1000 cm^{-1}, though in this case reductions were more significant. These variations of the spectrum suggested that changes occurred within the collagen structure that determined a decrease in the number of amide groups. The effect of these changes was probably responsible for the lower moisture content, the lowest measured among all the ageing procedures. Moreover, the maximum force at break, elongation, and both bending rigidity and compressibility indicated that the treatment made EL2 less elastic and less compressible.

The H150 treatment had a significant impact on both coated and fibrous layer. An increase in surface roughness was detected via image capture and processing and 2D scanning and, interestingly, SEM revealed the presence of particles spread throughout the top coating. The particles were composed of carbon and oxygen, which indicated a possible degradation of elements within the coating. However, no noteworthy difference was detected after ATR-FTIR analysis. The fibrous layer exhibited a shift of the amide II band which was attributed to the increase in the random coil collagen content (Bicchieri *et al.*, 2011). The moisture content was slightly higher than after H115 ageing, but it must be considered that H150 treatment only lasted 56 hours. The material's elongation increased to some extent, as also did the work for compression. Together with the considerations regarding the increased stiffness of these samples, the results indicated a general reduction of the mechanical properties of EL2.

The H+RH ageing environment induced statistically significant changes in surface roughness, in particular during the first exposure interval, that were detected via 2D scanning. After this interval the roughness values approached similar figures measured before ageing. Colour change between aged and unaged samples occurred on both the coated and fibrous layers and was greater on the latter. Despite this colorimetric change, SEM observations did not show significant differences in the fibres compactness. Micrographs of the bulk coating showed a less homogeneous cross-section even though the top coating did not seem affected. Interestingly, the C-H domain in the ATR-FTIR spectra highlighted the appearance of the same peaks detected after H115 ageing, possibly related to degradation phenomena of the PU. In addition, the assignment of the new peak at 1714 cm^{-1} confirmed that carboxylic acids were formed. On the fibrous layer side, the major changes were again related with the region between 1150 and 1000 cm^{-1}, again due to probable collagen structural changes (Valeika *et al.*, 2010). The pH of the extract solution after H+RH ageing was more acidic than the unaged and this represented the most significant pH change among all the degradative procedures. In contrast the moisture content exhibited a smaller reduction compared with the other degradative procedures. The reason for this behaviour was not clear and will need further study. The reduction in tensile properties, the increase in bending rigidity and the work for compression indicated a worsening of mechanical properties.

UV ageing did not seem to have affected the fibrous layer, though the UV radiation had a significant impact on the coating layer. The latter became redder and yellower, and ATR-FTIR detected the rise of the peak at 1714 cm^{-1} that this time was not accompanied by any other absorption. It is possible that similar degradation routes were at the base of the different behaviour of the samples after H115, H+RH and UV.

5.5.4 E-Leather® with Flame Retardant (EL3)

EL3 was the most interesting material from a degradation point of view, because it presented unexpected evidences of deterioration compared with the other man-made substrates.

H70 was the ageing condition that affected the EL3 material the least in terms of roughness and colour change (both on the surface and reverse face). Increases of the absorbance values were noticed in the C-O peak of the coating, while the fibrous layer presented variations of the peaks intensities after the first two intervals but not after the last one. These spectral changes were attributed to changes in the collagen molecule that were also probably responsible for the decrease of the pH value.

The H115 exposure procedure changed the roughness to some extent, but the deformation (bending) of the samples complicated the effective measurement of the parameter. This intrinsic bending may already be considered a sign of the material's degradation, and in fact the bending rigidity increased because more energy was required to bend the samples in the opposite direction. The colour difference of the coating was easily detectable after ageing, and the ATR-FTIR spectra showed the presence of the C=O stretch band already described for other samples. Some of the peaks associated with this absorbance in the previous materials were also found here (1103, 1065 and 1013 cm^{-1}), though the C-H domain consisted of two peaks and not three as in SY. This may indicate that the degradation followed a different route compared with other materials and that this degradation route did not involve CH_2 and CH_3 moieties. The fibrous layer showed a highly significant colour variation ($\Delta E = 7.06$) and the FTIR spectra exhibited marked changes in absorbance of a number of peaks, especially those attributed to amide III and C-O bond stretching. The moisture content was at its lowest level, as also the pH value of the aqueous extract. If the contributions of the other substrate's components was negligible, these results may be related with the variations observed in the ATR-FTIR spectra. As a consequence, changes in the collagen may have influenced the pH. The maximum force at break decreased in the machine direction while increased in the perpendicular direction, possibly as a result of the deformation of the samples.

The H150 ageing did not show evidence of a roughness increase using the image capture and processing system, but the 2D scanning effectively detected the change. Both the coating and fibrous layer presented a highly significant difference between the colour coordinates before and after ageing. This suggested that high temperature had a greater effect than the combined effect of heat and humidity on the colour variation of the fibrous layer components, differently from TL. The ATR-FTIR spectrum showed that a third peak appeared in the C-H region, though in a different position from the ones observed in the previous cases, and the C-O band absorption increased. The fibrous layer presented a very different spectral profile when compared to the unaged samples, and the intense vibration at 1390 cm^{-1} decreased markedly while the C-O band increased. Moreover, the amide II band shifted to the lower frequency indicating an increase of the collagen coil mode content. The moisture content decreased and the pH increased slightly, as already seen in TL samples. The former was in agreement with the results reported in literature (Thomson, 2005) while the second was probably the signal of the presence of ammonia and possibly other decomposition compounds. The only measurable effect concerning mechanical properties was the increased work for compression, which indicated a stiffening of the material.

A number of similarities were found between H150 and H+RH ageing, though the second affected the samples to a greater extent. The exposure procedure in the presence of high humidity resulted in a steep increase in the roughness immediately after the first interval and then the values decreased. While the colour difference between aged and unaged samples on the coating side was not significantly different ($\Delta E = 1.82$), on the fibrous layer its value reached 15.32 units. This figure was still lower than EL3 after H150 exposure and indicated that significant changes occurred within the hydroentangled layer. SEM analysis revealed the appearance of newly formed structures between the fibres that exhibited a similar shape to the one of bromine deposits formed in the convection oven during ageing. It was to these structures that the loss in flexibility was attributed to. ATR-FTIR spectra highlighted the reduction of the amide peaks and of the strong vibration at 1390 cm^{-1} while the one at 1016 cm^{-1} increased markedly. Despite these changes, the moisture content decreased to a lesser extent than after H150 and the pH value was the same as before the ageing. In addition, maximum strength and elongation did not change markedly and the only test that was able to identify variations of the mechanical properties was KES-FB3, where a clear pattern was recognisable. These findings suggested that, although significant changes occurred at the microscopic level, some of the physical properties did not vary accordingly. This was probably due to the different contribution of each part of the composite that effectively mitigated the negative impact on the whole material of one of its parts.

UV ageing of the EL3 material did not produce any detectable change in surface roughness, though the effect of UV radiation on the coating colour was greater (ΔE = 4.61) than in the other materials. ATR-FTIR spectra seemed to point out that the coating went through the initial stages of a degradation process. However, it is likely that also the dyes used to colour the coating underwent degradation. The mechanical properties seemed to be mostly unaffected by the ageing treatment, as already seen in the other materials.

5.6 Preliminary Summary

In this chapter aesthetical, chemical and physical properties were analysed in order to assess the impact that different accelerated ageing techniques had on the substrates under investigation. The detection of changes in the properties was used to identify signs of early degradation occurring within the different materials.

The early accelerated ageing simulations highlighted that SY was stable when subjected to moderate heat for 56 hours, while TL was damaged and more prone to shrinkage than the other two leather-based substrates. Crumple-flex studies, demonstrated that EL3 may present an intact top coating while its reverse side may be highly damaged. This should be always considered in case E-Leather® is found in a museum collection, because a good conservation state does not necessarily correspond to the integrity of the reverse side.

Aesthetic properties of TL and EL3 were clearly affected by heat and heat and humidity treatments and, in the case of TL, colour variations of the coating were correlated with those of the fibrous layer. EL2 roughness was less affected by the ageing treatments, though it was possible to identify changes after some of the procedures (H150 and H+RH ageing). The correlation of the colour change between front and reverse side of the samples was moderate, as in EL3. SY exhibited a marked increase in the roughness after H150 ageing, whilst the remaining procedures affected it only to a lesser extent. Lightness values of SY were the most relevant among the colorimetric parameters used to assess colour change, and there was a positive correlation between the two sides of the material.

SEM observations were useful to observe changes in the morphology of TL and EL3 fibrous layers, where the level of the fibres compactness increased and, in EL3, newly formed material started to be visible after the first interval of H+RH ageing. EL2 presented particles on the top of the coating after H150 ageing. Initially they were attributed to pigments but then it was discovered that were made of carbon and oxygen, possibly products of degradation of the polymeric coating. Their characterisation in following works may provide responses on the exact composition and correlation with degradation mechanisms. SY coating appeared smoother during SEM observations and this explained the increased gloss after H150 ageing.

EDX provided information on the presence/absence of flame retardant particularly within the coating, suggesting that the compound volatilised in TL while it only entered in contact with EL3 coating after treatment with heat. ATR-FTIR was more effective in providing insights in the degradation mechanisms occurred after treatment of all the materials. Evidences showed that changes in the absorbance intensities of the coatings occurred mainly after H150 ageing (all coatings), H+RH (EL2 and EL3) and H115 (EL2). The fibrous layers of TL, EL2 and EL3 behaved in a similar way, highlighting the sensitivity of the collagen to severe temperature (H150) and heat and humidity.

The measurement of moisture content emphasised some similarities between TL and E-Leather® substrates, such as the effect induced by prolonged moderate heat (H115). The moisture loss of the three materials after this ageing was the most significant compared with the other ones. In addition, the pH content of TL and EL3 were correlated, leading to the hypothesis that similar chemical degradation pathways may characterise the two materials despite the different type of tanning and additives they were subject to.

The similarities described above, in particular between TL and EL3, did not correspond to similarities of the physical properties. Tensile strength, elongation, bending and compression values of TL highlighted a significant deterioration of the properties after every ageing procedure. Tensile properties of EL2 and EL3 changed slightly but not in the same measure as in the case of TL and the change was even lower in the SY samples. Bending rigidity, however, changed significantly for E-Leather® after ageing, to such an extent that in some cases the stiffening did not permit the test to take place. Similar considerations are valid for compression tests that, particularly after H+RH ageing and H150, indicated that the material reduced its flexibility and compressibility.

During surface analysis via KES-FB4 the impact of the samples roughness became obvious. Observing the results obtained, it was possible to confirm that the suitability of the device is restricted to those cases where the material has a highly periodic pattern, e.g. woven of paper, in order to reduce the impact of the variable pattern on the measurement. Therefore, the validity of the results obtained using this instrument was scarce.

Finally, it was assessed that during measurements of colourfastness to rubbing the amount of colour transferred from the samples to the abrader after the ageing procedures increased mainly for TL, while it increased to a lesser extent in SY and EL3.

In conclusion, it is possible to summarise as follows:

- The analysis of the four substrates allowed to assess that mild heat (H70 ageing) did not affect in a significant way the samples. However, the other procedures resulted in different degradation routes characteristic of each substrate. In particular, high temperature and humidity determined significant changes within the fibrous substrates of TL and EL3. Also EL2 was affected by the H+RH ageing, but to a much lesser extent than the previous substrates;
- Moderate and severe heat (H115 and H150 ageing) also affected TL, EL2 and EL3 on a smaller scale. The changes occurred primarily on the fibrous layers and in a few cases, e.g. TL after H+RH, the coatings also deteriorated in conjunction with the reverse side;
- SY, on the contrary, was mainly degraded by the action of severe heat (H150), after which the coating exhibited the worst degradation. The presence of aramid fibres guaranteed stability to the synthetic leather fibrous layer.

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Chapter 6 Degradation Markers and Conservation Approaches

6.1 Introduction

Conservation practices, active and passive, are conducted on a daily basis in the conservation departments of many museums. When an institution does not own such a department, active conservation is delegated to external organisations that carry out the operations on their behalf. However, preventive conservation guidelines need to be put in practice by museums. This is normally done by following the guidelines provided by institutions that promote conservation, such as International Council of Museums-Committee for Conservation (ICOM-CC) Canadian Conservation Institute (CCI), and International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM).

The need for the identification of the early signs of degradation is a relatively new branch of the conservation. The understanding that plastics degrade at a faster rate than natural materials and that once degradation has started it is not possible to reverse the reaction (Shashoua, 2006) has highlighted the importance of studies that detect degradation in its early stages. The need for degradation markers has been addressed for wool and silk (Vanden Berghe, 2012) and some types of plastics (Lattuati-Derieux *et al.*, 2013). The research on PU has mainly focused on foams. Pellizzi *et al.* (2014) investigated the possibility of finding degradation markers using non-invasive methods that also provided information on parameters that otherwise would have required the use of invasive techniques. In the case of collagen based substrates, previous studies were focused on parchment and uncoated leather samples (Larsen *et al.*, 1994; Chaplin *et al.*, 2010; Abdel-Maksoud, 2011). The research in the innovative leather area did not focus on the evidence for degradation markers. It rather listed changes to different sample properties by testing them using invasive techniques (Palop *et al.*, 2008; Bacardit *et al.*, 2010).

In this chapter a list of degradation markers identified during the accelerated ageing studies will be presented. The correlation between 2D scanning and KES-F analysis was investigated and the results reported with a view to establishing damage markers.

The currently suggested conditions for storage and exhibition will be considered and a proposal storage and exhibition guidelines for leather-related materials will be made.

6.2 Assessment of the Effectiveness of Degradation Markers

As already emphasised, the processes leading to polymer degradation cannot be reversed (Shashoua, 2006) and this is also valid for some of the changes occurring in leather (Işik and Karavana, 2012). As a result, degradation can only slow down or increase and this makes the detection of early deterioration signs of primary importance.

Following the accelerated ageing treatments and material's characterisation it was possible to identify a number of degradation markers. These markers would ideally allow the effective detection at an early stage of the presence of an ongoing degradation phenomenon of materials that will be part of a museum collection. Moreover, the correlation between properties detected via non-invasive and invasive analysis (destructive and non-destructive) may ideally permit the assessment of certain mechanical properties without the need for sampling.

A list of degradation markers was collated after considering the effects that each accelerated ageing had on the properties measures in this work. This list is reported in Table 6-1 and provides a summary of the parameters that should be measured in order to assess whether the properties worsened after exposure. This implies that tests should be carried out on items that become part of a collection, e.g. after acquisition, and they should be repeated after a certain amount of time. In most of the cases the variation (indicated with Δ) between the parameters will constitute the actual degradation marker. In other cases, such as for ATR-FTIR, the change will be identified by the shift of the peaks or the appearance of a new vibrations.

It must be always remembered that the variation of a property, however, will not be necessarily related with other properties. In particular, changes occurring at the microscopic level may not have obvious correlation with the ones occurring at the macroscopic level. This explains why there is the need for studies that focus on multi-property profiling.

Technique	Measured Properties	Effect	Degradation Marker
Appearance	-	Macroscopic change of appearance	Δ Gloss
Image Capture and Processing	Roughness	Variation of grey value SD	Δ SD
2D scanning	Roughness	Variation of grey value SD	Δ SD
Spectrophotometry	Colour coordinates	Variation of L*a*b*	Δ E*
SEM	Coating roughness and thickness and bulk coating homogeneity	Change of coating roughness and thickness, presence of voids and exposed particles within the coating cross-sections	Δ Coating waviness and thickness
SEM	Fibres compactness, deposits	Difference in the distance between the fibres bundles, deposits form between fibres	Δ Leather bundles compactness, appearance of unidentified material
EDX	Elemental composition	Change of the flame retardant distribution	Bromine presence/absence
ATR-FTIR	Molecular composition of coating	Variation of methylene moieties absorption, appearance of carbonyl group peak	Δ C-H peaks comprised between 2850 and 3000 cm^{-1}, new C=O peak at 1714 cm^{-1}
ATR-FTIR	Molecular composition of fibrous layer	Shift from helical to random coil, change of amide (I, II, III) peaks intensities (collagen-related)	Peak at 1540 cm^{-1}, and Δ peaks 1340 cm^{-1} (amide III), 1540 cm^{-1} (amide II) and 1650 (amide I)
KES-FB2	Bending rigidity and recovery	Variation of flexibility	Δ B and Δ 2HB
KES-FB3	Work for compression and compressibility	Variation of compressional properties	Δ WC and Δ Compressibility (%)
Fastness to crocking	Colour transferred after rubbing	Change of colourfastness	Δ Colour transferred in units

Table 6-1: Degradation markers associated with the effect of the ageing procedures

6.3 Correlation of Degradation Data

Many authors conducted studies on the change of chemical and physical properties after natural or accelerated ageing (Hansen *et al.*, 1991; Lovett and Eastop, 2014; Li *et al.*, 2016). Those studies relied on the evaluation of the variation of the properties with time, and estimated the correlation by visually comparing the trends (Pellizzi *et al.*, 2014) while in some cases they also used statistical analysis (Larsen, 2008). However, the correlation between changes of properties measured with non-invasive and invasive techniques is less common. As a result, some authors call for this type of data because of the restrictions found in sampling specific type of collections, e.g. for library items (Bicchieri *et al.*, 2011).

A revision of the ageing results and the evaluation of possible relationships between the properties was performed. The correlation (*r*) between some of the parameters that were measured during the ageing procedures was evaluated and tested for significance level. The selection of the parameters was based on the number of measurements available (e.g. ageing intervals) and on the type of information that was possible to extrapolate if the correlation was proved successful. The aim was to evaluate the existence of a linear relationship between the parameters and to confirm whether the correlation between the results was arbitrary or not.

A set of requirements was identified in order to select the degradation markers suitable for the purpose of this research, according to the list reported in Table 6-1:

- it must provide a quantitative value;
- it must represent the result of measurements conducted at variable ageing times;
- the non-invasive marker should refer to changes in properties that can be measured if only one side of the item is accessible, e.g. colour change via spectrophotometry can be easily measured on the top coating of a car seat in a historical car, but it could not be assessed on the fibrous layer because that would require sampling or disassembling the car seat.

In this study the standard deviation (SD) of grey values was used as a non-invasive measure of the surface roughness. This parameter was thought to be associated with roughness changes occurring both on the coating and fibrous layer, as seen in Chapter 5. It was observed that, on several occasions, changes affecting roughness also affected mechanical properties, in particular the bending rigidity (B) and work for compression (WC). These properties were measured via KES-FB2 and KES-FB3 devices that were classified as invasive and non-destructive. In their turn, B and WC may provide an insight on other characteristics of the samples that would require destructive investigations. For this reason the correlation between SD values and B, and SD values and WC were considered of primary interest.

A number of correlation analyses were carried out using different datasets (different "sample" size). The first trial separately considered the results obtained from each ageing procedure and each material. The second trial jointly considered every ageing procedure and every material. The third trial considered the results of every ageing conducted on the same substrate, but the substrates were considered separately.

The Spearman's rank correlation analysis was initially considered to analyse the correlations between the parameters and the p-values associated with the correlation. This test is used in those cases where the values are considerably skewed. However, it was not possible to calculate the statistical significance of the results because the test required a greater number of data, e.g. a higher amount of ageing intervals. In fact, Spearman's correlation requires at least 4 degrees of freedom, while in this work the degrees of freedom associated with the measurement were 3 (Spearman's df = number of measurement - 2). As a result, the evaluation of the correlation between SD and B values and between SD and WC was not possible using this test.

The Pearson's test was then used to calculate the correlation and significance of the correlation (p-value). The results were reported in Table 6-2; only one case shows a statistically significant correlation (p-value < 0.05). These results indicated that using this dataset no significant linear correlation was found neither between the superficial roughness measurement via 2D scanning and the bending rigidity nor between roughness and work for compression. Consequently, although in some cases the roughness values changed because of phenomena taking place within the substrate, it was not possible to assess that those phenomena simultaneously and in equal measure affected the mechanical properties.

When focusing on the *r* results, the SD values of all the H70 and H115 aged samples appeared to correlate well with both B and WC, particularly for TL, SY and EL2 samples. However, for TL-H115 (r = -0.9), SY-H115 (r = -0.72) and EL2-H115 (r = -0.95) the correlation had a negative sign, indicating that the higher the roughness the lower the bending rigidity. This indicated an opposite trend compared to the one observed. For example, when EL2 was subjected to H115 and tested, the roughness increased and samples were so rigid in the warp direction that after the first interval it was not possible to calculate the B value in both directions. Though, the same samples here were the only ones to exhibit statistical significance of the correlation. On the one side, some limitations of the Pearson's test were at the base of the low significance, because the analysis is sensitive to skewed distributions and to outliers. The graph below (Figure 6-1) shows an example of correlation between SD and B values in TL samples. It is evident that the results were not homogeneously distributed and this reduced the level of significance of the analysis. On the other side, significance may increase when a greater number of measurements are collected, even if this does not imply that the level of correlation will also increase.

	r (B)	**p-value (B)**	**r (WC)**	**p-value (WC)**
TL-H70 Roughness	0.6	0.39	-0.92	0.07
TL-H115 Roughness	-0.9	0.09	-0.67	0.32
TL-UV Roughness	-	-	0.03	0.9
SY-H70 Roughness	0.82	0.17	0.22	0.77
SY-H115 Roughness	-0.72	0.20	0.61	0.38
SY-H+RH Roughness	-0.46	0.53	0.55	0.44
SY-UV Roughness	-	-	-0.5	0.49
EL2-H70 Roughness	0.93	0.06	-0.21	0.78
EL2-H115 Roughness	-0.95	0.04	0.63	0.08
EL2-H+RH Roughness	0.28	0.71	-0.61	0.38
EL2-UV Roughness	-	-	-0.57	0.42
EL3-H70 Roughness	-0.05	0.94	-0.48	0.51
EL3-H115 Roughness	0.56	0.43	0.74	0.25
EL3-H+RH Roughness	-	-	0.22	0.77
EL3-UV Roughness	-	-	0.11	0.88

Table 6-2: Pearson's correlation values (r) and p-values for the properties SD and B, and SD and WC of all the samples considered separately

Certainly, it would be interesting to conduct the same analysis increasing the number of intervals in order to evaluate whether the correlation would become statistically significant.

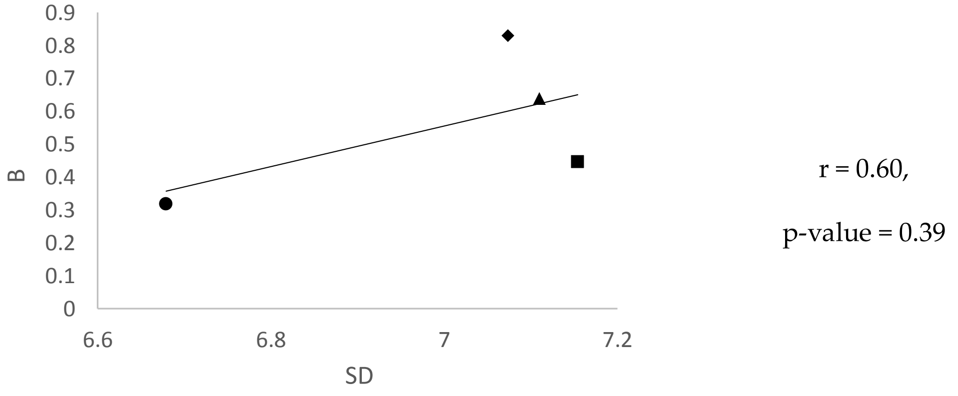

Figure 6-1: Correlation between roughness (SD) and bending rigidity (B) of TL samples after H70 ageing at different ageing times. Circular markers: 0 hours; rhombus markers: 56 hours; triangular markers: 112 hours; square markers: 168 hours. On the right, the correlation value and p-value associated with the measurement are reported

The second trial for the correlation analysis was conducted by jointly evaluating all SD values for the roughness and the bending rigidities without distinguishing on the basis of the substrate. The aim was to increase the size of the statistical sample and, as a consequence, improve the significance of the correlation. However, the significance of the results did not improve (p-value > 0.05) and, in addition, the correlation between SD and B decreased (r = 0.11). Similar results and graphic output were also obtained when the correlation between SD and WC was analysed.

The third trial was conducted by separately considering each material but grouping together all results of the ageing procedures. In the previous chapters it was noticed that each of the substrates was characterised by its own properties. Therefore, considering all the substrates at once may have a great impact on the error associated with the measurement. The results of this analysis are reported in Table 6-3.

	r (B)	p-value (B)	r (WC)	p-value (WC)
TL- Roughness	-0.80	0.01	0.75	0.04
SY- Roughness	0.47	0.11	-0.24	0.35
EL2- Roughness	0.23	0.44	0.06	0.82
EL3- Roughness	0.87	0.04	0.15	0.57

Table 6-3: Pearson's correlation values (r) and p-values for the properties SD and B, and SD and WC for each group of materials

The results obtained for SY and EL2 samples were not significant and they also exhibited poor correlation. However, this analysis highlighted that a linear correlation between the roughness and both the bending rigidity and work of compression existed for TL samples. It is interesting to notice that a strong negative relationship (p-value = 0.01) was identified between SD and B, indicating that higher rigidities corresponded to lower roughness values. Indeed, when the TL samples were analysed via 2D scanning it was observed that the roughness decreased both during the H115 and H150 ageing. This effect was attributed to the shrinkage of the collagen fibres and led to the samples stiffening. The samples subjected to the H115 procedure showed increased bending rigidity and the ones subjected to H150 were so stiff that a bending test was not feasible. The results also showed that higher roughness values were correlated with higher work for compression and this was in partial disagreement with the results reported in chapter 5. The H115 aged samples presented an initial increase of the work for compression followed by a decrease. Further investigations are required in order to better understand these results.

Another interesting finding concerned the EL3 samples, that were the most damaged and the ones that presented the highest roughness variation after TL. A very strong positive relationship (r = 0.87, p-value = 0.04) was found between the roughness values and the bending rigidity. This confirmed that the greater the roughness the stiffer the sample, which was in agreement with the results obtained after accelerated ageing. In particular, the H150 and H+RH procedures determined a marked increase of the roughness that in both cases did not permit to conduct the bending analysis with the KES-FB2 device.

It was therefore assumed that the roughness values detected via non-invasive 2D scanning can be potentially used to identify variations in the bending rigidity of TL and EL3. Nonetheless, it was noticed that when the roughness increased and the flexibility decreased other degradation phenomena were likely to be involved. Though, further analysis of the correlation with invasive techniques should the carried out to achieve a better understanding of other related phenomena.

One of the outcome of these findings is that if in the near future E-Leather® SL3 UL will become part of a museum collection it will be possible to gather preliminary data on its conservation state by observing its roughness. If the material will be tested as soon as it enters the collection, the progress of its degradation could be monitored. A way to implement the use of degradation markers is to include them in condition reports, which are useful tools that describe the conservation state of an object in a collection. The BS EN 16095:2012 standard describes their use and the way in which they should be filled in and used as a record (British Standards Institution, 2012). In particular, the use of non-invasive methods has been described as favourable within the section 'recommended practices'. One outcome of this thesis could be the proposal, after the necessary adjustment to the method, of including the roughness evaluation within the above standard as a recommended content.

6.4 Preservation Routes

The importance of preserving and conserving the material facet of items and artworks and the implications for other spheres of items, such as the social and cultural one, has been debated for a long time (Marontate, 2013) and it was briefly introduced in Chapter 2. Also for this reason, this thesis mainly focused on the materiality as the starting point to highlight the need for new preservation practices. Although preventive conservation measures are available for leather from national and international conservation institutes, they are normally based on the observation of the degradation pathways of previously collected objects. As a result, preventive conservation guidelines are suitable for a larger number of items but they are not specific enough to cover materials with certain attributes, such as innovative hybrid products.

In the past this, approach was effective because the type and variety of items collected was limited, though in the last century the multitude of polymaterial and composite objects like synthetic leathers has introduced manifold challenges. These new materials are characterised by different degradation pathways, as was emphasised in the previous chapters. Consequently, new approaches are needed to understand when these materials and objects are actually starting to degrade to such an extent that their integrity is compromised.

The following paragraphs describe the currently ‘accepted’ preventive conservation practices applied to leather and textiles in the light of the degradation routes observed in Chapter 5.

6.4.1 Preventive Conservation

The different patterns of degradation occurring in leather and related materials have been presented in the previous chapter. Because of the different composition and degradation of leather and related materials, the need for more dedicated guidelines became evident. In this paragraph the general guidelines defined by some of the main conservation institutes and standardisation bodies will be reported. Indication of the most harmful parameters for innovative leather-related materials, derived from the studies conducted in this thesis, will be given and their relationship with the guidelines described.

6.4.1.1 Established Preventive Conservation Guidelines

Organic materials are more prone to degradation than inorganic ones, therefore all the substrates studied during this thesis are likely to be subject to accelerated degradation phenomena if not carefully controlled. Preventive conservation guidelines for tanned-leather highlight the need for proper storage conditions and the presence of support able to minimise physical deformations (Canadian Conservation Institute, 1992). Similar considerations are also valid for textiles and plastics or polymeric materials (Canadian Conservation Institute, 2015a; Canadian Conservation Institute, 2015b). Guidelines concerning composite materials were not found, though, and institutions dealing with this type of substrates should refer to one of the guidelines that describe preventive practices for one of the composite components. Nevertheless, a number of issues would be associated with this approach.

The Canadian Conservation Institute (CCI) reports that organic materials should be normally stored in the dark. It suggests to store leather objects in an environment with temperatures ranging between 18 °C and 20 °C and relative humidity between 45 % and 55 % (Canadian Conservation Institute, 1992). The CCI also reports that attention should be paid to RH variations which, where possible, must be avoided and to temperature and illumination. The temperature may rise easily when leather objects are placed in confined environments (Canadian Conservation Institute, 1992) and this may result in accelerated degradation processes. Illumination may interact with the leather dyes leading to fading, hence it is best to restrict the lighting conditions to 150 lux (undyed leather) or 50 lux (dyed leather) while avoiding the presence of UV radiation (Canadian Conservation Institute, 1992). The British Standards Institution (2010) defined the best storage conditions in a slightly different way. Instead of providing a range of temperatures and humidity for organic materials, the standard emphasises the need for a thorough evaluation of the previous storage conditions (British Standards Institution, 2010). In addition, it stresses on the importance of understanding whether temperature and/or humidity are priorities for the conservation and on the need for maintaining those conditions that the item became acclimatised to (British Standards Institution, 2010).

Regarding textiles, the CCI suggests temperatures of about 20 °C and reports that low temperature (5 °C) can also be used as an effective tool of preservation because it does not endanger natural fibres (Canadian Conservation Institute, 2015b). On the contrary, raising the temperature above the recommended 20 °C reduces textiles lifetime, in agreement with the Arrhenius equation. The relative humidity is of higher concern because levels below 40 % render fabrics more brittle and susceptible to breakage, while above 70 % the growth of microorganisms is facilitated (Canadian Conservation Institute, 2015b). UV radiation should be totally excluded while for illumination 50 lux is the maximum suggested value for minimising the degradation. For long-term storage, however, textiles should be stored in the dark and care must be taken to avoid extreme humidity conditions.

When looking at the directives for plastic objects it is interesting to notice that the CCI provides guidelines are not as specific as for the previous materials. The negative impact of oxygen is reported, 65 % is suggested as the maximum limit for humidity, and illumination should not exceed 150 lux. No temperature limit is specified (Canadian Conservation Institute, 2015a) and this is likely to be related to the different sensitivity of plastics to temperatures (Shashoua, 2008). A reason for the lack of information regarding plastics is that the category comprises a large number of materials and products that are relatively new. Waentig (2008) has conducted research in this area and revised the publications on the history, characterisation, ageing, conservation and storage of the main plastic families in their different forms, from fibres to rigid and soft foams. She confirms that UV radiation must be excluded and oxygen should be avoided. In addition, Waentig suggests that the relative humidity should be controlled between 50 % and 55 %, the temperature should be maintained below 20 °C and illumination should not exceed 50 lux (Waentig, 2008).

Although the guidelines do not seem to noticeably differ, there are some key differences in the parameters that must be considered. One example for damage caused by the wrong preventive conservation procedure due to inexact identification can be the one of an object that is thought to be made of synthetic leather but is actually made of leather. The polymeric coating that can be present on both substrates, for example, can lead to the wrong identification and a certain type of degradation would be expected. As a consequence, the preventive plan could be based on the CCI guidelines for leather and plastic. Because the levels of relative humidity allowed in this case (maximum of 55-65 % RH depending on the standard) would be higher than those suggested for leather (maximum 55 % RH) this may increase the rate of degradation. Similar considerations are valid in the case of leather composites. Additionally, the presence of additives that can volatilise should not be underestimated, because even if the substrate was effectively identified these detrimental additives may lead to premature degradation or may endanger other objects exhibited in proximity.

6.4.1.2 Recently Introduced Guidelines

Over the past few years, greater attention has been paid to the effect that certain factors and parameters may have on collections made of mixed materials. This is due to the increasing variety of items that are hosted in museum storage facilities, e.g. archives and libraries, and that would normally require different temperature and humidity conditions. The aim of using the same parameters for different collection items is to apply less restrictive environmental conditions for storing objects composed of manifold materials without endangering them. As a result, new guidelines for the conservation of items have been recently established: BS EN 16893:2018 and BS 4971:2017 have been approved in February 2018 and June 2017, respectively. The former provides specifications for existing and new buildings where heritage collections are stored and exhibited, whilst the latter focuses specifically on management of archive and library collections.

In 2011, Thickett *et al.* described the approach used by English Heritage to identify groups of objects defined as 'unstable', referring to those items that need strict control over envirnmental parameters in order to be preserved (Thickett *et al.*, 2011). The publication highlighted the non-invasive techniques used by the organisation to identify these unstable groups of objects. It also emphasised the importance of choosing cost-effective preservations methods and environmental conditions suitable for a variety of items/materials. Three years later, Xavier-Rowe *et al.* (2014) reported on the evolution of the work conducted by English Heritage and they described how the collaboration between curators, conservation scientists and engineers helped to create a cost-efficient storage space for archaeological and architectural collections. Further work has been conducted following this path.

The current BS 4971:2017 standard can be referenced when leather and related materials are considered. It refers to both 'traditional' and 'non-traditional' materials encompassing different leather and plastic types used in archives, and therefore includes recommendations that can be valid for innovative and composite leathers. The standard takes into account that archive collections may be made of mixed media. It specifies that decisions on environmental parameters for archives and library collections should consider both the type of materials stored and the long-term effect of storing those materials under specific conditions (British Standards Institution, 2017 p. 7). Moreover, it specifies that conditions should be chosen in such a way that the conservation of temperature sensitive items is prioritised (British Standards Institution, 2017 p. 26). Cool temperatures are preferred to warm temperatures since the latter increase the rate of decay, and the range of accepted temperatures should not exceed the temperatures of 23 °C and 13 °C for sensitive materials. In terms of RH, the limits are set at 60 % and 35 %.

The BS EN 16893:2018 is another standard whose consideration is suitable in this context because it lists the requirements for buildings where collections are stored and exhibited. Clause 4.3.3 specifies that information regarding the upper and lower limits of temperature, RH and their average, along with the limits for light exposure and UV should be specified in order to minimise items' deterioration. This clause further highlights the need for a clear understanding of the conditions that can be highly detrimental for materials in collections (British Standards Institution, 2018 p. 12). Annex B and Annex C report tables describing the 'relative risk of damage and deterioration due to temperature' and 'relative risk of damage and deterioration due to relative humidity' (British Standards Institution, 2018 p. 34, 37). The tables emphasise the high sensitivity of leather and plastics, in particular to hydrolysis. Temperatures considered safe for long term storage can range from -10 °C to 2 °C for materials sensitive to temperature, as some types of plastics; from below 0 °C to 12 °C for materials with moderate sensitivity; from below 0 °C to 20 °C for the remaining materials. RH above 40 %, 45 % and 55 % can be detrimental for highly, moderately and low sensitive materials respectively. In order to maintain the desired conditions in a storage facility, BS EN 16893:2018 describes the steps that should be made before building the facility or before renovating an existing one.

It should be noted that the British Standard guidelines display greater flexibility in terms of temperature and relative humidity recommended for specific objects, compared with those mentioned earlier. Moreover, greater attention has been paid to the ability of the storage facility to allow fluctuations, with 1 °C of difference in 24 hours considered the optimum. This indicates a shift in the way environmental parameters for collection storage are described and it was useful to elaborate the following section.

6.4.1.3 Remarks for the Preventive Conservation of Innovative Leather-Related Materials

As noted above, Clause 4.3.3 of BS EN 16893:2018 highlights the need for a clear understanding of the conditions that can be highly detrimental for materials in collections (British Standards Institution, 2018 p. 12). Hence, the use of the data obtained during this thesis can be used for obtaining this type of information. The results of tests conducted after accelerated ageing procedures showed that some conditions greatly affected all the materials, therefore they should be avoided. In the majority of the cases, however, the procedures had a different impact on the four substrates. In order to establish a common preventive conservation plan valid for all materials, it would thus be necessary to restrict the conditions of preservation also for the least sensitive substrate, that is SY.

The four materials showed that H70 ageing did not produce significant changes of the properties, indicating that this temperature did not affect the products in a substantial manner during the time frame used for the test. UV ageing determined a greater variation of the properties, in particular in TL and EL3, induced modifications of the coating colour and molecular structure.

The effect of high heat and relative humidity, and particularly their fluctuations, caused a significant shrinkage in chrome-free samples. The results of H+RH ageing demonstrated that humidity variations have a significant impact on the chemical and mechanical stability of the samples containing leather fibres (TL, EL2 and EL3). Here changes in colour, roughness, pH, moisture content and compressibility highlighted the worsening of the substrates' properties (see relevant sections in Chapter 5). Avoiding drastic changes of environmental parameters becomes therefore of primary importance during any operation, from storage to transport of collections. These fluctuations were identified as the most damaging factor for both the TL and EL3 materials, though the type of damage differed.

In addition, the presence of flame retardants was demonstrated to have detrimental effects on the substrate as a whole, particularly in the case of EL3 and during H+RH ageing. The formation of new material between the HE face of EL3 was demonstrated via observations with SEM and they were attributed to processes of recrystallisation after the decomposition of brominated flame retardant. Two considerations must be made: one regards the use of exhibition/storage cases and the other the dust formation. Care must be taken if EL3 has to be stored in a confined environment, e.g. within a display case. Previous work conducted by Thickett *et al.* (2005) has emphasised the importance of air circulation in display cases to minimise the degradation due, among other things, to the deposition of exudates. This would become important for EL3 preservation because the instability of flame retardant could result in exudates that in the long-term might damage collected items placed in cases. In addition, the release of the flame retardant, followed by the formation of a dust (Rauert, 2014), would become potentially detrimental for other objects if EL3 was exhibited in proximity to other items.

The damage on EL2 samples was much less evident than in the other leather-based materials after every ageing procedure, therefore the preventive conservation conditions may be considered generally less restrictive than those for TL and EL3. The absence of flame retardant was considered as one of the reasons that provided greater stability to the substrate, which mainly suffered the effects of high dry heat (H150). H+RH ageing also affected the material by changing the colour and both chemical and mechanical properties, but to a minimum extent.

Finally, SY was affected to an even lesser extent by the accelerated ageing procedures, and the optimum conditions for preservation may be similar to those described for textiles. The only accelerated ageing that affected the material was H150, which induced clear changes in the aesthetical properties of the coating and modifications of its molecular structure.

On the basis of all the previous considerations, the following remarks should be remembered when storing or exhibiting leather-related materials:

- Exposure to UV radiation should be avoided in order to preserve the original coloration and molecular structure of collected items. Even short term exposure to UV radiation can in fact produce a considerable damage;
- High values of RH, e.g. between 60 % and 95 %, must be excluded because they facilitate hydrolysis. High values over a short period may result in drastic fluctuations in the following period, when environmental parameters return towards lower values. In addition, when flame retardants are present, they can promote the formation of new, unwanted solid compounds as in the case of EL3;
- Along with the RH value difference (size of RH fluctuation), also the rate of RH change is of primary importance. Intervals chosen for this research were composed of 56 hours where samples were subjected to constant temperature and relative humidity. After that time, samples were subjected to a rapid change of conditions that, in some cases, was enough to determine a deterioration of the properties. As a result, it is anticipated leather and composite leather objects have to be moved to spaces with temperature and relative humidity parameters different from those the object is acclimatised to, should be slowly conditioned to the new conditions over a suitable time frame;

- Dry heat can be highly detrimental because it increases the reaction rate within the material, therefore the temperature surrounding the item should be controlled also during transport. This aspect should be also considered when collections are located outdoor, e.g. in the case of museums collecting vehicles that are exposed outdoor.

These remarks, together with the guidelines for archives and library collections, may be useful in the case items containing leather-related materials not fully characterised are acquired by an institution and there is no detailed documentation on their composition. Subjecting these items to the described conditions is unlikely to endanger them and would allow to gain time for conducting the necessary investigations. However, if an item is already part of a museum collection where it became acclimatised to different conditions, attention should be paid when the item needs to be moved. During the transition from a condition to the other the item must be monitored for signs of change because this is essential to avoid excessive stresses, as also highlighted by previous standards (British Standards Institution, 2010).

Further studies are required in order to define with certainty the best preservation plan for E-Leather® substrates. In order to do so, a study should focus on how each factor impacts on the material when subjected to different conditions of increasing heat, relative humidity and irradiation (Luxford, 2009). Therefore future studies aimed at assessing the best preventive conservation plans should follow this design. However, the above guidelines should take into account all the components of the material, the approved standard guidelines and the degradation pathways observed in this thesis.

6.5 Preliminary Summary

- A list of invasive and non-invasive degradation markers for the substrates under investigation was identified. Some of these markers were substrate-specific. In TL samples major markers of deterioration were roughness (SD values), colour coordinates (ΔE*), coating waviness and thickness, compactness of leather bundles and absence of bromine within the coating, Changes of gloss and reduction of the coating waviness were found to be detrimental for aesthetic properties of SY, but only after H150. EL2 presented degradation markers associated with the collagen amide (I, II and III) deterioration and with the colour variation of both coating and fibrous layer. EL3 markers were often related to the presence of flame retardant, which had a clear effect on roughness and colour coordinates. The presence of flame retardant within the coating, as also the observation of newly formed material within the fibrous layer, were considered degradation markers. In addition, changes in the vibrations of N-H and O-H bonds and amide region of the reverse face were identified as markers.

- Some markers were common to more than one substrate. The most useful evidences came from roughness values, bending rigidity and work for compression. Other interesting markers were the C-H peaks accompanied by the appearance of a new absorption in their region, and the formation of a new peak attributed to C=O stretching (both SY and EL2 coatings).
- The three most common degradation markers, one representing non-invasive analysis and the other two representing invasive ones, were chosen in order to investigate their possible correlation. It was found that 2D scanning results were correlated with bending rigidity results for TL (strong negative correlation) and EL3 (strong positive correlation) samples.
- Important remarks for reducing the risk of degradation during storage and exhibition, and valid for all the studied substrates were drawn up. These remarks would be particularly useful in the future in cases where the identification of the material is not certain. However, because different factors affected the substrate's degradation in variable ways, more focused studies will be necessary to describe substrate-specific guidelines.

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Chapter 7 Conclusions and Future Work

7.1 Main findings

In this work, one of the main objectives was to investigate which currently available technologies museum staff could effectively use to discriminate between natural, artificial leather and composite leather/textile substrates. The focus was placed on non-invasive techniques and their comparison with invasive techniques, which showed that:

- Inexpensive, non-invasive methods such as visual investigation and stereo-microscopy, conducted on the surface and reverse of the materials, allowed to differentiate between TL, SY and E-Leather® substrates. However, it was not possible to distinguish between E-Leather® without flame retardant (EL2) and with flame retardant (EL3);
- ATR-FTIR, also a non-invasive technique, could be used to successfully differentiate the natural and man-made materials. In particular, the analysis of the fibrous layer allowed distinguishing and characterising all four substrates. The EL3 samples were recognised because of the presence of peaks attributed to the flame retardant-collagen interaction;
- The investigation of the material's cross-sections via the invasive SEM coupled with EDX spectroscopy also provided a definitive way to differentiate TL, SY and E-Leather®. Nevertheless, the discrimination between EL2 and EL3 was only possible by analysing the fibrous layer based on the emissions of bromine in the flame retardant;
- The applicability of the KES-F graphic output to differentiate the studied substrates was assessed and it was found that the KES-FB2 and KES-FB3 could be successfully used for this purpose. The diverse internal structure of the materials and the different interaction of their parts produced distinguishable graphic outputs. This was particularly evident during the bending test (KES-FB2), though also the compression tester provided encouraging results. Indeed, these findings demonstrated that more studies are needed to understand the full potential of these devices in a museum context.

Another objective of the research was to study the effect of some of the most damaging degradation factors on the studied substrates in order to gather information on how the materials may deteriorate in the future. Here, the focus was placed on detecting the early signs of degradation, by means of invasive and non-invasive techniques, to help conservators with the assessment of the collection's conservation state. Interesting findings in this area of the study were:

- Severe heat and high heat and humidity ageing were the most damaging procedures for the leather-based substrates (TL, EL2 and EL3), confirming the sensitivity of collagen fibres to high temperatures and to the combination of high temperature and humidity. TL's dimensional stability was considerably affected (considerable shrinking was observed), whilst EL3 maintained its dimensional stability but other properties changed. EL2 demonstrated to be less affected than the other leather-based substrates. The other procedures, apart for mild heat ageing, also induced variations of some of the properties that became obvious after chemical and mechanical analysis. SY was visibly damaged only by severe heat ageing, with a greater effect on the coating that resulted in a change of the substrate's appearance. High heat and humidity treatment affected the bulk coating and, to some extent, the top coating, though the material seems mostly unvaried. The higher stability of this material was attributed to the presence of aramid fibres as supporting fabric;
- Although severe heat ageing and high heat and humidity treatment were the most damaging procedures for all substrates, the actual effect on the properties of the materials was different. This suggested that the different materials responded in variable ways to the accelerated ageing procedures. As a results, it is expected that the natural degradation pathways of these materials will differ and, therefore, the identification of the substrate will become of primary importance in museum context.
- The analyses conducted on the substrates at different ageing times allowed to understand what properties could be considered as markers for their degradation. The variation of the standard deviation of the lightness (SD in chapter 5), measured via photography or 2D scanning, was considered as a promising non-invasive degradation marker common to all the substrates. Similarly, changes in the colour coordinates, described by the ΔE* value, could be used as non-invasive markers of modifications occurring within the coating or dye chemical structure. In addition, variations of the colour coordinates can identify changes, which occurred in the fibrous layer. The appearance of new absorptions in the ATR-FTIR spectra, e.g. at 1714 cm^{-1} in the spectra of aged PU coatings, and the shift of peaks attributed to specific bonds, e.g. the shift of the absorption of amide II from 1540 cm^{-1} to 1530 cm^{-1} in the leather-based substrates, can be used as non-invasive markers. The increase in the gloss of the SY samples may be considered as a substrate-specific marker. In some occasions the variations in the ATR-FTIR

absorptions were interpreted as signals of changes that affected also other properties. For example, the shift of the amide II bond of collagen may be related to the deterioration of leather fibres that led to changes of moisture content and pH (detected via invasive methods). The mechanical behaviour of the substrates changed as a result of the ageing procedures, and the most interesting results were obtained through non-destructive bending and compression testing (KES-FB2 and KES-FB3);

- It was confirmed that, although non-invasive techniques allowed an evaluation of the global conservation state, detailed data to characterise the damage were only obtained via invasive techniques. One example was the discovery of a newly formed matrix that surrounded the hydroentangled fibres in EL3. This matrix, attributed to the flame retardant evaporation and recrystallization, was not visible by the naked eye and only SEM was able to assess its presence.
- The correlation between the non-invasive degradation marker SD and the invasive, non-destructive bending rigidity was analysed. It was observed that in TL samples these parameters had a strong negative correlation (r = -0.80), while in EL3 there was a strong positive correlation (r = 0.87). Ideally, this correlation could be used to determine the presence of a damage that, along with altering the appearance of the material, may also affect some of its mechanical properties.

The ultimate goal of this thesis was to evaluate if, in agreement with the observed degradation routes of the substrates, the description of a common preservation plan for the four substrates was possible.

- The current guidelines for storing and exhibiting leather, textile and plastic objects in museum collections were examined and observed with the accelerated ageing results. Remarks that could be used in the event of uncertain identification of the substrate were provided. The importance of excluding UV radiation, high temperature (e.g. during storage or transport) and humidity fluctuations were recognised to be of primary importance. These considerations would become essential if leather or E-Leather® containing flame retardants were considered.

7.2 Future work

Both immediate and perspective research directions were identified in the final part of the project and are reported below. At the end of Chapter 2, the question was raised of how to address the issue of studying innovative materials that may enter collections in order to prevent their premature degradation. A novel approach, called ProCoCo (Proactive Collaborative Conservation), was proposed as a way to tackle the problem of the reduction in public funding assigned to museums and other institutions while increasing the awareness on the degradation routes of innovative materials.

7.2.1 Immediate Research Directions

Several research directions were identified while working on this thesis and were highlighted in the text. In this section the most relevant research routes, strictly related with the main findings and their possible application within and outside of museums, are reported.

- This research emphasised that discrimination between leather and man-made substrates by means of non-invasive techniques can be challenging. In this case inexpensive methods that may potentially be used by museums of any size were applied. However, only a limited number of non-invasive techniques were tested and it is likely that broader studies comprising different devices could provide remarkable results. The use of imaging techniques, e.g. thermal imaging, 3D scanning and reflectance transformation imaging (RTI), could be effective in identifying different support's characteristics and the effect of ageing on the substrate. The availability of these devices will increase and their price will probably decrease in the next decades, therefore studies that focus on their usability are advisable.
- Photography and 2D scanning provided encouraging results, though the accuracy of photography was not as high as the one of scanning. In addition, the use of SD values only provided information regarding one parameter of the roughness (peak's height), limiting the effectiveness of the measurement. More investigations should be carried out to identify methods able to provide quick responses comprising other parameters of the signal, e.g. its period;
- The invasive tests carried out for this thesis were mainly conducted on new samples and on samples after the complete set of ageing, at 56 or 168 hours. However, a more detailed insight into the variation of the materials throughout ageing could be achieved by conducting invasive analysis after each ageing stage. For example, measuring the pH of the substrate after each ageing interval would allow comparisons with ATR-FTIR spectroscopy results. Similarly, DSC could provide an insight into the stability of the leather at the different ageing stages. This type of evaluation would require a considerable amount of time, thus it would be better to restrict the research to one substrate at a time;

- The flame retardant in TL, SY and EL3 was identified as one of the components that caused considerable changes within the substrate, in particular in the case of TL and EL3. The mechanism of interaction between flame retardant and the collagenous matrix should be further studied in order to understand how to minimise negative effects associated with it. Also, mass spectrometry could be used to characterise the volatile fractions released from the different substrates containing flame retardants. This would allow developing specific guidelines for collecting substrates that contain flame retardants, avoiding the risk of contaminating other objects in collections;
- Changes in pH and moisture content after the ageing procedures were attributed to modifications of the collagen molecule and were identified via ATR-FTIR. It was noticed that similar pH variations occurred in TL and EL3 samples, although they were subject to different tanning methods. A thorough analysis of their amino acids content, for example by using ion-exchange High Performance Liquid Chromatography (HPLC), could provide an indication of the prevalent mechanism of deterioration. This would permit to understand if chrome and chrome-free leather are characterised by similar degradation pathways;
- The colourfastness test highlighted that ageing may cause greater sensitivity of the coating to continuous rubbing. This result suggested that, even if dusting and dry cleaning operations are conducted with extreme care in museums, in the long term the items may deteriorate because of the loss of dyes as a consequence of rubbing. Similar studies could be conducted by substituting the dry cloth used during this research with a wet cloth. This could reproduce to some extent the effect of wet cleaning on the substrate;
- The materials in this research were all studied without tensioning the samples to represent an ideal situation where the substrate is free to move in any direction. However, in most of the cases substrate’s movement is restricted, in particular in the case of leather and synthetic leather, such as in the case of upholstery leather. It would be interesting to study the behaviour of these substrates when subjected to tensioning, because tension minimises the mobility of samples and could induce cracks after cycles of heat and relative humidity;
- Finally, the most significant research to conduct after this preliminary work of thesis would evaluate the design of substrate-specific guidelines for storage and exhibition. In order to do so, kinetic studies that measure the activation energy of deterioration would be required, according to previous

work conducted on silk. In addition, the long-term, natural ageing of the substrates could be measured by storing materials under monitored conditions. This reference material could be then used as a comparison for samples subjected to simulated ageing, an approach used in previous studies on vegetable-leathers.

7.2.2 Prospective Research Directions: Proactive Collaborative Conservation

After revising the guidelines for leather, textiles and plastics it became evident that a gap exists within the different areas of conservation. The importance of preventive conservation practices is undeniable and it is essential to promote this practice within both established institutions and less known ones. However, in some cases this practice is not effective enough to prevent deterioration. This is particularly true in the case of innovative materials which comprise a number of components, additives and finishing compounds. The same components found in diverse objects, e.g. leather fibres and polymeric coating may lead to different changes of the properties of those objects. As a consequence, it is evident that current preventive conservation guidelines do not cover the complexity of modern and contemporary materials. But how is it possible to deal with this issue, in particular in a period in which the museum and heritage sector is experiencing a reduction in funding availability?

The following paragraphs describe what has been called Proactive Collaborative Conservation (ProCoCo), a framework that would permit museums and other institutions to gain information regarding the degradation of innovative materials through the collaboration with private companies. Differently from the previous chapters, these paragraphs are more policy-oriented and allow one to look back at the whole thesis as a first example of ProCoCo involving two of the final partners: a conservation scientist and a manufacturing company.

7.2.2.1 The Context

Cultural heritage is a fundamental patrimony that reminds people of their roots, social battles, historical background and achievements. UNESCO (United Nations Educational, Scientific and Cultural Organisation) divides cultural heritage in tangible and intangible (UNESCO, 2017). Intangible heritage refers to performing arts, traditions and rituals. Tangible heritage refers to objects that represent a recognised testimony of cultural and/or social events or steps forwards in the form of expression. The UNESCO subdivision of tangible heritage comprises movable, immovable and underwater cultural heritage. They respectively include books and manuscripts, sculptures, paintings and so forth (movable), archaeological sites and monuments (immovable), and underwater cities or ruins and shipwrecks (underwater) (UNESCO, 2017). Indeed, these objects tend to degrade with time and institutions are actively trying to slow down this process to preserve them. To date natural heritage is also considered a form of cultural heritage, though it will not be discussed because it is out of the scope of this thesis as also is intangible heritage.

Conservation is crucial in order to preserve tangible cultural heritage, because it protects this type of patrimony and ensures its future enjoyment. Organisations such as ICOM-CC (International Council of Museums – Committee for Conservation) and ICCROM (International Centre for the Study of the Preservation and Restoration of Cultural Property) are active in promoting conservation practices and developing a common language to allow the use of a consistent terminology in this field (ICOM-CC, 2008). These organisations suggest guidelines to improve stewardship and maintenance and are equipped to tackle to some extent many of the common issues encountered during the conservation of traditional, natural materials. However, the deterioration of modern and contemporary materials has introduced new issues that have often led to overlook the effects of degradation (Keneghan, 1996) and have finally caused irreversible damage to collections. It is unlikely that organisations such as ICOM and ICCROM alone will be able to sustain the weight of investigating the broad variety of new materials in their manifold forms available in museum collections. Therefore novel systems should be found and put in place in order to gather information that is useful to preserve these items.

The concepts of sustainability may provide a platform to start collaborations to help museums to accomplish this task. Since 1969, when the word sustainability was first used to promote the idea that economic growth should not cause damage to the environment, the term 'sustainable development' has been developed and optimised (Adams, 2006). The well-known Brundtland Report stated that 'Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs' (Brundtland *et al.*, 1987). This means that any activity conducted today to satisfy human's needs should not interfere with the ability of doing the same in the future. Growing attention has also been given to the three pillars of sustainable development: economic growth, environmental protection and social progress. As a result, a number of national and international directives have been developed to comply with these concepts. Efforts in this direction have been made within and outside of museums.

Companies are required to satisfy certain standards and comply to regulations in order to limit their impact on the environment during production (COTANCE & Industrial All, 2012). One the one side, this has triggered research towards materials with lower environmental impact (CORDIS (European Commission), 2013). On the other side, the understanding of how products deteriorate still requires more attention because it would help to assess the actual lifecycle of materials (Gowda and Babu, 2008). Similarly, museums are introducing sustainability in their policies (Madan, 2011), though their goals are normally limited to the reduction of carbon footprints and, to a greater extent, to achieve the economical sustainability of the institution (Arts Council England, 2013; ICOM, 2013). The evaluation of conservation practices has also started to be under the spotlight, with some authors calling for less restrictive ranges of temperature and humidity in order to minimise fossil fuels consumption (Schäfer, 2014). Nonetheless, this would require more studies focused on material's degradation that involve the use of human and economic resources that, as already said, are limited.

A possible solution may be the introduction of a systematic form of collaboration between product's manufacturers and institutions that may potentially preserve those products. This approach may become a supplementary source of funding for museums, not alternative to public funding, by providing a service to manufacturers that in turn will have a clearer idea of the long-term degradation of their products. Indeed, the approach would be of greater interest for those institutions that store and collect modern and contemporary object, but it would not be restricted to them.

7.2.2.2 Generalities of the ProCoCo Approach

The name of the approach was designed to comprehend and identify its essential aspects. The term 'proactive' has been already used in the heritage context and its significance has been recognised by some authors (Drdácký *et al.*, 2005; Rozell, 2014). Nonetheless, in some occasions preventive and proactive are used as synonyms. In this case the term refers to the characterisation of degradation processes that may potentially take place within a substrate before it becomes art or cultural heritage. 'Collaborative' refers to the presence of stakeholders external to museums that will be actively involved in the collaboration with conservators and conservation scientists. Indeed, 'conservation' refers to the actions performed in order to protect tangible cultural heritage (ICOM-CC, 2008). A possible conflict between the terms may be perceived, in particular between proactive and conservation. However, the desire of creating this approach with the specific aim of preserving valuable items included in collections is made clear by adding the term conservation.

ProCoCo is intended as a form of conservation aimed at increasing the understanding of the processes leading to degradation in substrates that have never been subject to conservation studies. This approach requires the collaboration between the conservation staff of a cultural institution, the institution and a private company. New knowledge can be generated by increasing the dialogue between the participants, because each of them has different types of expertise. Focusing on the assessment of the early signs of degradation, ProCoCo will provide valuable data that museums will be able to use in the future in case the material under investigation will become part of a collection. In addition, manufacturers may gather important information that can be used to improve some characteristics of their substrate or to design strategies for disposal and reuse.

ProCoCo may have a broad impact on both movable and immovable heritage, though its implications can be easily understood when innovative and composite materials are considered. A multitude of items made out of synthetic fibres, foams, rigid plastics, and composites have been and are currently used in textiles, automotive, building and aerospace applications. These items already constitute a challenge today (Ayrey and Hewes, 2017) and they will probably become more present in museum collections in the near future. Efforts to conduct research in this area have been made in the last 15-20 years (Shashoua, 2012), though the amount of funding available for museums remains one of the main issues that limit research. By involving stakeholders interested in the results of this type of research, part of the financial restrictions could be reduced. In addition, the resulting income could cover the cost of urgent conservation treatments.

In order to understand the possible implications of this type of approach, an example is provided. Protein fibres, in particular those derived from soya bean and casein, have been widely studied during the past century and they were commercially produced during the World War II (Brooks, 2009). They were characterised by interesting properties that allowed them to effectively substitute wool and other natural fibres (Brooks, 2005). However, their production stopped after the end of the war probably for two main reasons. Firstly, they were replaced by the newly developed and cheap synthetic fibres and, secondly, they presented some issues when worn of a strong odour and poor tensile strength (Brooks, 2009). In the last 20 years these fibres have been re-discovered and new manufacturing methods were implemented for the sake of reducing the current dependence from oil-derived fibres (Rijavec and Zupin, 2011). It would be interesting to see what would be the outcome of collaboration projects between those institutions that took care of the limited number of items developed in the 20th century and the research groups that are now working to create a new generation of protein fibres.

7.2.2.2.1 How ProCoCo Works

One of the possible criticisms that can be raised to the ProCoCo is that it is not clear how the access to funding should be secured and who should apply for the capital to conduct the research. At this stage, the initial mechanism requires more investigations to understand all the possible sources of funding and the application procedures. Nonetheless, it is possible to propose some solutions that may be further evaluated before the ProCoCo is implemented, possibly considering the option of running workshops where interested stakeholders are involved. This type of approach has been applied in other fields, in particular when policies oriented towards the sustainability of a service are considered, and it is based on the backcasting principles (Robinson, 1982).

One reasonable option is that, once ProCoCo will be implemented, manufacturing companies will contact the government, or an alternative funding body, that will consider the request to establish the collaboration for the investigation into the degradation of a material. A list of museums or institutions that may be interested in conducting research in that area will be provided and a first contact will be established between the company and the institutions. Associations such as the Museum Association, active in the UK, already have lists of museums that could serve for this purpose (Museum Association, 2017). Once the most suitable partner is identified, the stakeholders will prepare a joint application to obtain the funding.

The funding application should ideally explain research objectives, accelerated ageing procedures that will be used, project timeline and the advantages that each partner will be able to achieve. In addition, particular attention should be paid to the project's long-term benefits, clarifying in what way ProCoCo is instrumental to increase the knowledge of the material or its sustainability, and how this can impact on cultural heritage. The partners will finally define the project's budget and, if the funding is granted, one-third of it will be allocated to the manufacturer while the remaining two-thirds will be assigned to the museum.

Because the project needs to be advantageous for all of the partners, the material will be studied using techniques that are typical of both industrial and museum sectors. Invasive techniques, which are normally used in industry, will be combined with non-invasive and possibly non-destructive ones. Data will be collected both before accelerated ageing and after a number of ageing stages, in order to gather information on the evolution of the degradation. A list of degradation markers will be created and stored to allow the effective assessment of the conservation state in the event that the material will enter in the museum collection. The evaluation of an object's condition will be possible by benchmarking the object against the data collected during ProCoCo.

The creation of a Joint Protocol with registration number and title of the project will be the major result of this conservation approach. The document may be stored in a dedicated databank where both companies and museums can share information on materials. In case patents limit the use of these documents, specific safeguards must be agreed upon to protect sensitive information.

7.2.2.2.2 The Partners

ProCoCo requires three participants in order to take place: a company that provides the substrate to be tested, a public or private institution that collects objects similar to the company's product, and the conservation department affiliated with the institution.

Manufacturing companies can be of different types and sizes, therefore a selection should be made to identify which are the most appropriate stakeholders for the ProCoCo. The involvement of big companies, especially corporations, with museums has sometimes been criticised because of the pressure from the first to re-consider public positions of the second (Collins, 2015). This means that these companies should be subject to stricter control mechanisms in case they decide to become involved in the ProCoCo. Nevertheless, young businesses and start-ups have often different managerial structures and are often open to collaborations. Moreover, smaller businesses might be understaffed or might have a limited amount of people able to conduct studies on materials degradation, if any. This research area, though, can be fundamental for the development of more sustainable products (Ljungberg, 2007). As a result, becoming involved in this type of project may offer a great help to these companies. Indeed, the funding deriving from the ProCoCo will also offer an incentive for the company to reinvest capital in the optimisation of its products.

The other two participants, the organisation that hosts objects similar to the ones provided by the company and its conservation department, can be part of the same institution or not. The role of the institution within the ProCoCo is obvious, because the approach may become central for the future preservation of items in its collection. In the short-term the ProCoCo funding may be used to conduct necessary remedial conservation or to improve preventive conservation. In the long-term the approach will minimise the need for remedial conservation. Several authors acknowledged museum's ability to influence society referring to their capacity of capturing, sharing and bridging different visions and perspectives of social, political and economic issues (Sandell, 1998; de Varine, 2008). Not only these institutions are the custodians of civilisation, societal, natural values and much more, they also hold the clues of material's degradation. As a result, they should be considered the guardians of invaluable scientific knowledge and should be treated as such.

The departments involved with the conservation of objects can provide an invaluable source of information due to the different professionals that are part of it.

Conservators and restorers may offer their knowledge in terms of material degradation and suggest possible ways to conserve items similar to the one under investigation. Conservation scientists are also becoming increasingly present and valued in museums for their efforts in studying degradation processes and possible solutions to tackle them (Corbeil, 2015). Corbeil's intervention on the occasion of the ICCROM international conference highlighted the idea that conservation institutions should be considered as 'agents of change' (Corbeil, 2015). She referred to conservation institutions, which are different from conservation departments because their goal is to guarantee that the suitable practices are applied on a regional and national level. Though, in the author's opinion, this idea is also applicable to museums and their conservation departments. The mixture of competences may provide a service similar to the one offered by material testing laboratories. However, here the additional benefit lies in the fact that conservators and conservation scientists constantly deal with degraded objects of different types. Therefore, in many cases, they are aware of the actual degradation one should see in the long-term, also when more than one material is used for the same item.

7.2.2.2.3 Avoiding Interference

As mentioned in the previous paragraph, some criticisms rose in the near past regarding the interference of private companies with museum decisions, programmes and exhibitions (Collins, 2015; Macalister, 2015). These criticisms were related to the alarming possibility that intrusions may put pressure on museums to present facts in a manner that is not totally truthful. Indeed, this would constitute a major problem and the real motivations that justify the financial support would be far from the philanthropic subsidy that it should represent. However, financial help is indispensable for museums and other institutions that need to support themselves in a climate of economic recession, where cuts to public funding for cultural heritage are frequent (Settembre Blundo *et al.*, 2017).

Along with sponsorship and patronage, that represent established forms of support towards museums and institutions, the Public Private Partnership (PPP) has been recently presented as an example of collaboration between the public and private sector (Settembre Blundo *et al.*, 2017). In the PPP the private sector provides the capital and manages a public service or asset, hence the typical benefits and concerns of outsourcing activities have been expressed (Wang and Zhao, 2014). These three types of collaboration have in common the dominant position of the private sector in comparison with the heritage organisation, where the latter requires the help of the former in order to economically sustain itself.

ProCoCo promotes a different vision of museums, where they become actively involved in a broader context that exceeds the boundaries of the institution. Being a mutually beneficial collaboration, ProCoCo will be based on the equality of the parts involved and every participant will be as important to the project as everyone else.

7.2.2.2.4 Limitations

Three main limitations were identified while the ProCoCo was developed and will be briefly presented. First, the human capital necessary to conduct the ageing procedures; second, the need for suitable facilities; third, the danger of infringing patent rights.

It is undeniable that a large number of people would be required to draft the funding application and to carry out laboratory operations such as accelerated ageing and degradation tests. This would indeed interfere with routinely conservation. However during ageing procedures samples are stored within ageing chambers for a number of hours and during those hours the usual operations can be conducted without compromising the daily work of the personnel.

Facilities, in the form of laboratories equipped with analytical instruments and ageing chambers, constitute one of the crucial elements of the ProCoCo approach. Small museums or institutions may struggle with this aspect, though the funding provided by the scheme may cover the price of simple equipment able to deliver meaningful results.

Products can be covered by patents that impose limits to sharing information related with them, as in the case of E-Leather® (Bevan, 2005). Inappropriately sharing data regarding patented materials may result in complicated legal issues. Consequently, the protection of sensitive data should be further discussed before the implementation stage, for example in a workshop with the stakeholders.

Another kind of limitation is related to the need for concrete bureaucratic help during the phase of implementation of ProCoCo. This phase requires the intervention of government and funding agencies at the national and international level. In particular, these bodies should promote the need for the public awareness of material's lifecycle. Certainly, the degree of consciousness has increased in recent years (White *et al.*, 2005; Sherburne, 2009), though much more can be done. Endorsing a holistic vision of manufacturing products by including an institution that is a guarantor of the public interest may help in achieving this goal. In addition, it must be noticed that the whole ProCoCo concept would not be able to play its part without the recognition of the central role of museums.

Such limitations should not deter possible stakeholders from investigating strategies to collaborate within the ProCoCo framework. As in any approach, in fact, also here there are limitations, though the potential benefits exceed these limitations.

7.2.2.3 Expected Outcomes

Change is often accompanied by scepticism and criticisms. Indeed, not every change has a positive impact on society, environment, or their elements, and sometimes it can be difficult to predict its long-term effects. For this reason, a long period of discussion should proceed the implementation of the ProCoCo in order to gain the best possible overview of its positive and negative aspects. However, the advantages that can be derived from the ProCoCo may be significant for society as a whole, thus a thorough debate should also consider the opinion of the public.

On the one side, it is difficult to predict every possible negative impact that ProCoCo may have, especially on museums. Uncertainty and inability to clearly visualise possible futures may result in further reductions to the funding availability. On the other side, the current need for new sources of funding and the push of some branches of the conservation sector is fuelling the idea that there is a need for change (Corbeil, 2015; Settembre Blundo *et al.*, 2017).

The main advantages of ProCoCo can be summarised as follow:

- Companies will become more aware of the degradation pathways of products they manufacture and will be able to design them in a more sustainable way;
- Museums and institutions involved with heritage will have access to new products before they become part of their collections, becoming more conscious of possible degradation issues in the future;
- The same institutions will have the possibility to study patented materials overcoming the difficulty of identifying additives that may interfere with the correct material’s conservation;
- Artists and designers that collaborate with museums will become more aware of possibilities and limitations of products that they may want to use for their creations.

In a world where sustainability is becoming a major point of discussion and a crucial theme to improve all aspects of human-environment interaction, ProCoCo may offer a great service. It would help to design more sustainable products and would support museums to become not only the custodians of social and cultural values, but also an active participant to the change of society.

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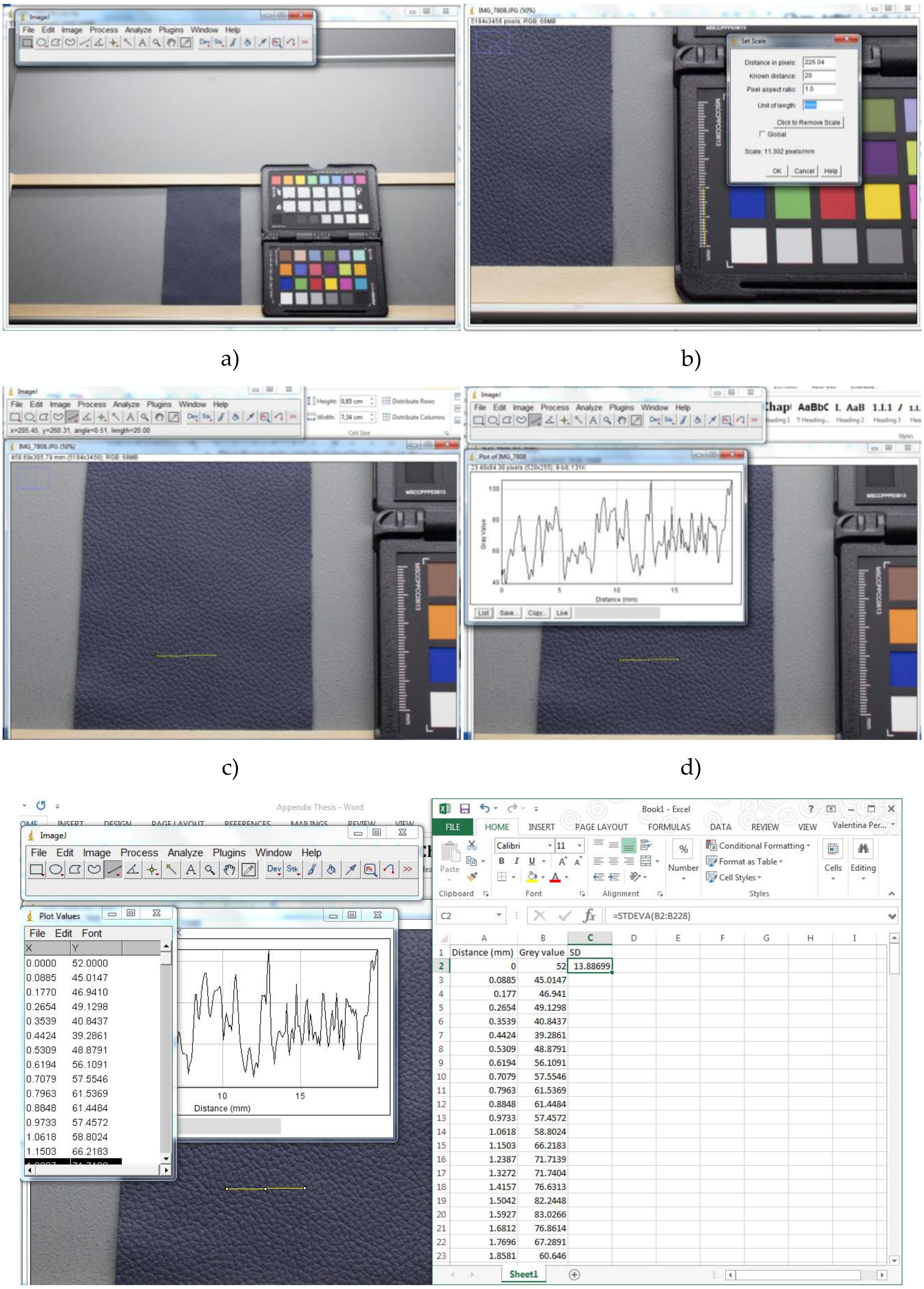
Appendix

A. Surface roughness calculation via image processing

The image processing method tested in this thesis to assess variations in the surface roughness, particularly for the coating of the samples, was performed following the steps reported below:

- The image (acquired with camera or 2D scanning) was imported in the ImageJ free software (Figure A-1a);
- The scale was set by using the ColourChecker ruler (or the grey patches in the case of 2D scanning) included in every image (Figure A-1b);
- A length of 2 cm was tested by drawing a horizontal line on the sample (Figure A-1c);
- The *Plot Profile* tool was used to obtain the grey values of the selected line (*Analyze* and *Plot Profile*) and a command window appeared containing the profile of the selected region (Figure A-1d);
- A list of the grey values along the tested distance was provided by pressing *List* in the command window;
- These values were processed in Excel and the standard deviation calculated (Figure A-1e);
- The standard deviations of three measurements (for each of the three samples) was then used to calculate the surface roughness variation.



Distance in pixels: 226.04
Known distance: 20
Pixel aspect ratio: 1.0
Unit of length: mm
Click to Remove Scale
☐ Global
Scale: 11.302 pixels/mm

X	Y
0.0000	52.0000
0.0885	45.0147
0.1770	46.9410
0.2654	49.1298
0.3539	40.8437
0.4424	39.2861
0.5309	48.8791
0.6194	56.1091
0.7079	57.5546
0.7963	61.5369
0.8848	61.4484
0.9733	57.4572
1.0618	58.8024
1.1503	66.2183

C2 =STDEVA(B2:B228)

	A	B	C
1	Distance (mm)	Grey value	SD
2	0	52	13.88699
3	0.0885	45.0147	
4	0.177	46.941	
5	0.2654	49.1298	
6	0.3539	40.8437	
7	0.4424	39.2861	
8	0.5309	48.8791	
9	0.6194	56.1091	
10	0.7079	57.5546	
11	0.7963	61.5369	
12	0.8848	61.4484	
13	0.9733	57.4572	
14	1.0618	58.8024	
15	1.1503	66.2183	
16	1.2387	71.7139	
17	1.3272	71.7404	
18	1.4157	76.6313	
19	1.5042	82.2448	
20	1.5927	83.0266	
21	1.6812	76.8614	
22	1.7696	67.2891	
23	1.8581	60.646	

a) b)

c) d)

e)

Figure A-1: Screenshots describing the procedure for the calculation of the roughness with ImageJ

A. ATR-FTIR Spectroscopy

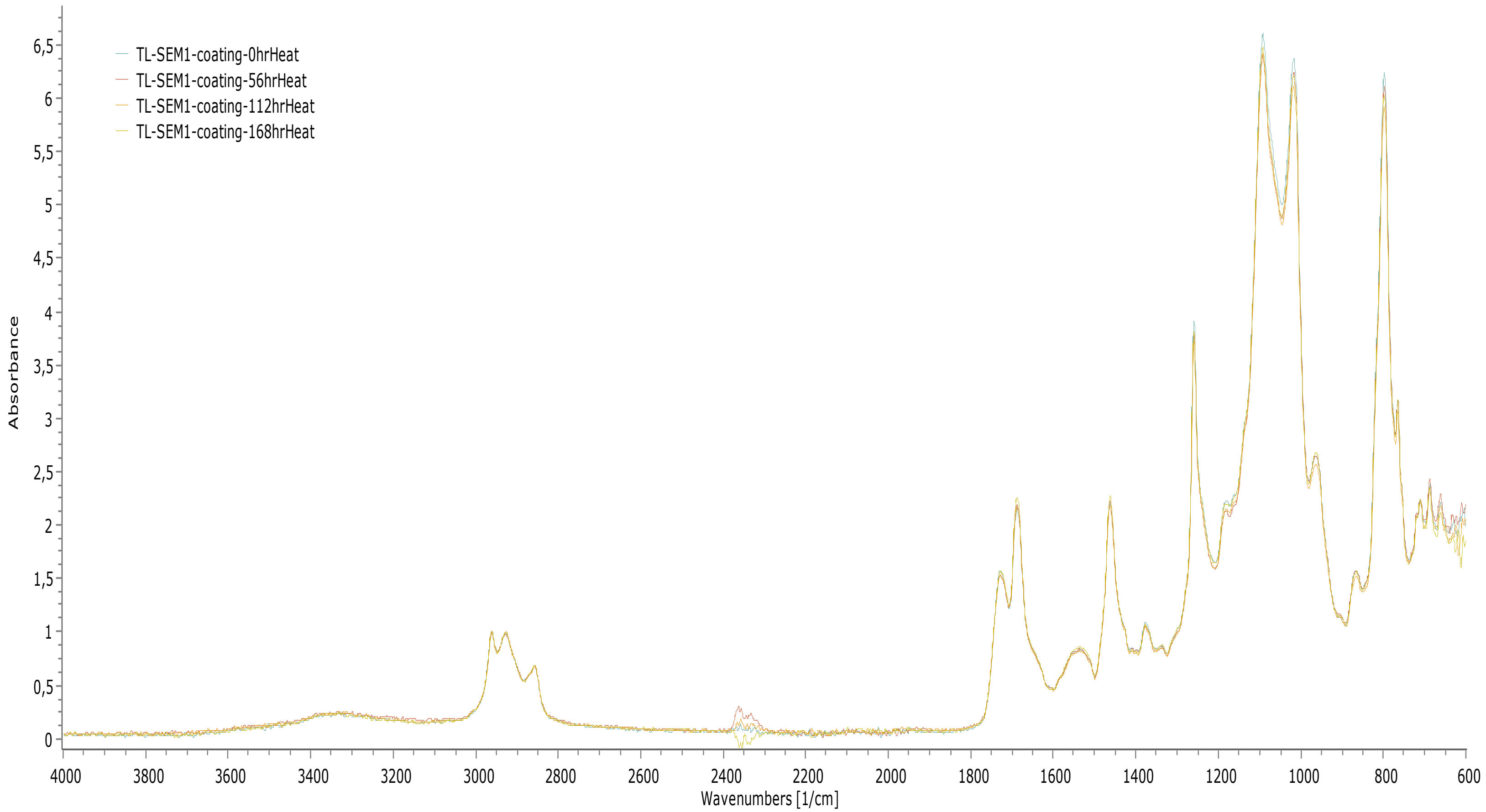


Figure A-2: ATR-FTIR spectrum showing absorbance peaks of TL coating after H70 ageing

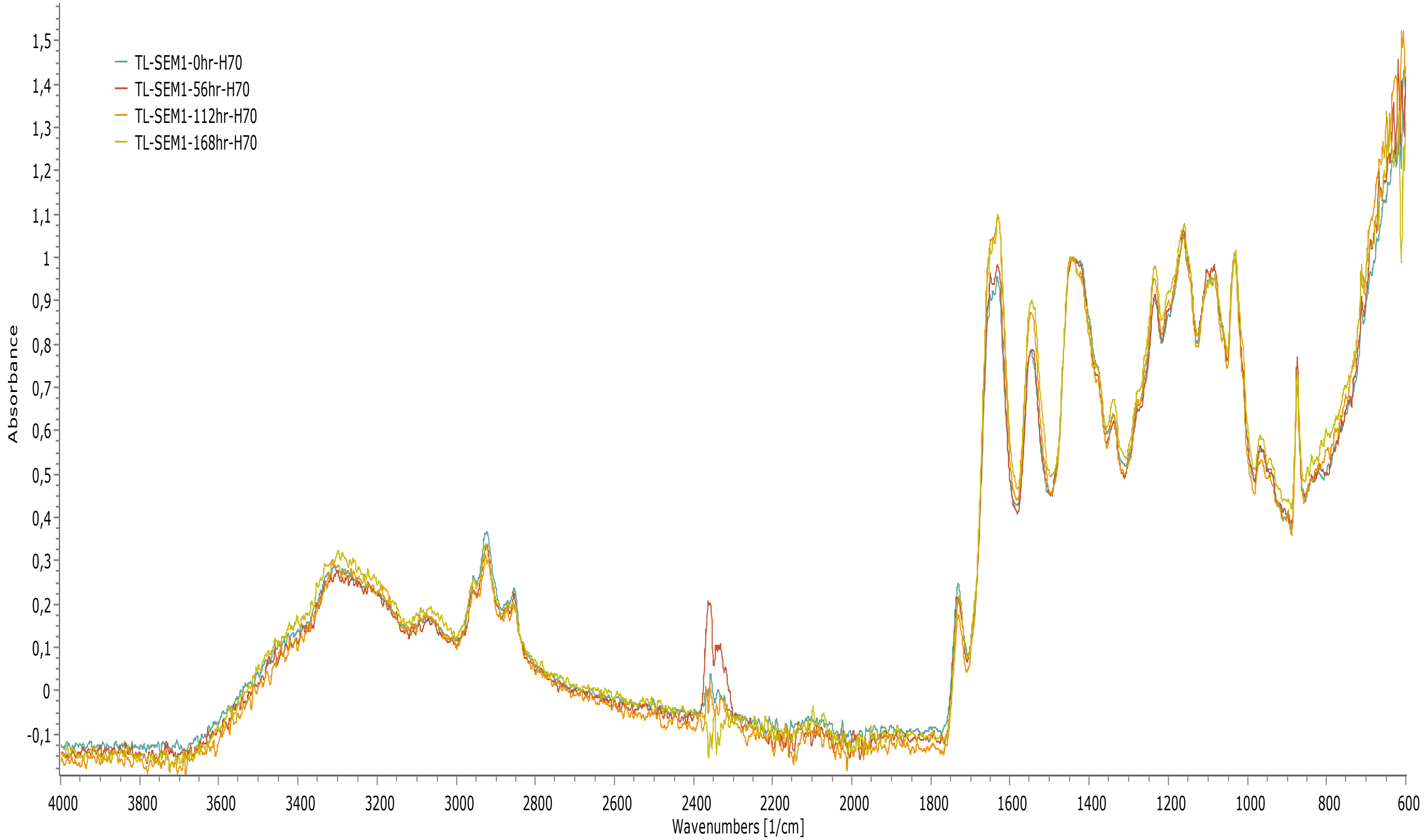


Figure A-3: ATR-FTIR spectrum showing absorbance peaks of TL fibrous layer after H70 ageing

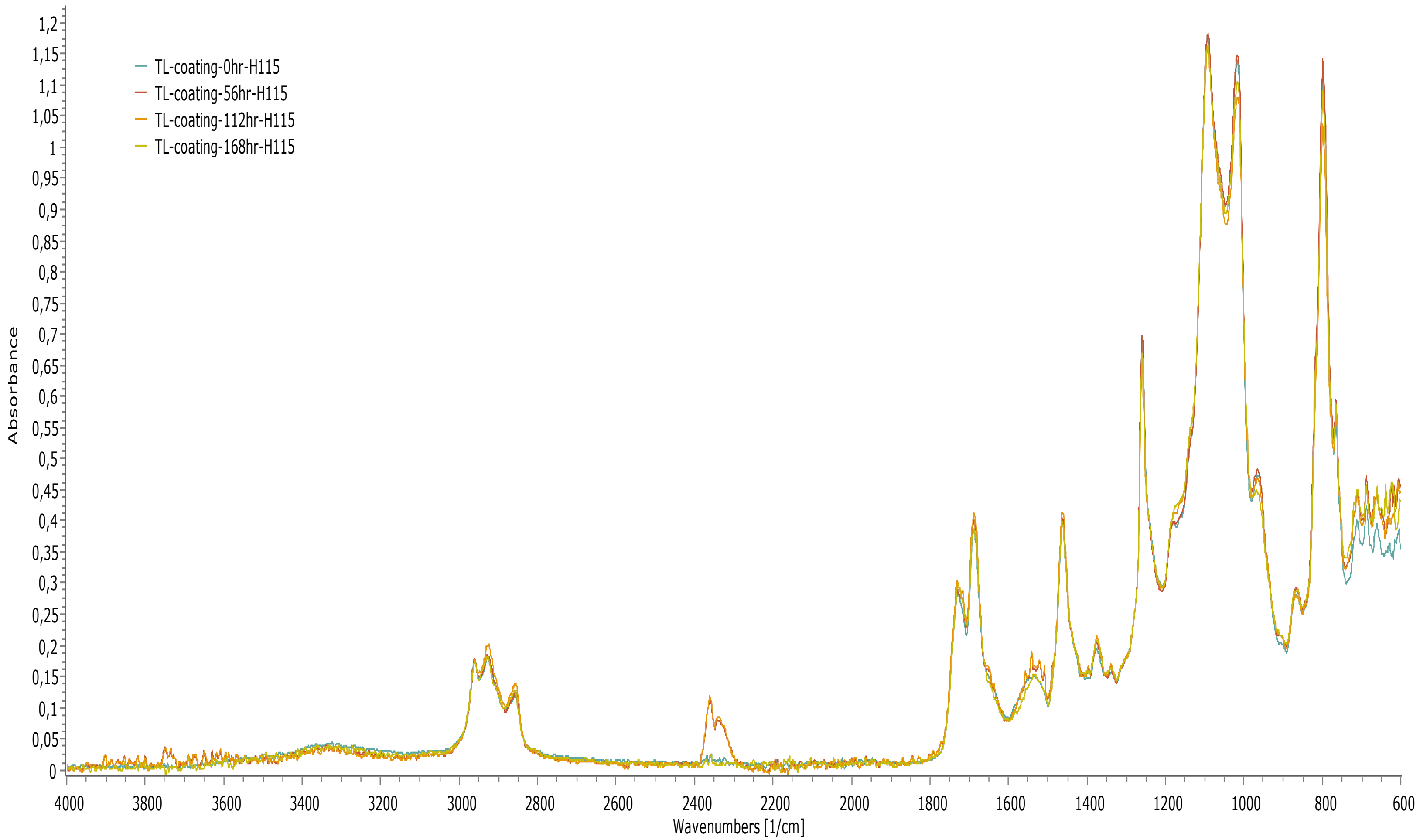


Figure A-4: ATR-FTIR spectrum showing absorbance peaks of TL coating after H115 ageing

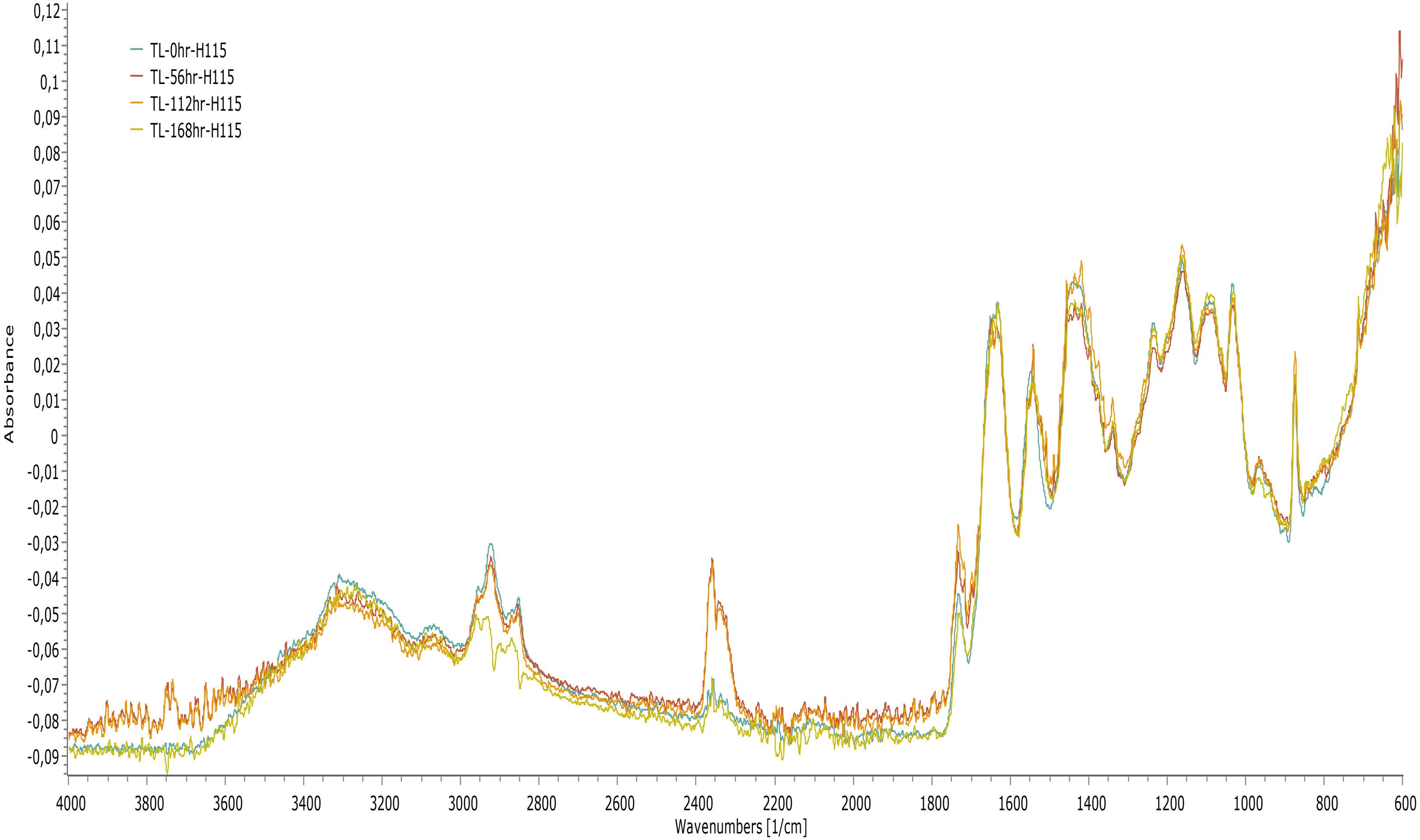


Figure A-5: ATR-FTIR spectrum showing absorbance peaks of TL fibrous layer after H115 ageing

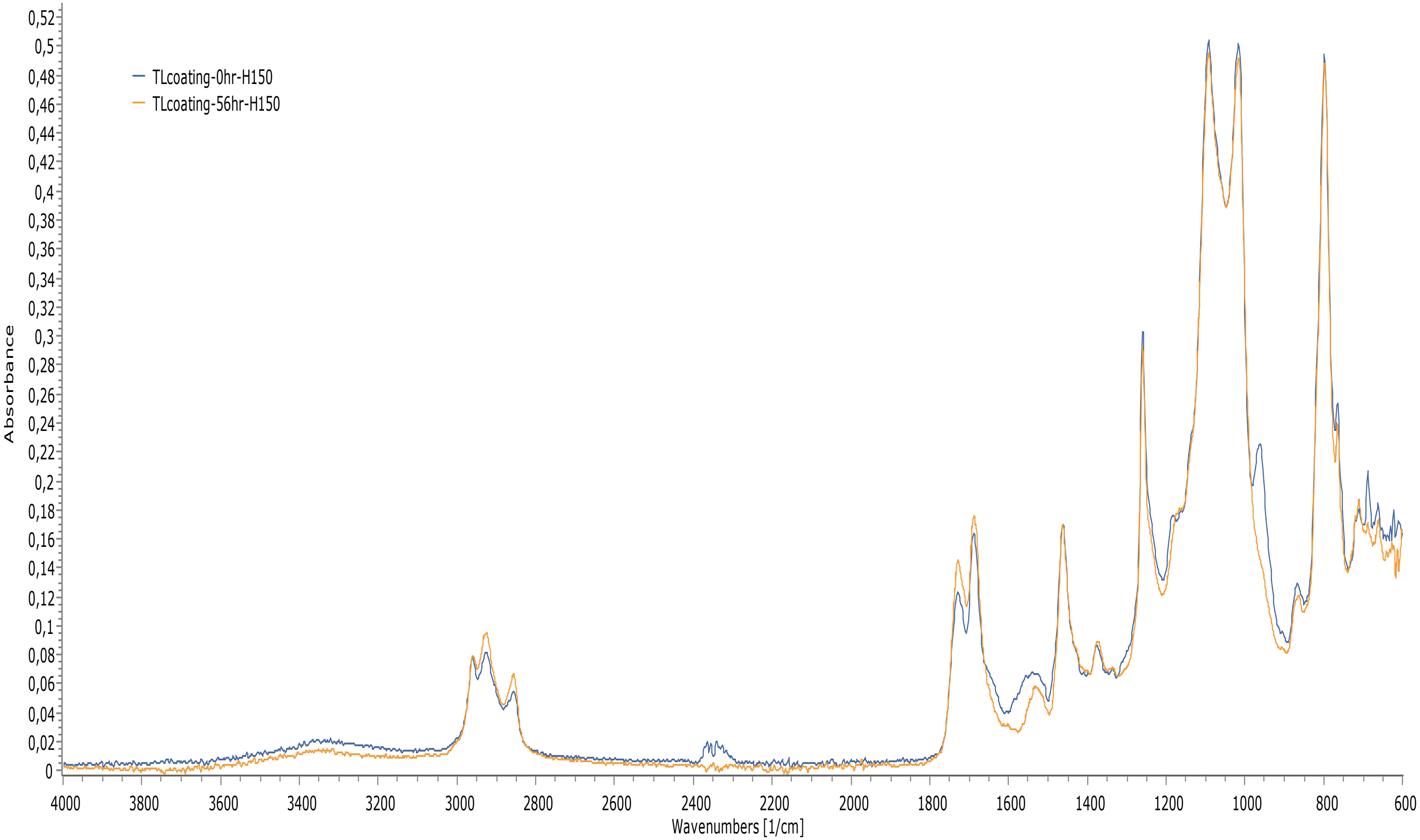


Figure A-6: ATR-FTIR spectrum showing absorbance peaks of TL coating after H150 ageing

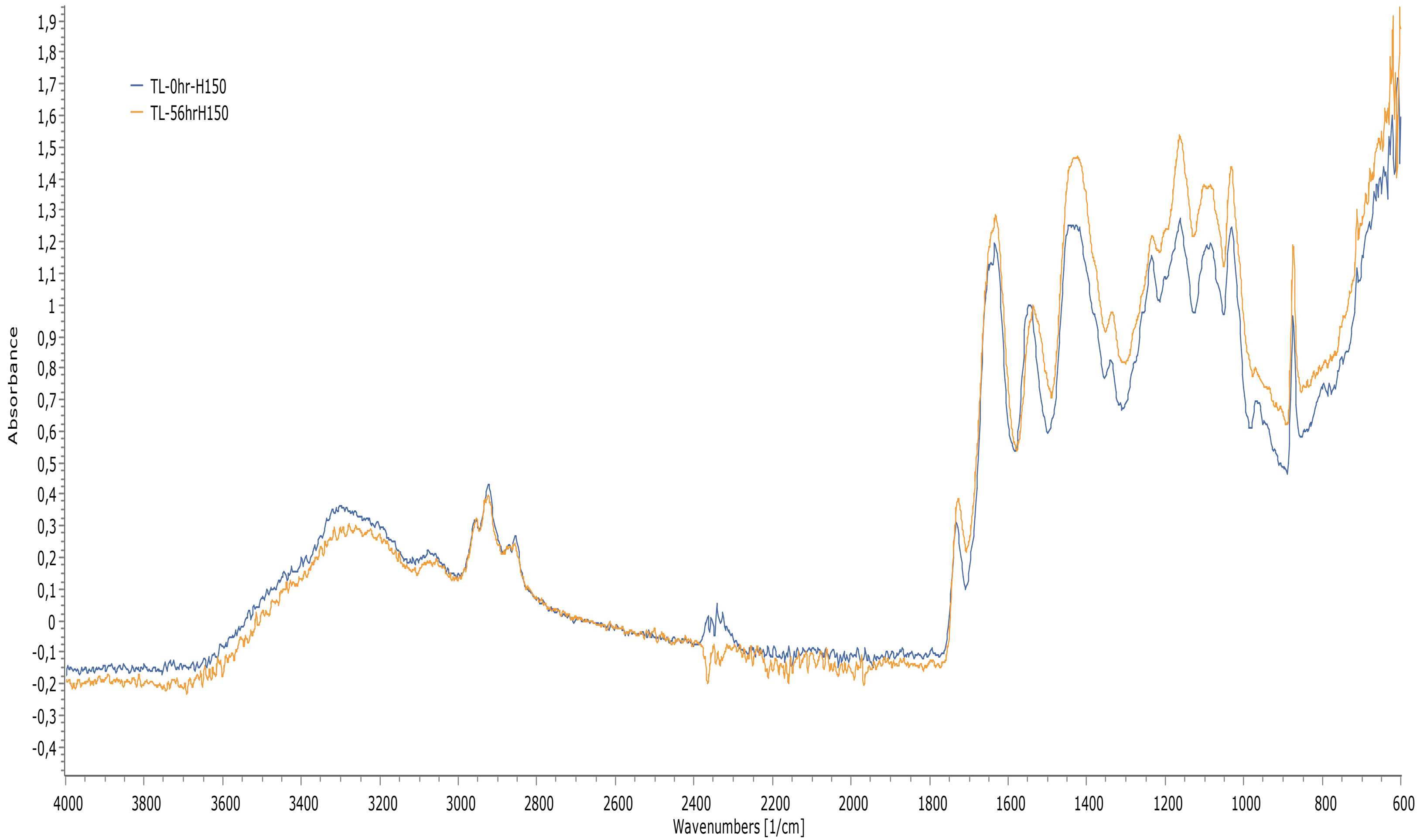


Figure A-7: ATR-FTIR spectrum showing absorbance peaks of TL fibrous layer after H150 ageing

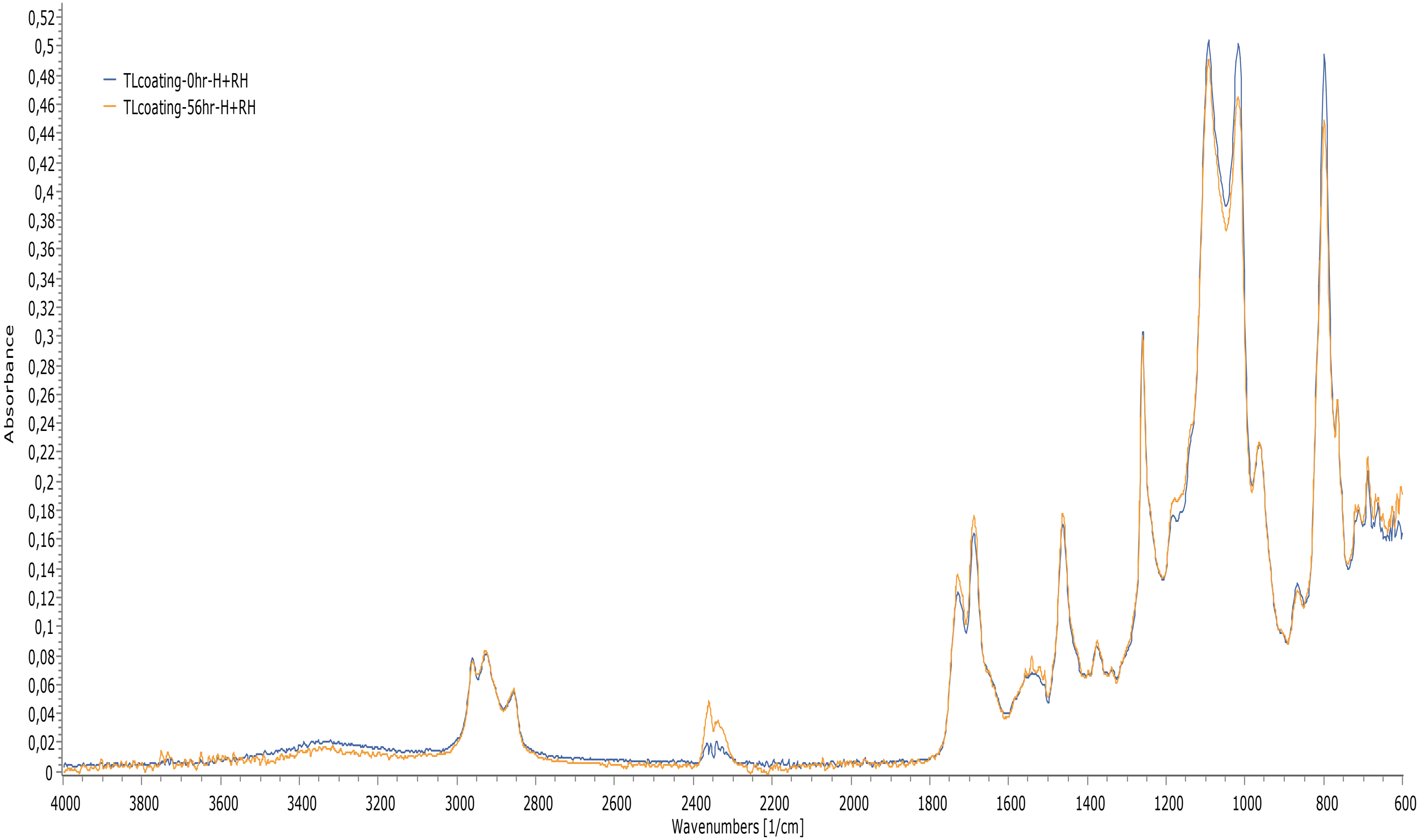


Figure A-8: ATR-FTIR spectrum showing absorbance peaks of TL coating after H+RH ageing

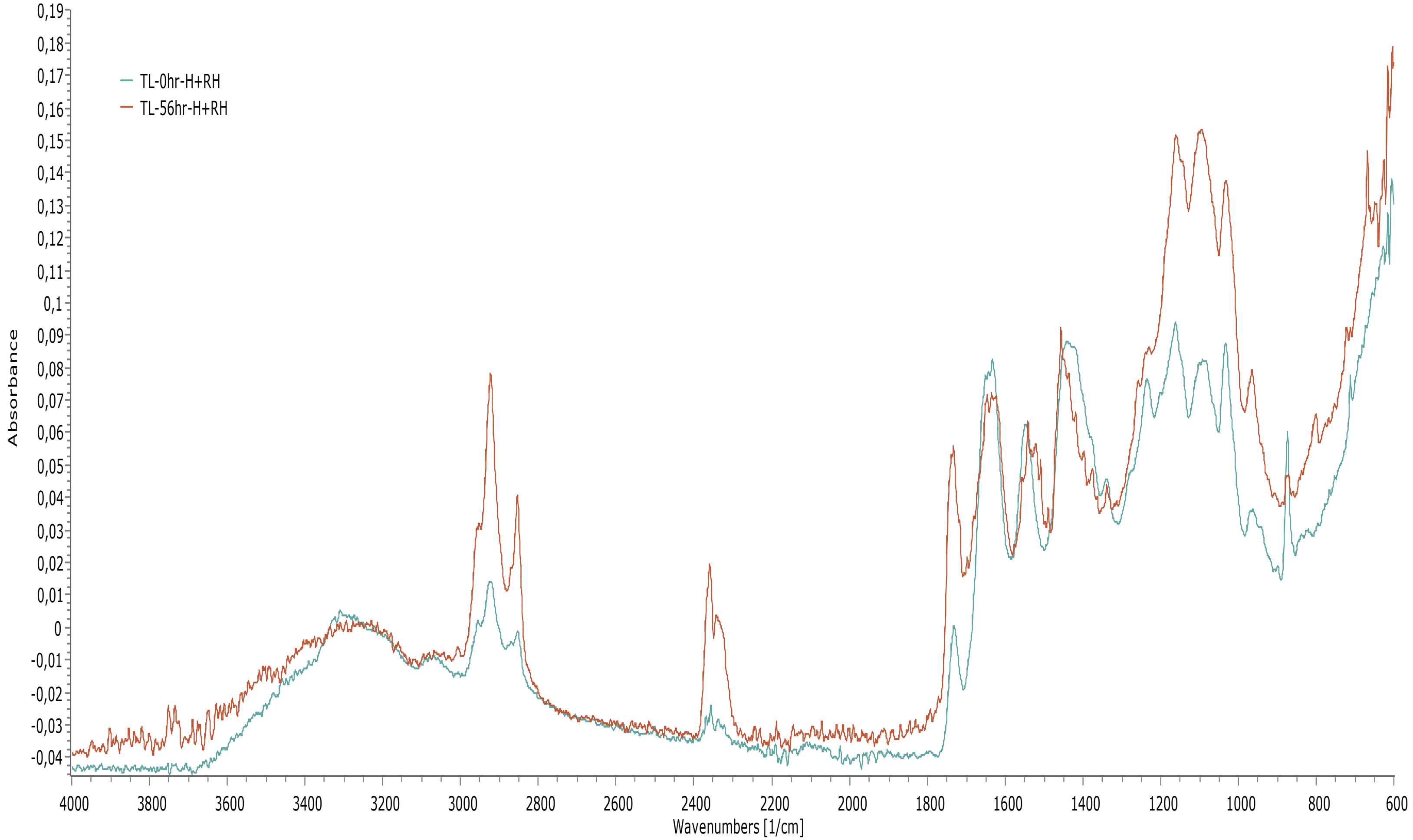


Figure A-9: ATR-FTIR spectrum showing absorbance peaks of TL fibrous layer after H+RH ageing

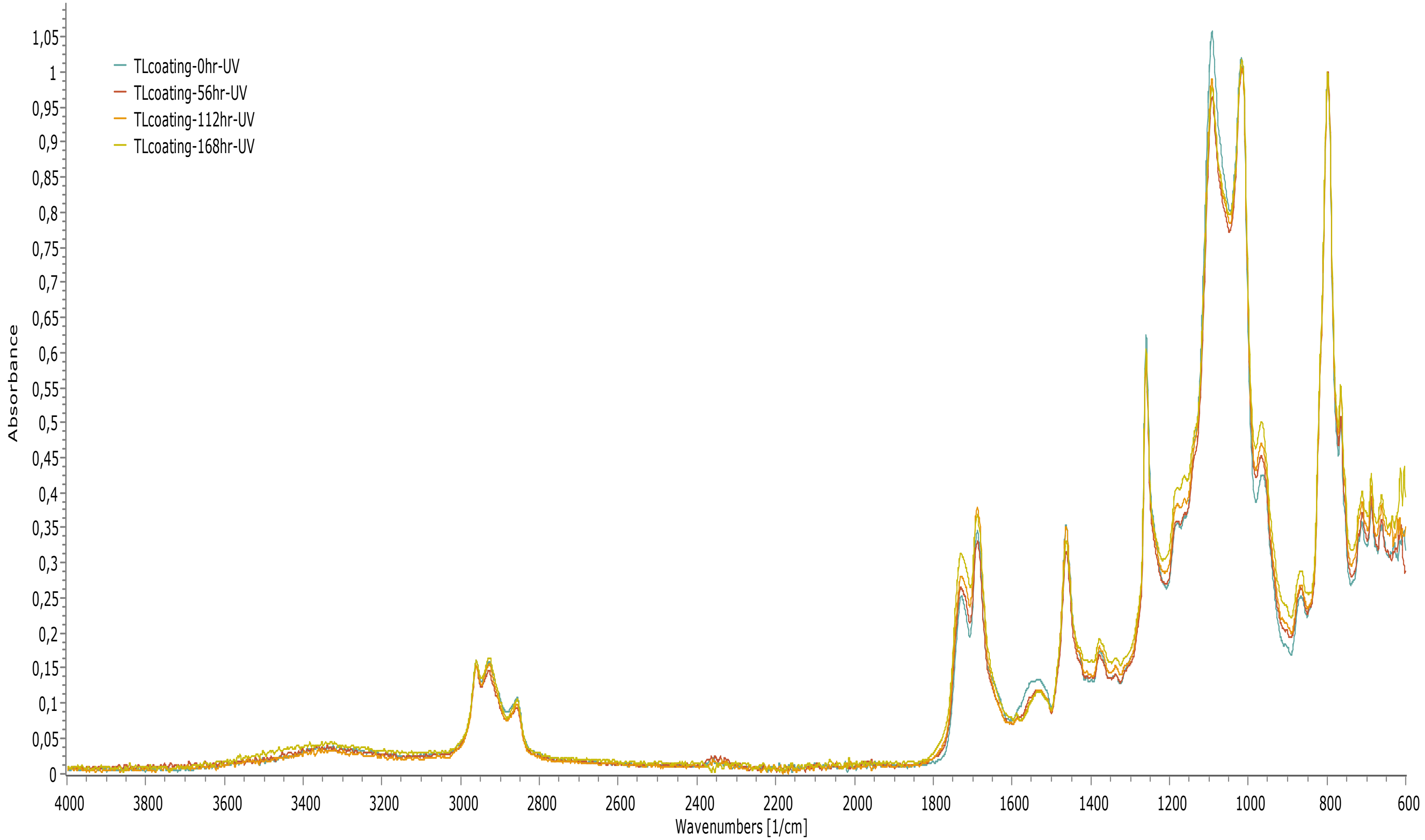


Figure A-10: ATR-FTIR spectrum showing absorbance peaks of TL coating after UV ageing

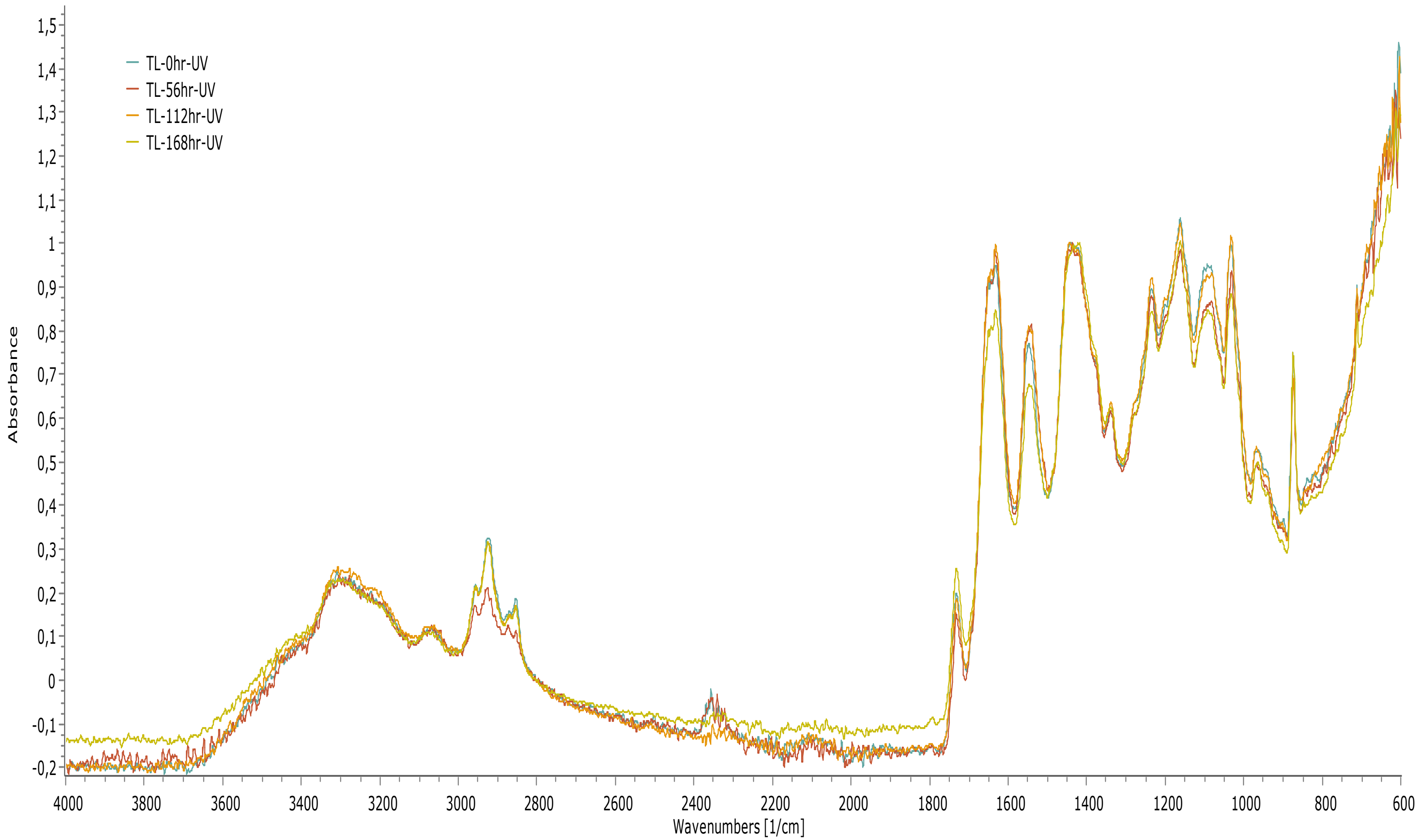


Figure A-11: ATR-FTIR spectrum showing absorbance peaks of TL fibrous layer after UV ageing

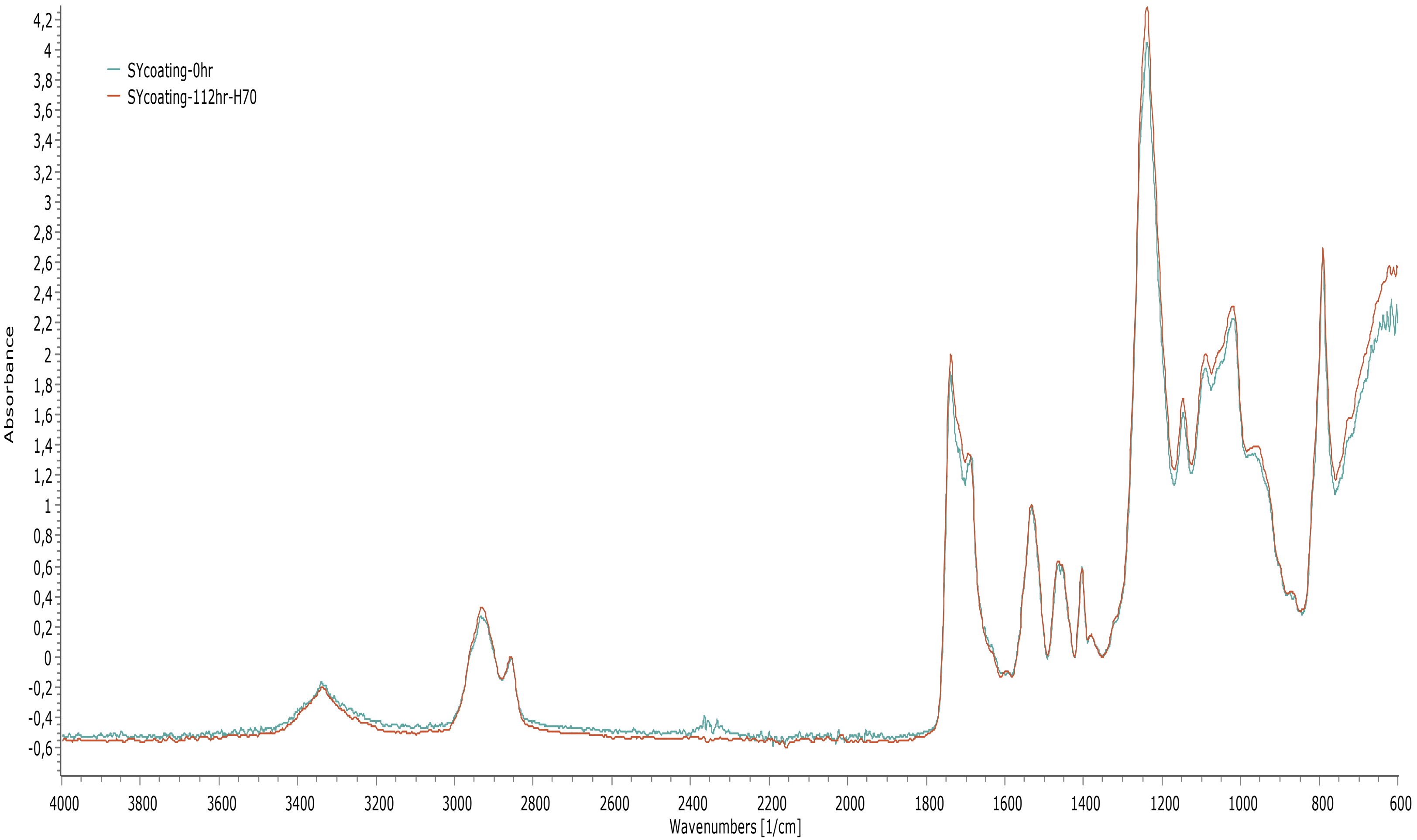


Figure A-12: ATR-FTIR spectrum showing absorbance peaks of SY coating after H70 ageing

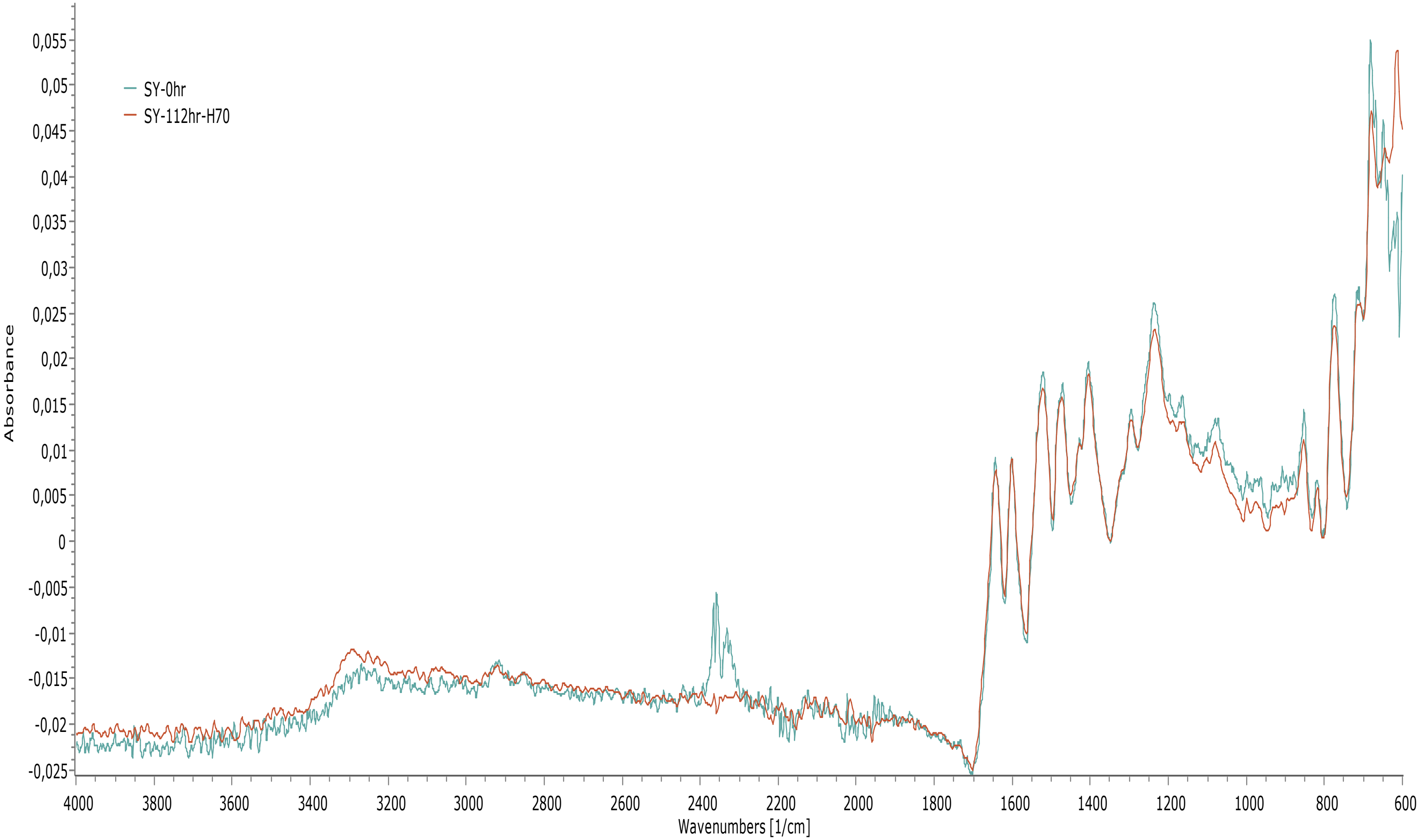


Figure A-13: ATR-FTIR spectrum showing absorbance peaks of SY fibrous layer after H70 ageing

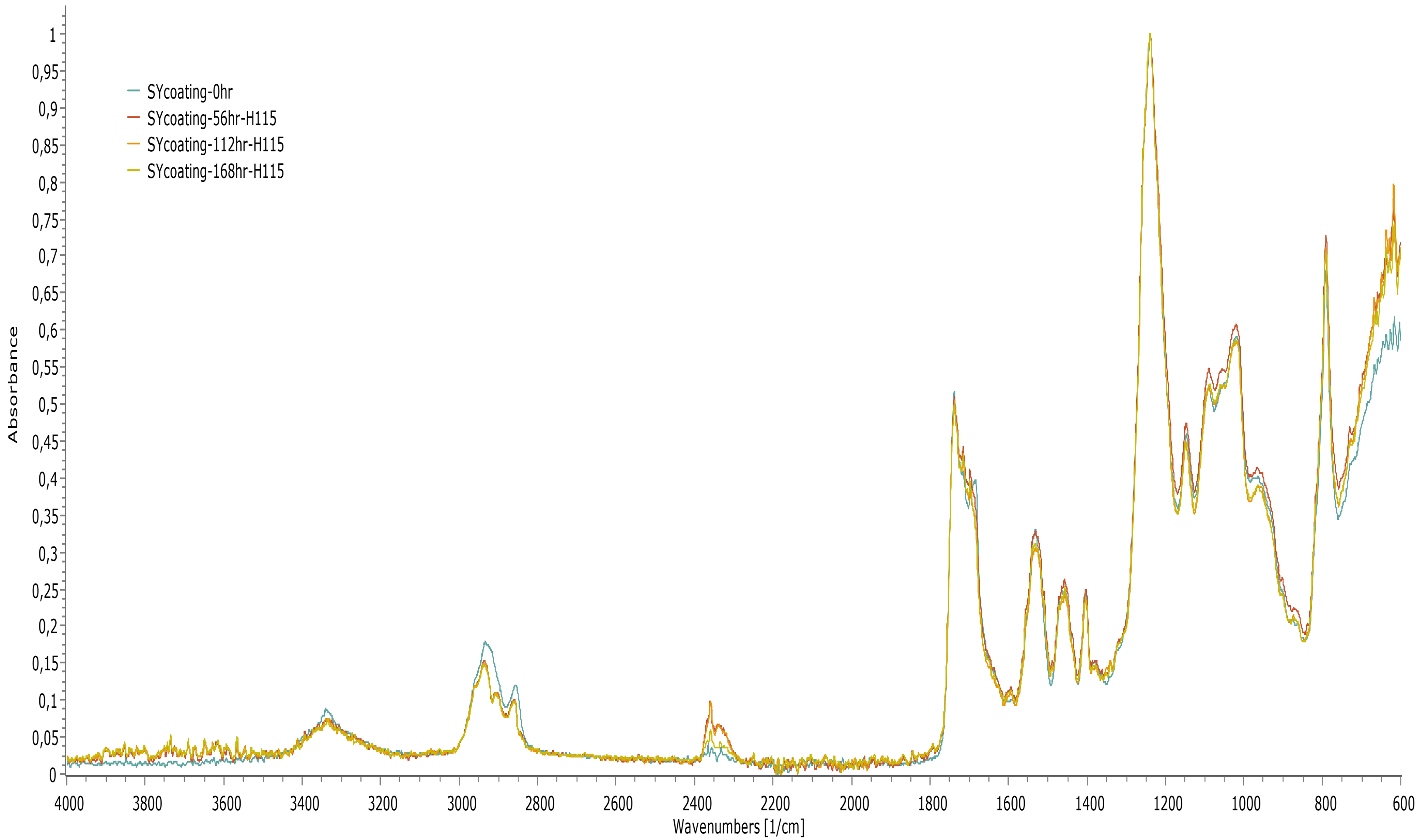


Figure A-14: ATR-FTIR spectrum showing absorbance peaks of SY coating after H115 ageing

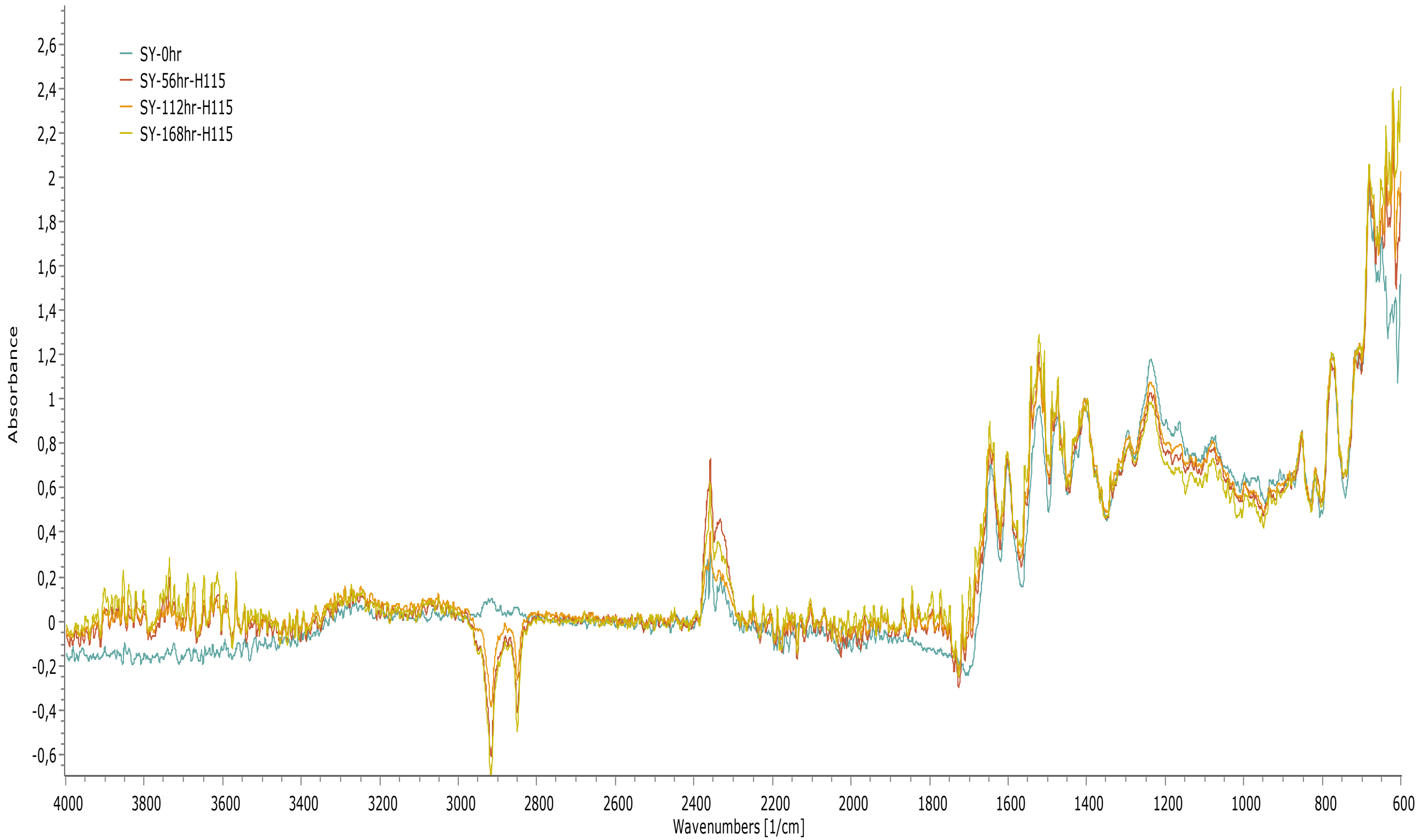


Figure A-15: ATR-FTIR spectrum showing absorbance peaks of SY fibrous layer after H115 ageing

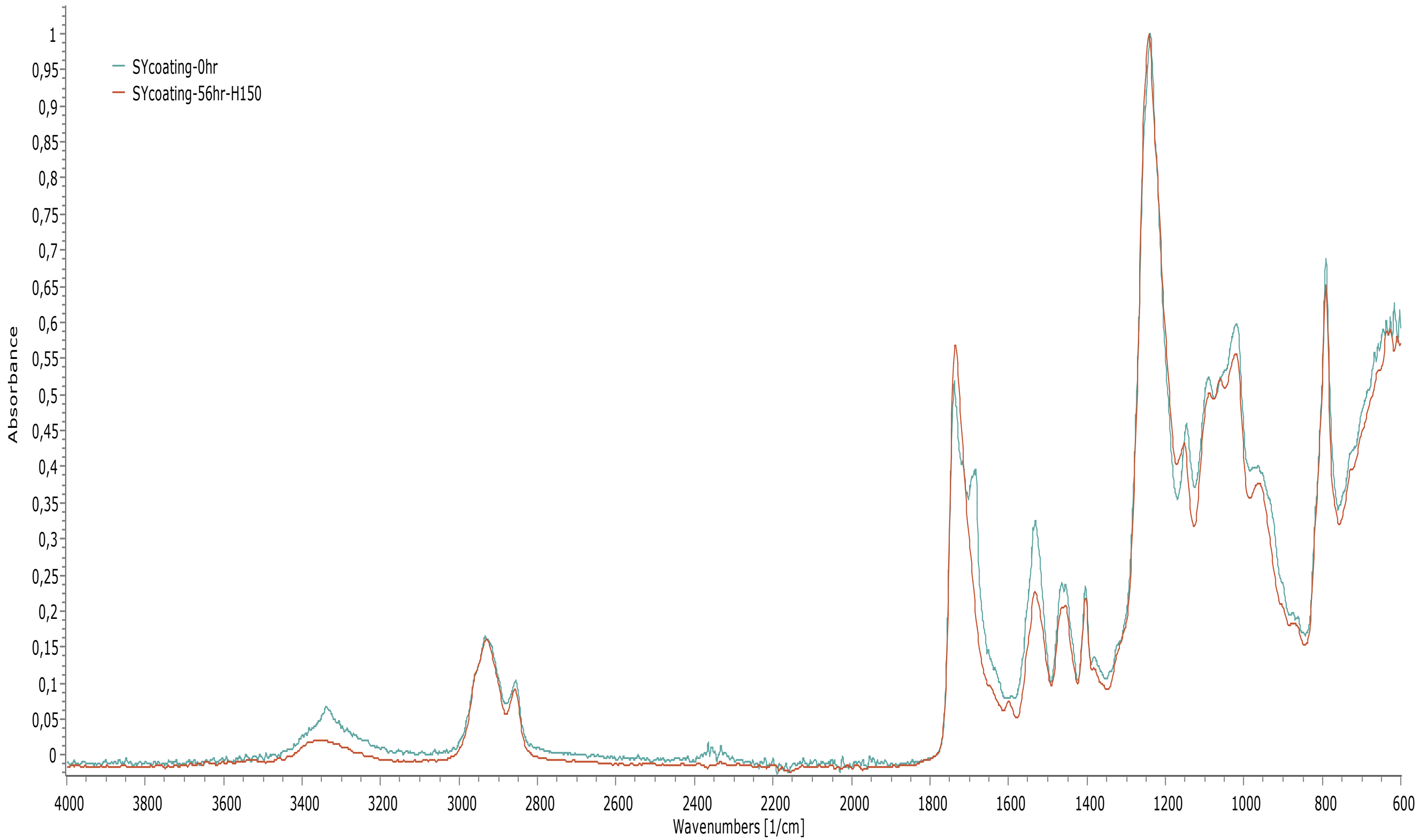


Figure A-16: ATR-FTIR spectrum showing absorbance peaks of SY coating after H150 ageing

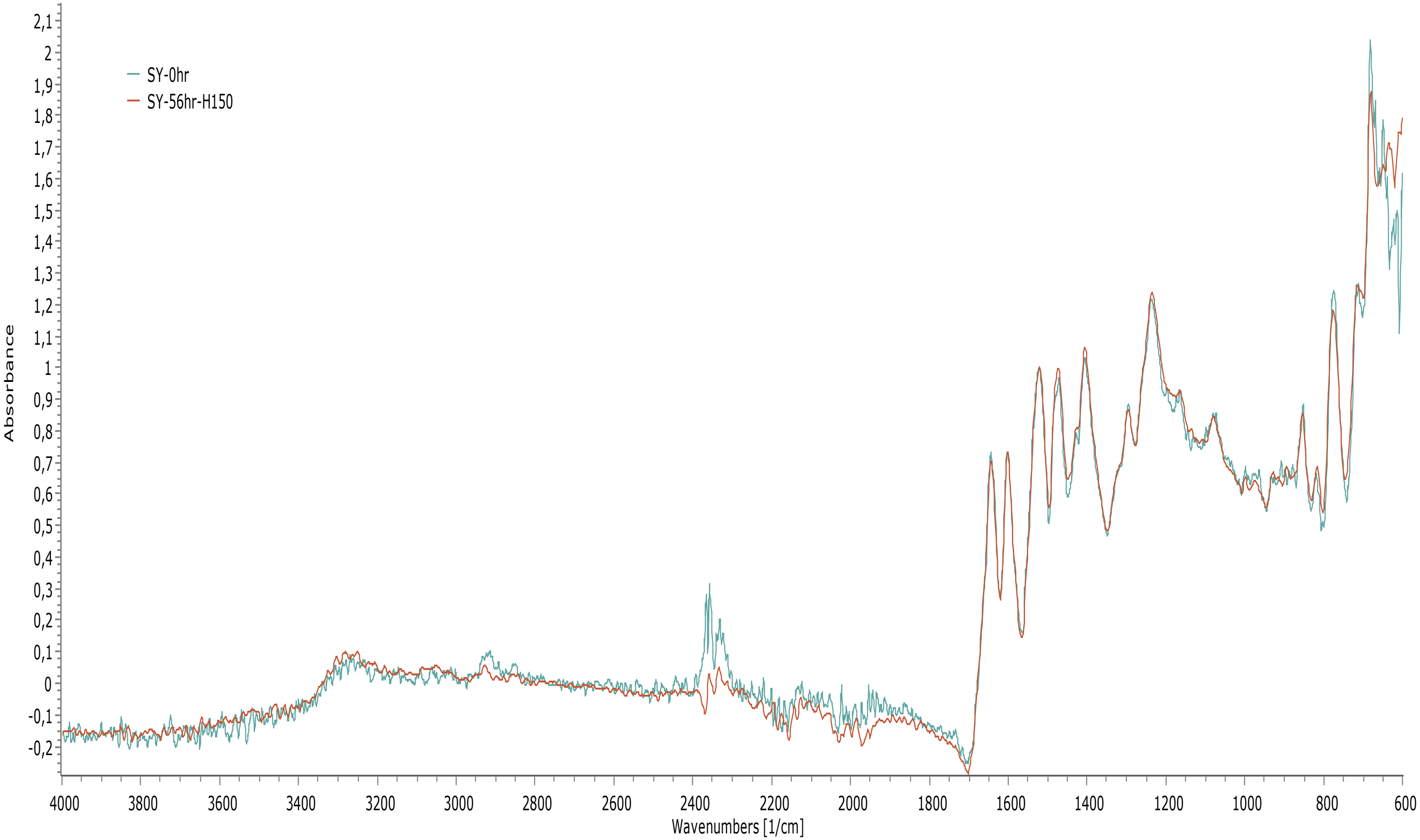


Figure A-17: ATR-FTIR spectrum showing absorbance peaks of SY fibrous layer after H150 ageing

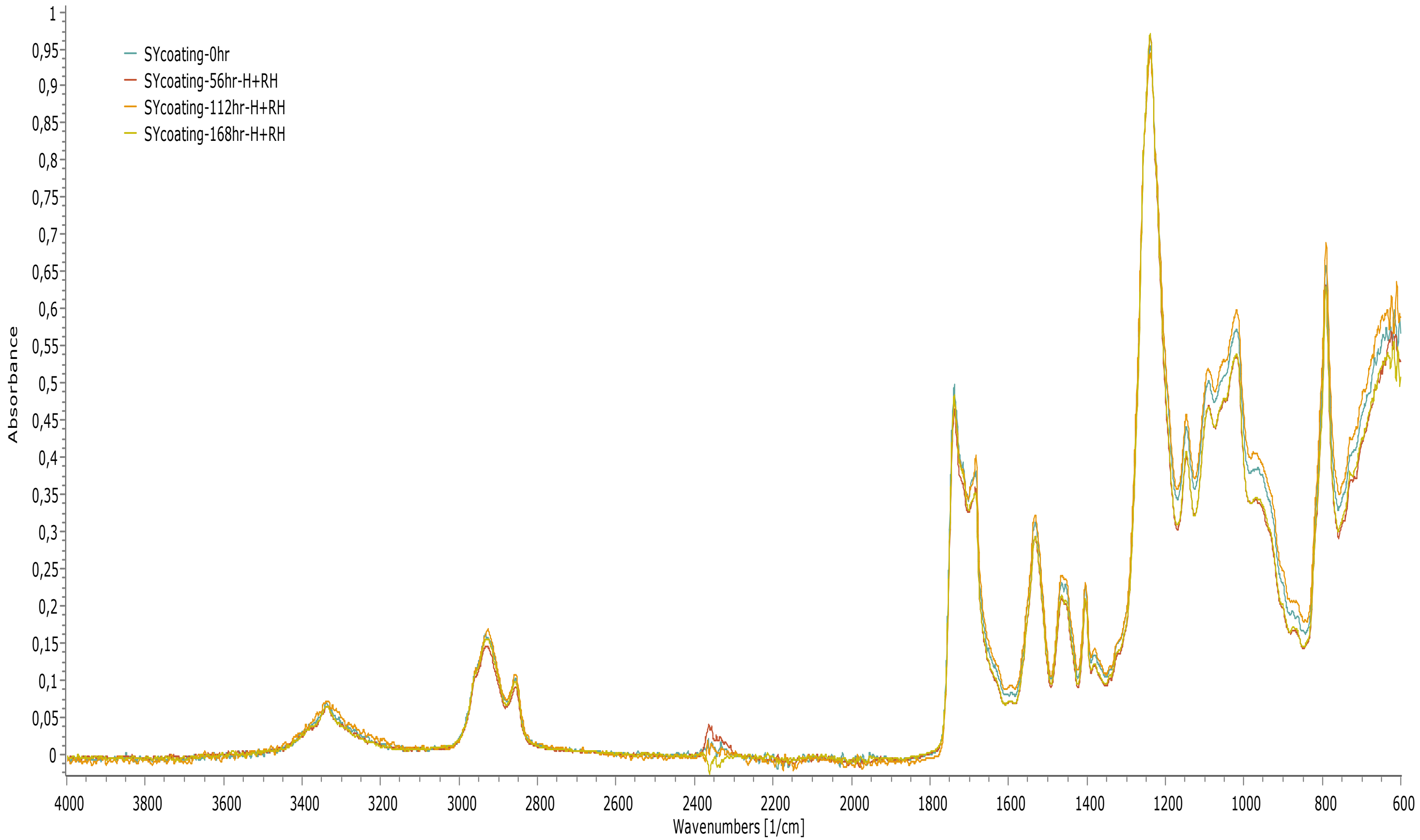


Figure A-18: ATR-FTIR spectrum showing absorbance peaks of SY coating after H+RH ageing

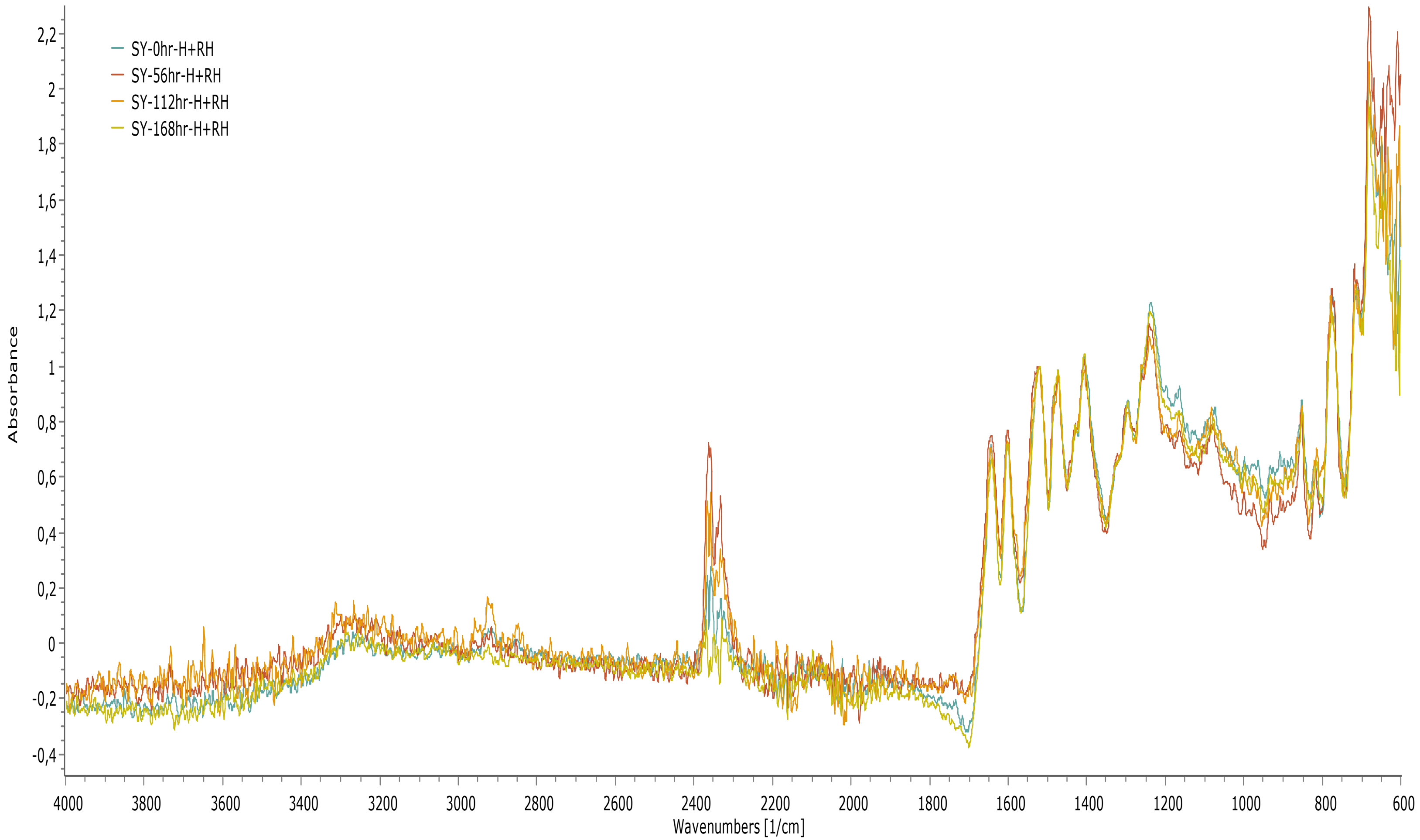


Figure A-19: ATR-FTIR spectrum showing absorbance peaks of SY fibrous layer after H+RH ageing

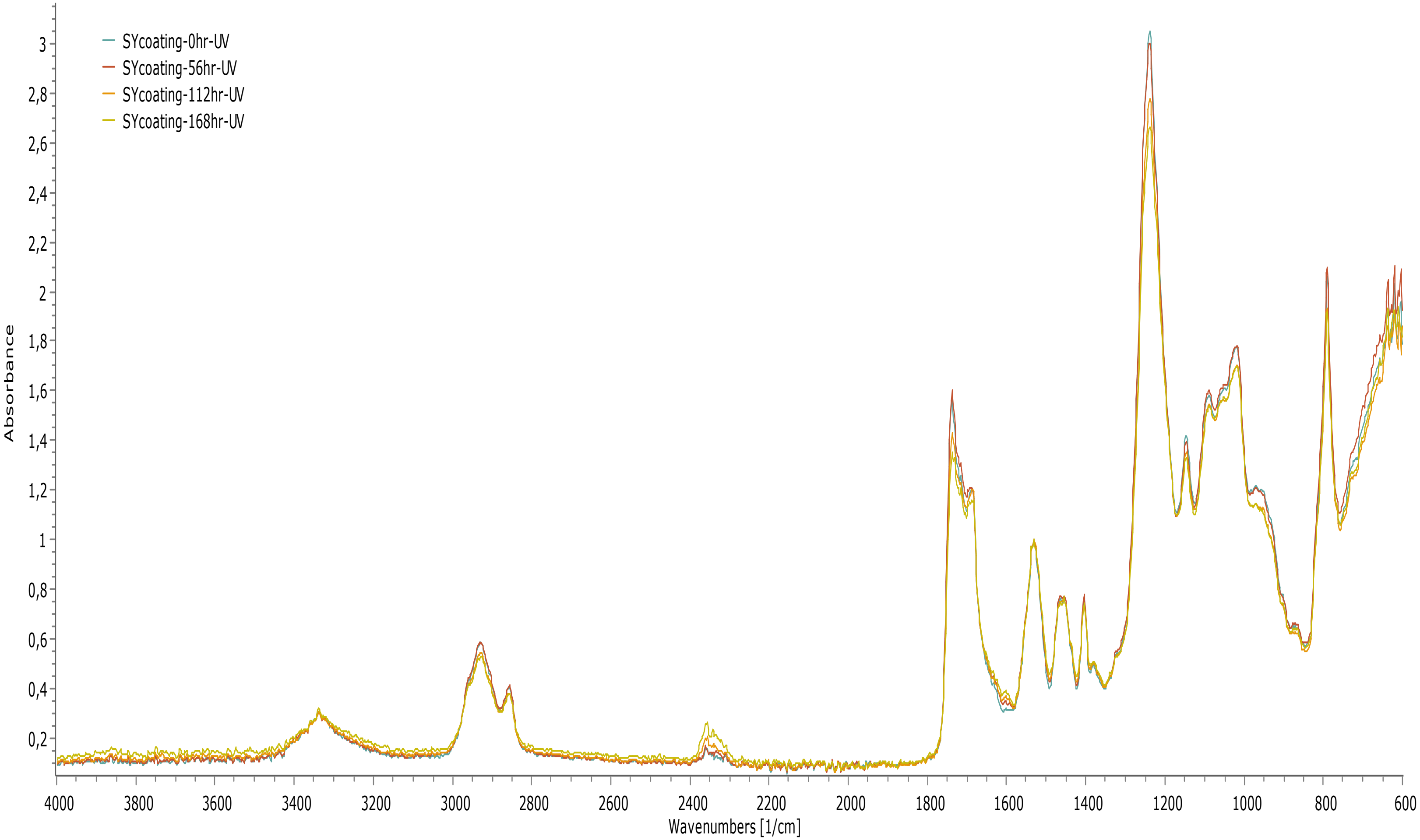


Figure A-20: ATR-FTIR spectrum showing absorbance peaks of SY coating after UV ageing

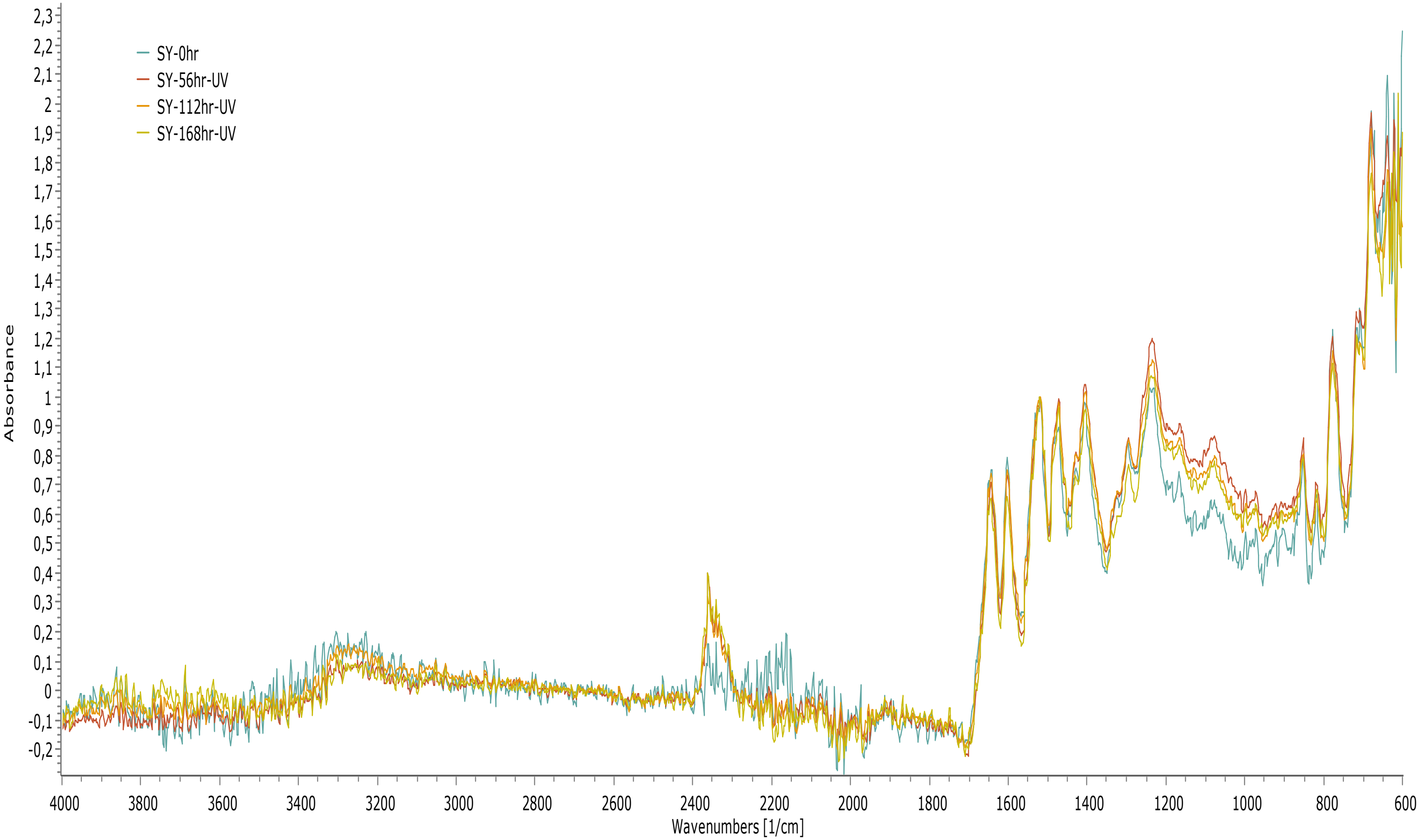


Figure A-21: ATR-FTIR spectrum showing absorbance peaks of SY fibrous layer after UV ageing

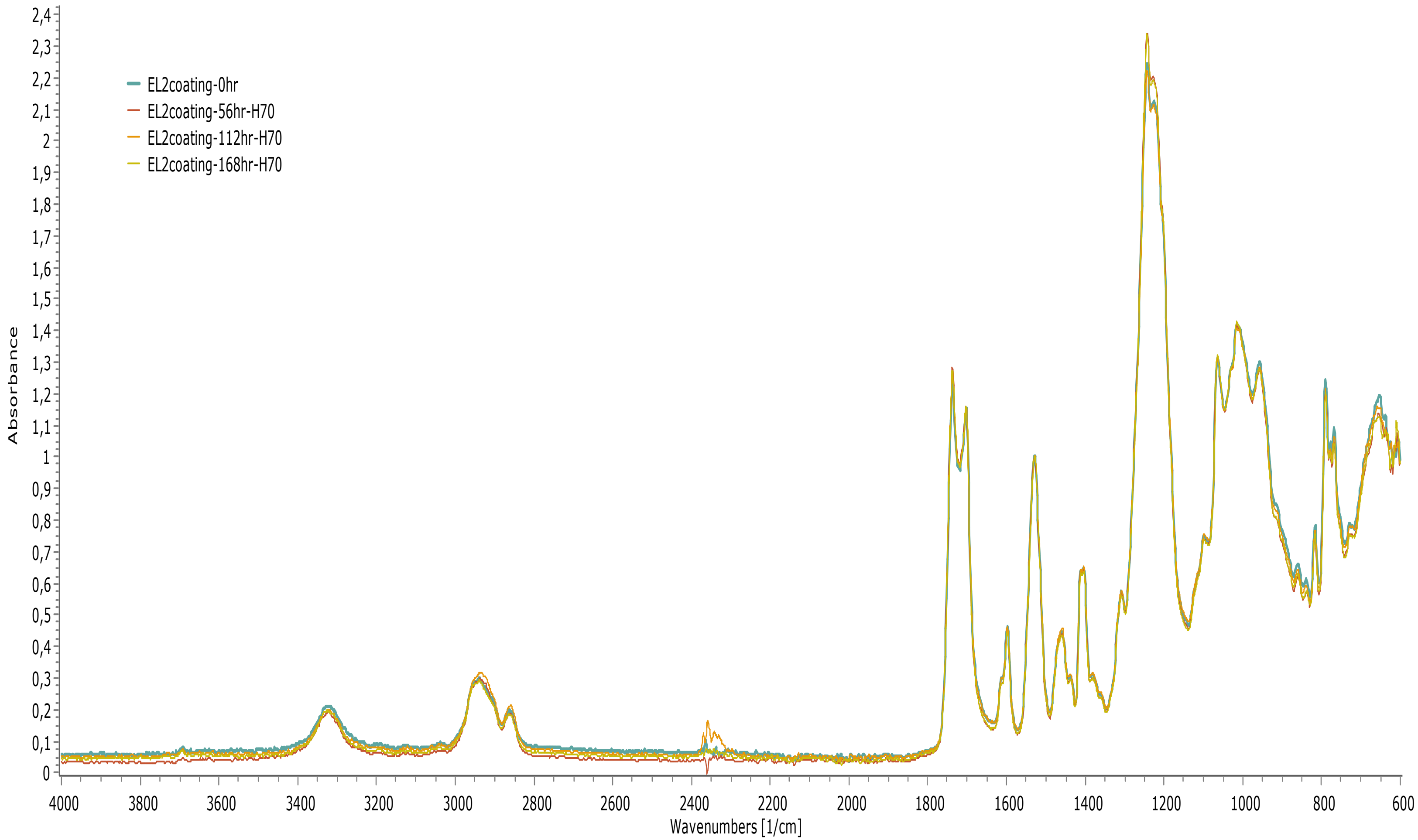


Figure A-22: ATR-FTIR spectrum showing absorbance peaks of EL2 coating after H70 ageing

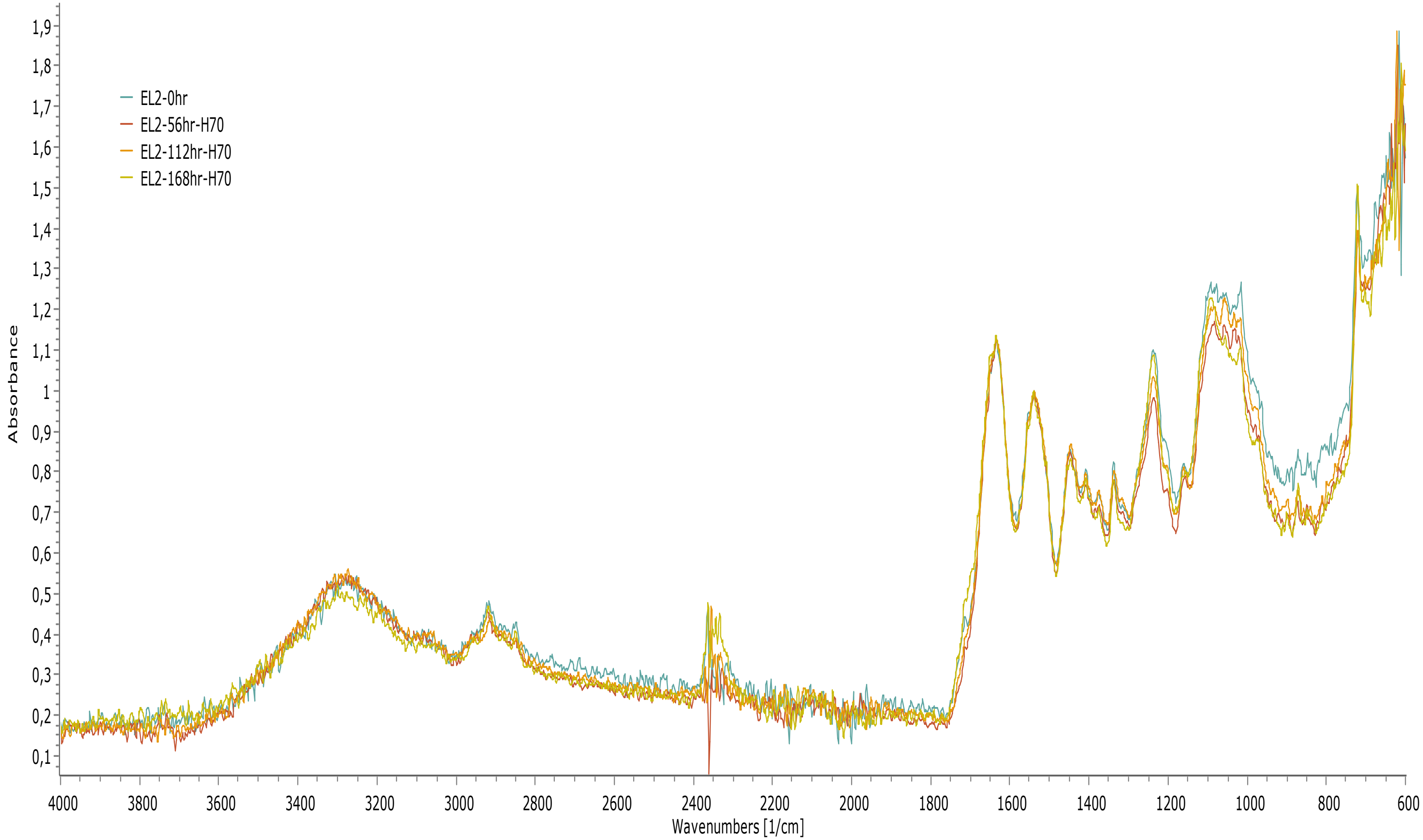


Figure A-23: ATR-FTIR spectrum showing absorbance peaks of EL2 fibrous layer after H70 ageing

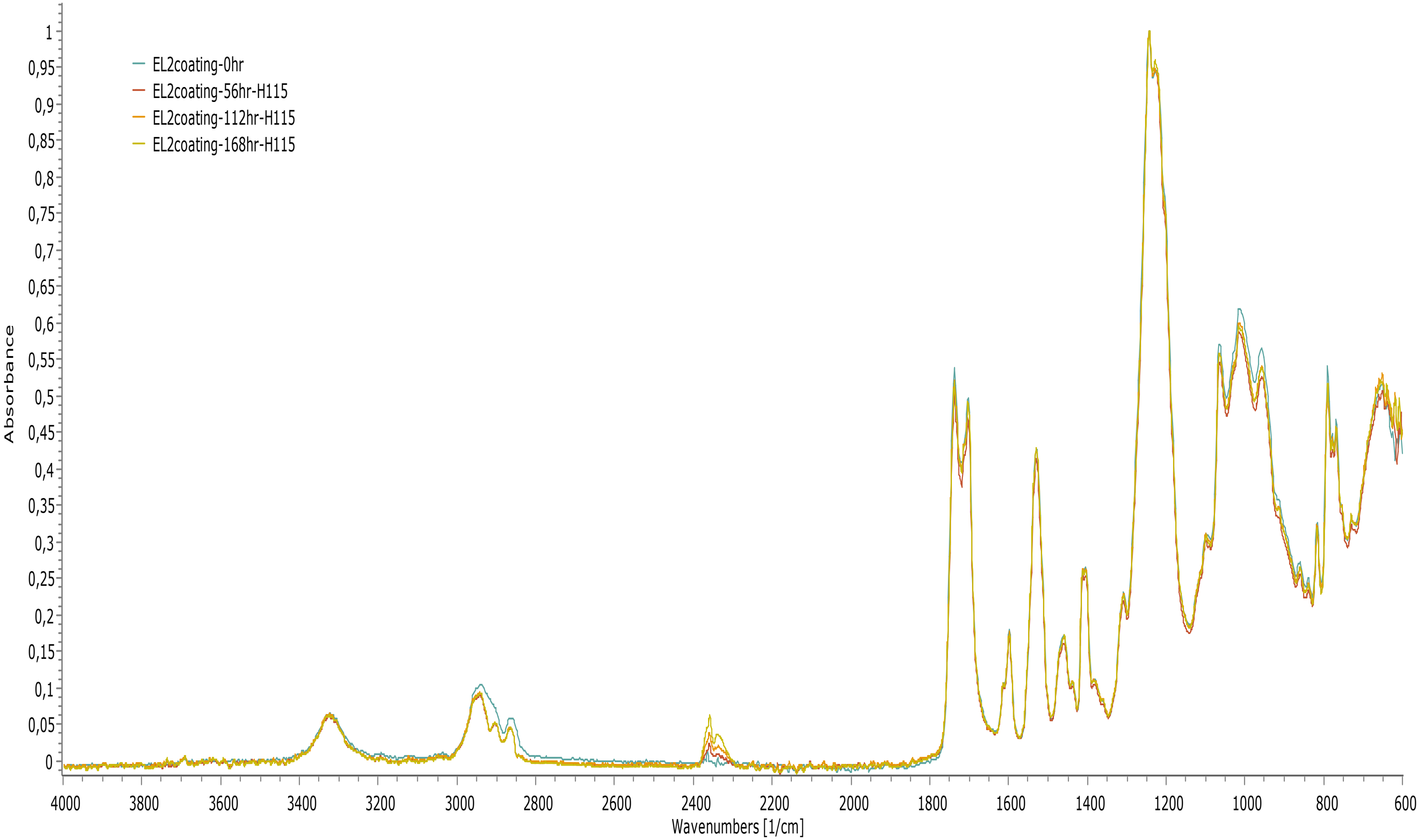


Figure A-24: ATR-FTIR spectrum showing absorbance peaks of EL2 coating after H115 ageing

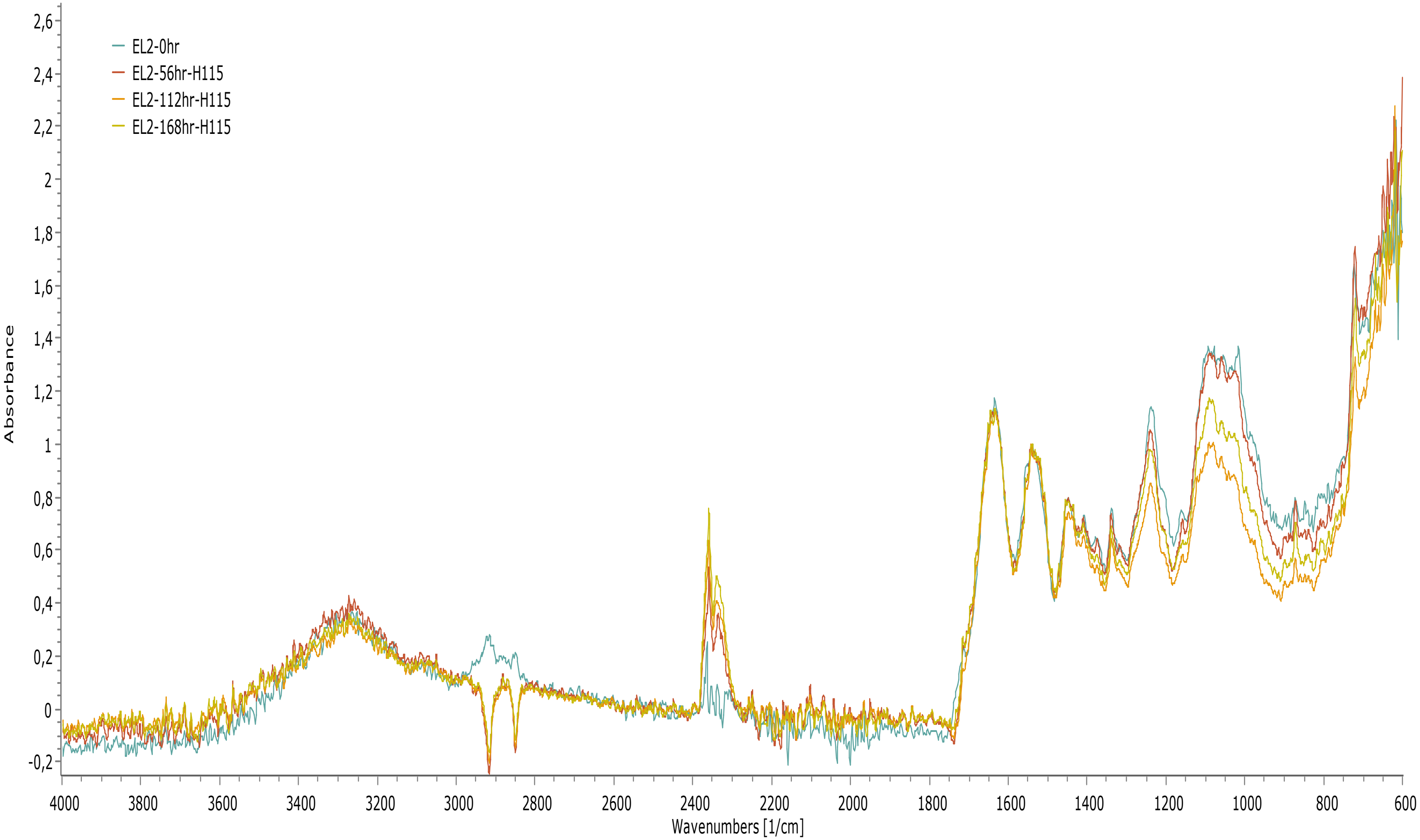


Figure A-25: ATR-FTIR spectrum showing absorbance peaks of EL2 fibrous layer after H115 ageing

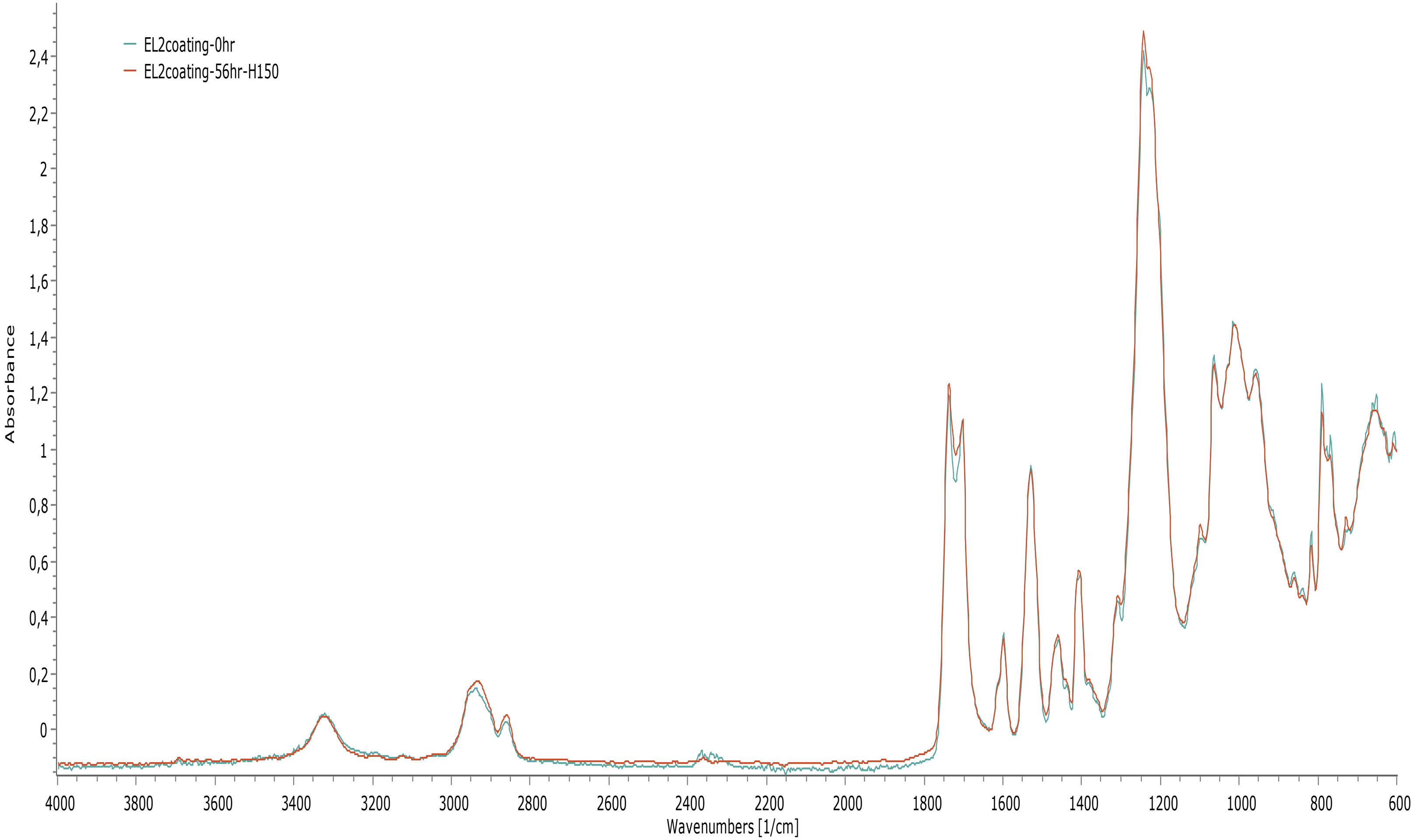


Figure A-26: ATR-FTIR spectrum showing absorbance peaks of EL2 coating after H150 ageing

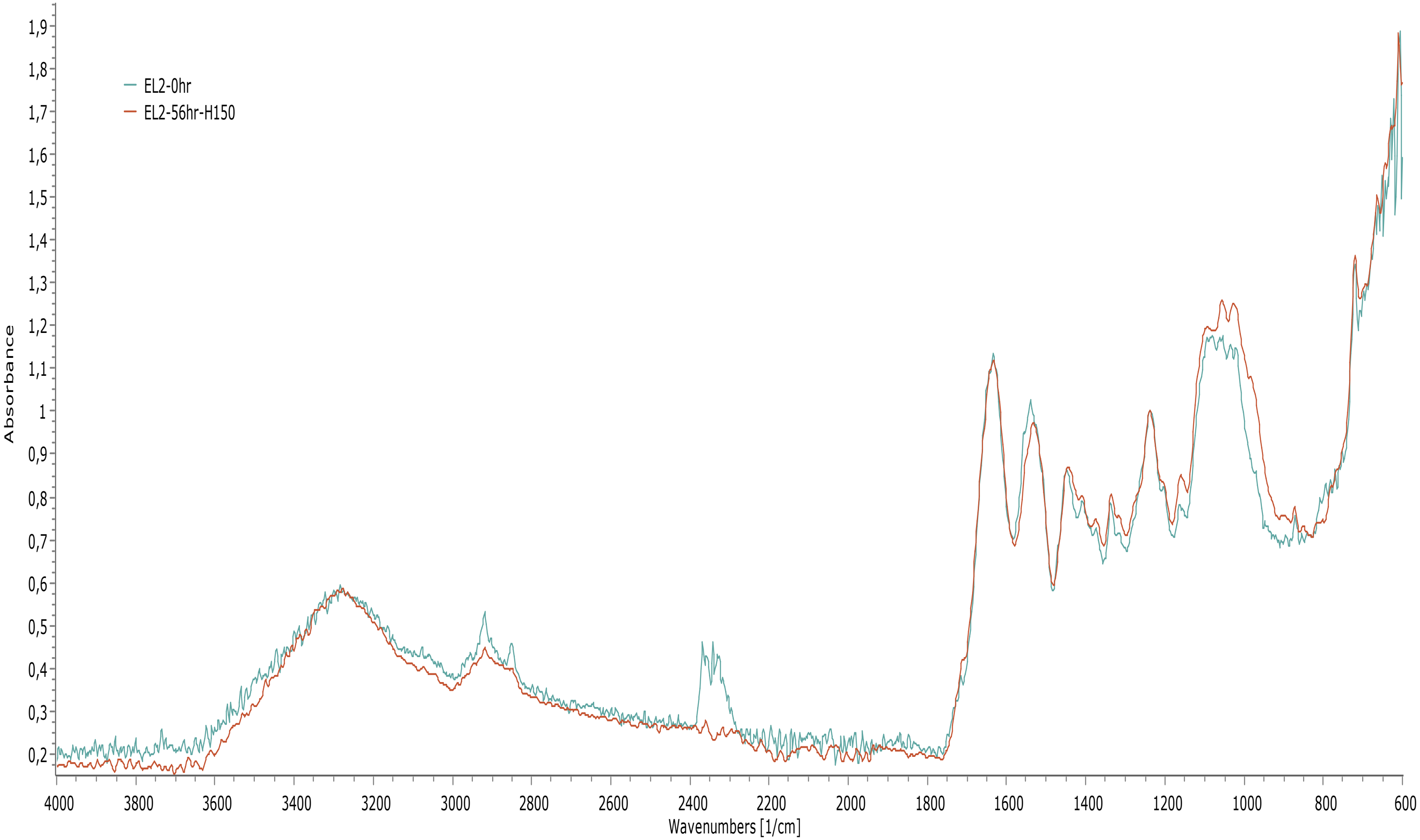


Figure A-27: ATR-FTIR spectrum showing absorbance peaks of EL2 fibrous layer after H150 ageing

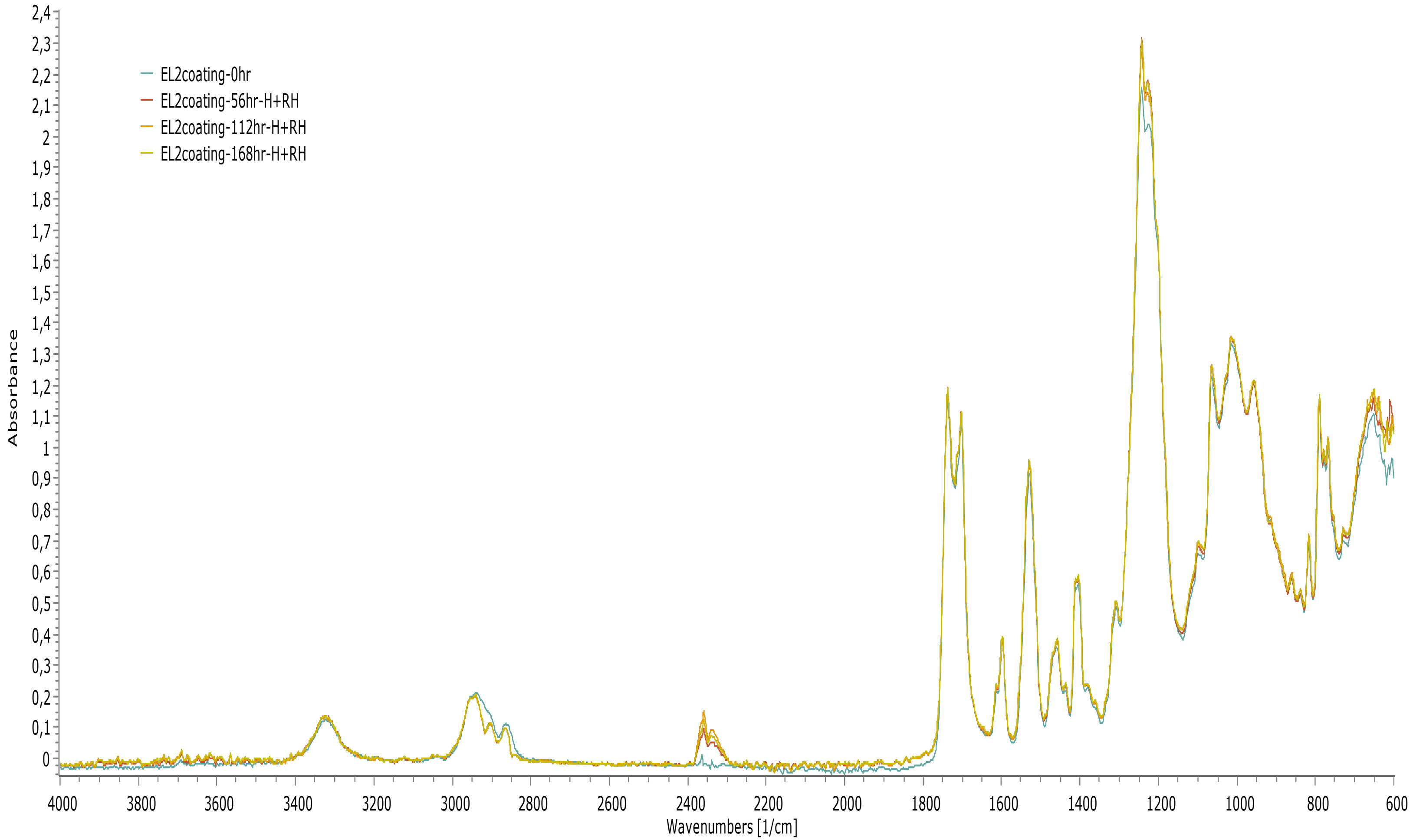


Figure A-28: ATR-FTIR spectrum showing absorbance peaks of EL2 coating after H+RH ageing

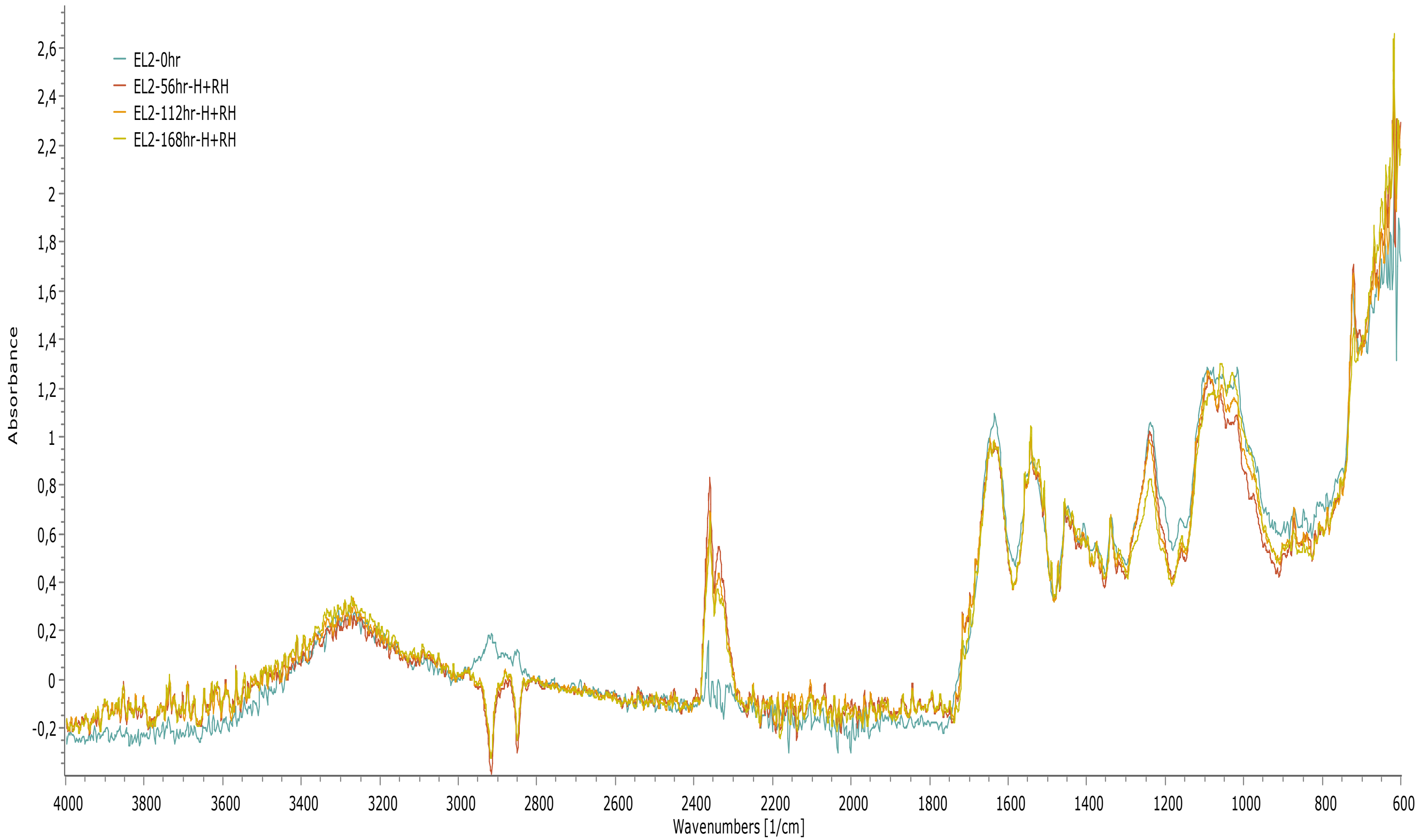


Figure A-29: ATR-FTIR spectrum showing absorbance peaks of EL2 fibrous layer after H+RH ageing

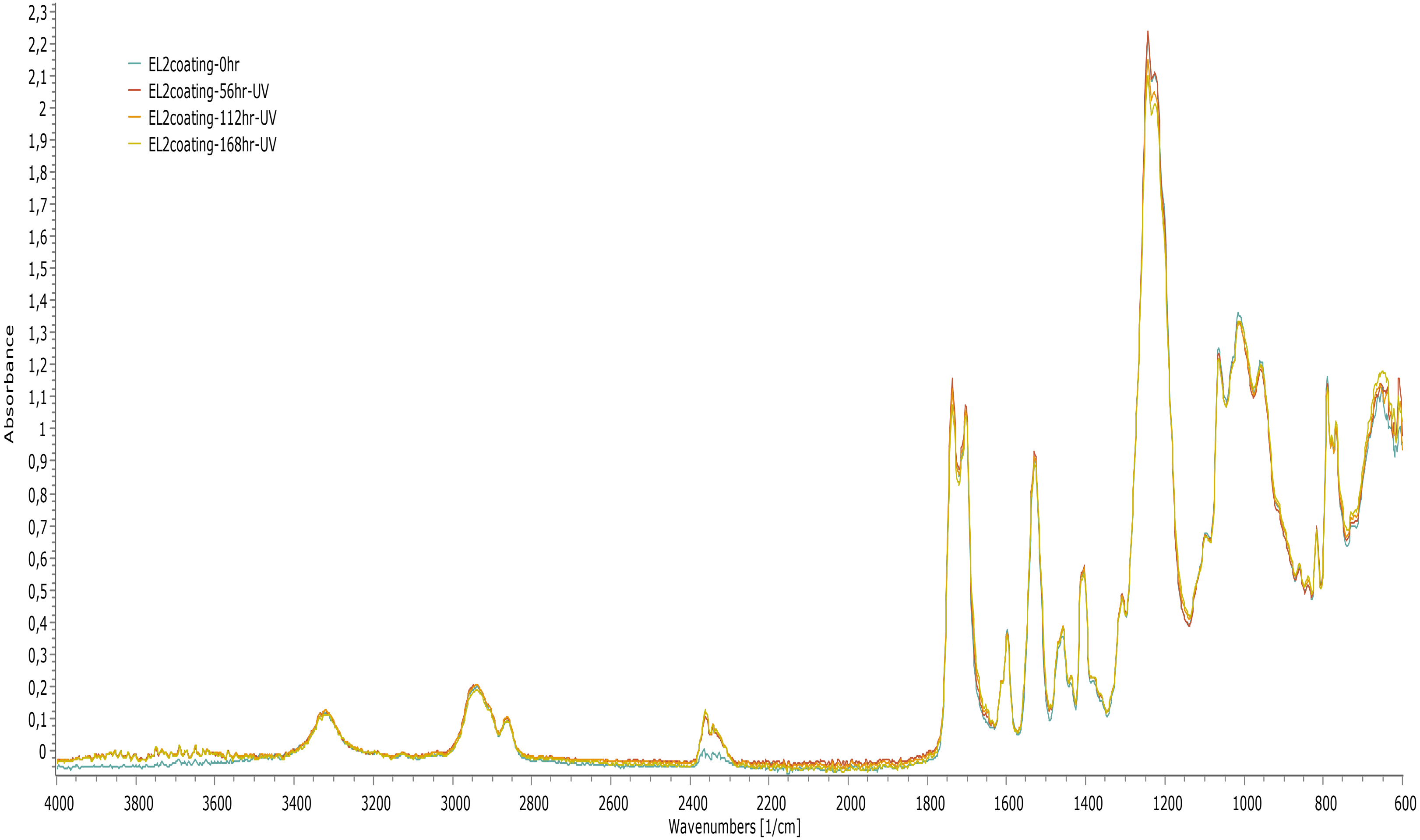


Figure A-30: ATR-FTIR spectrum showing absorbance peaks of EL2 coating after UV ageing

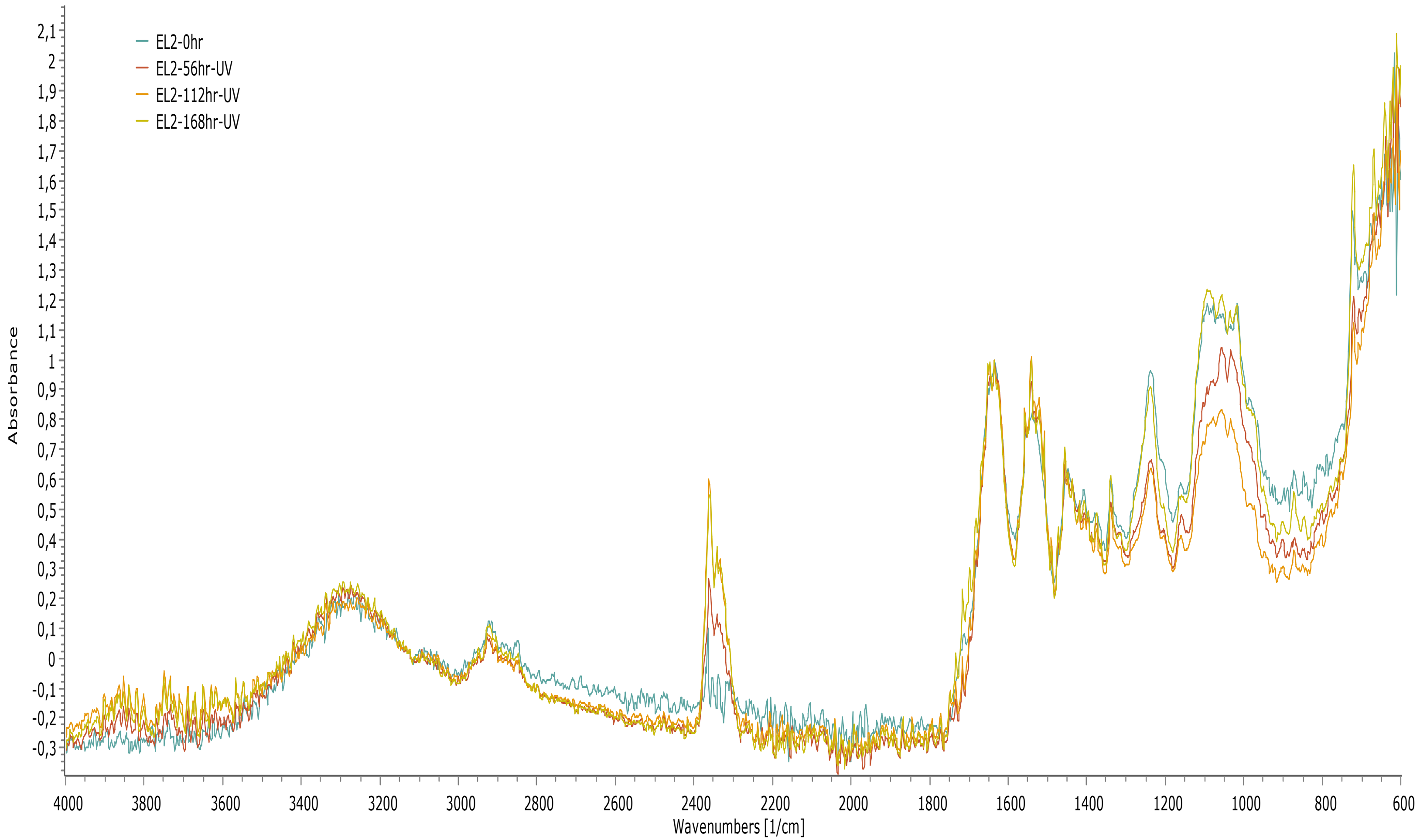


Figure A-31: ATR-FTIR spectrum showing absorbance peaks of EL2 fibrous layer after UV ageing

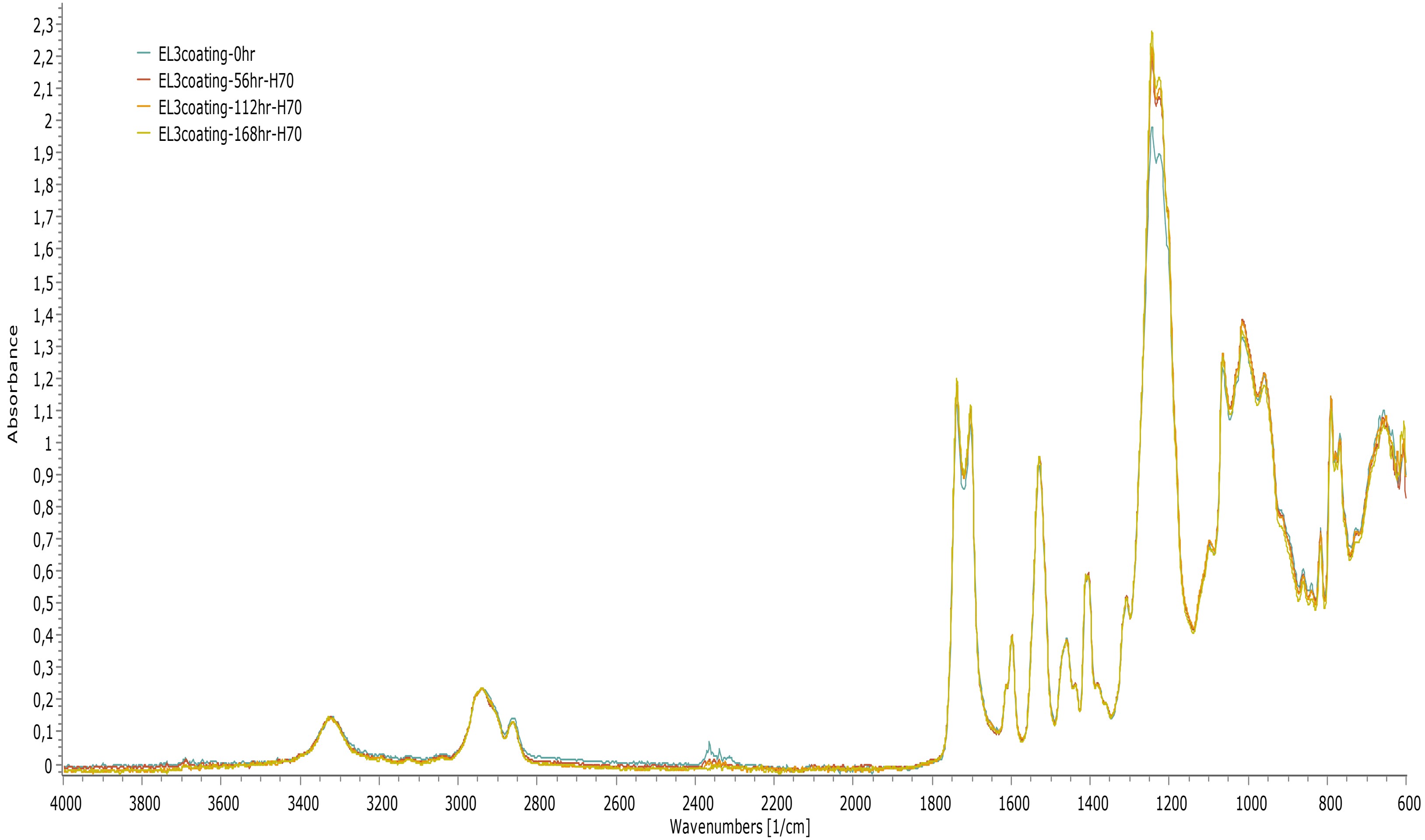


Figure A-32: ATR-FTIR spectrum showing absorbance peaks of EL3 coating after H70 ageing

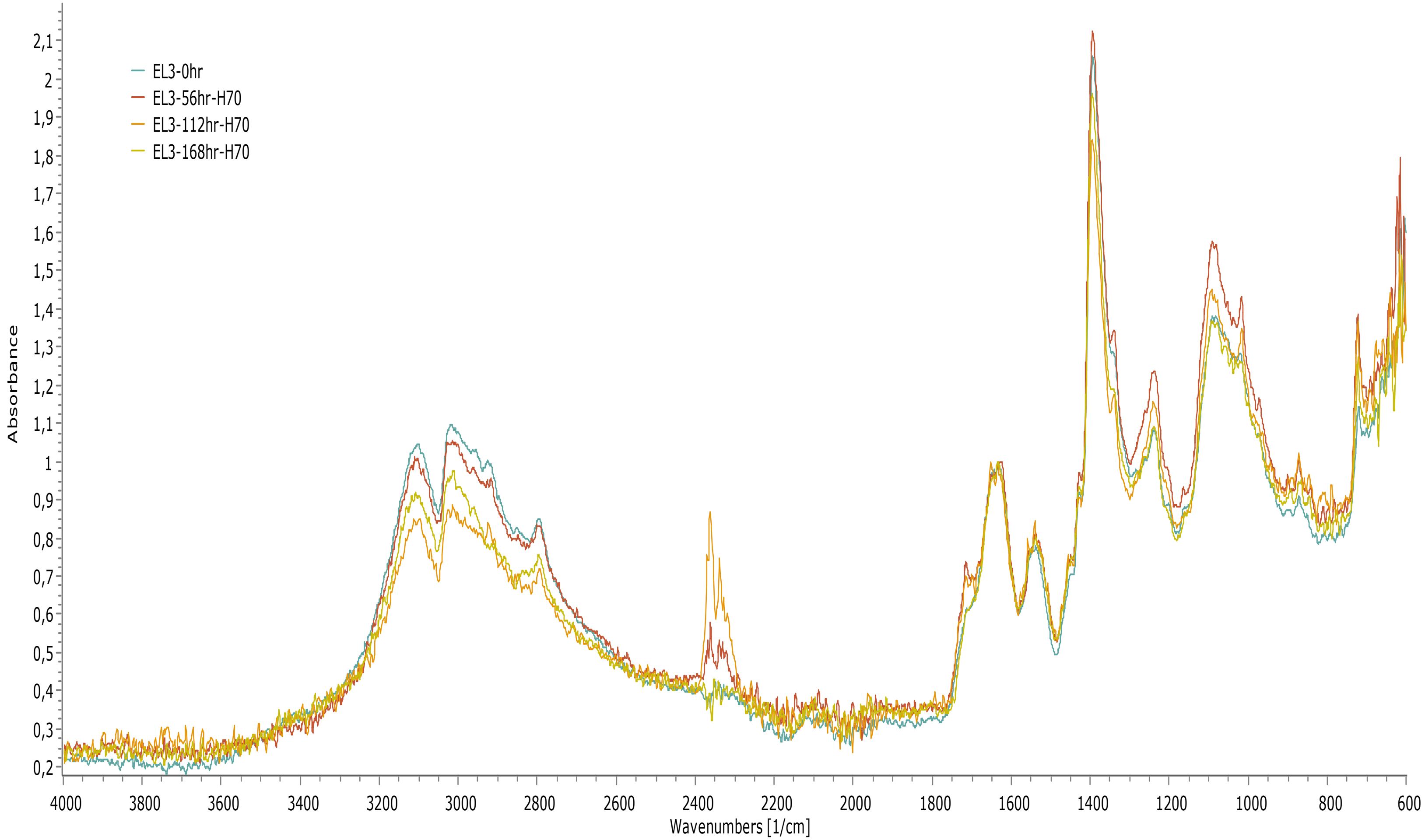


Figure A-33: ATR-FTIR spectrum showing absorbance peaks of EL3 fibrous layer after H70 ageing

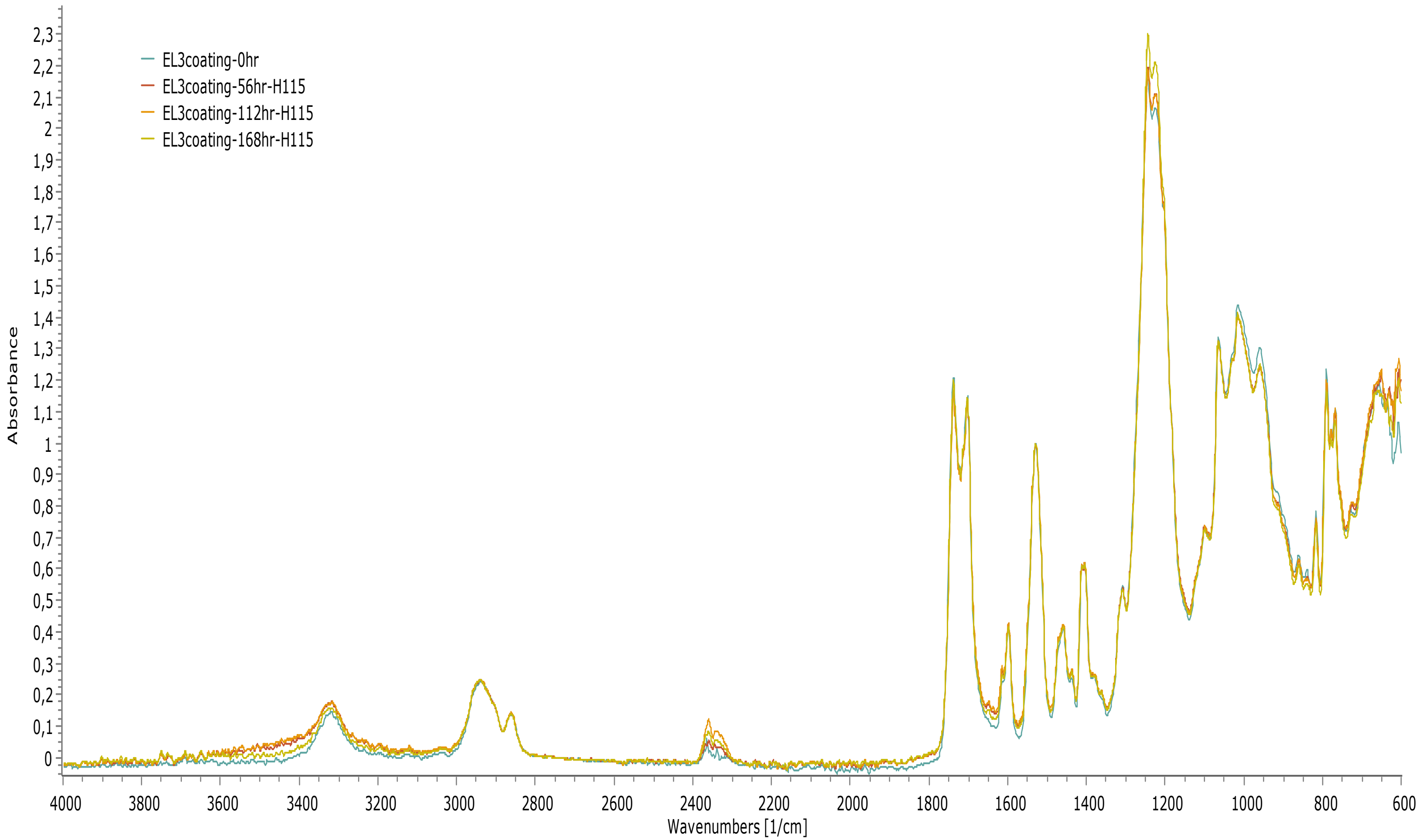


Figure A-34: ATR-FTIR spectrum showing absorbance peaks of EL3 coating after H115 ageing

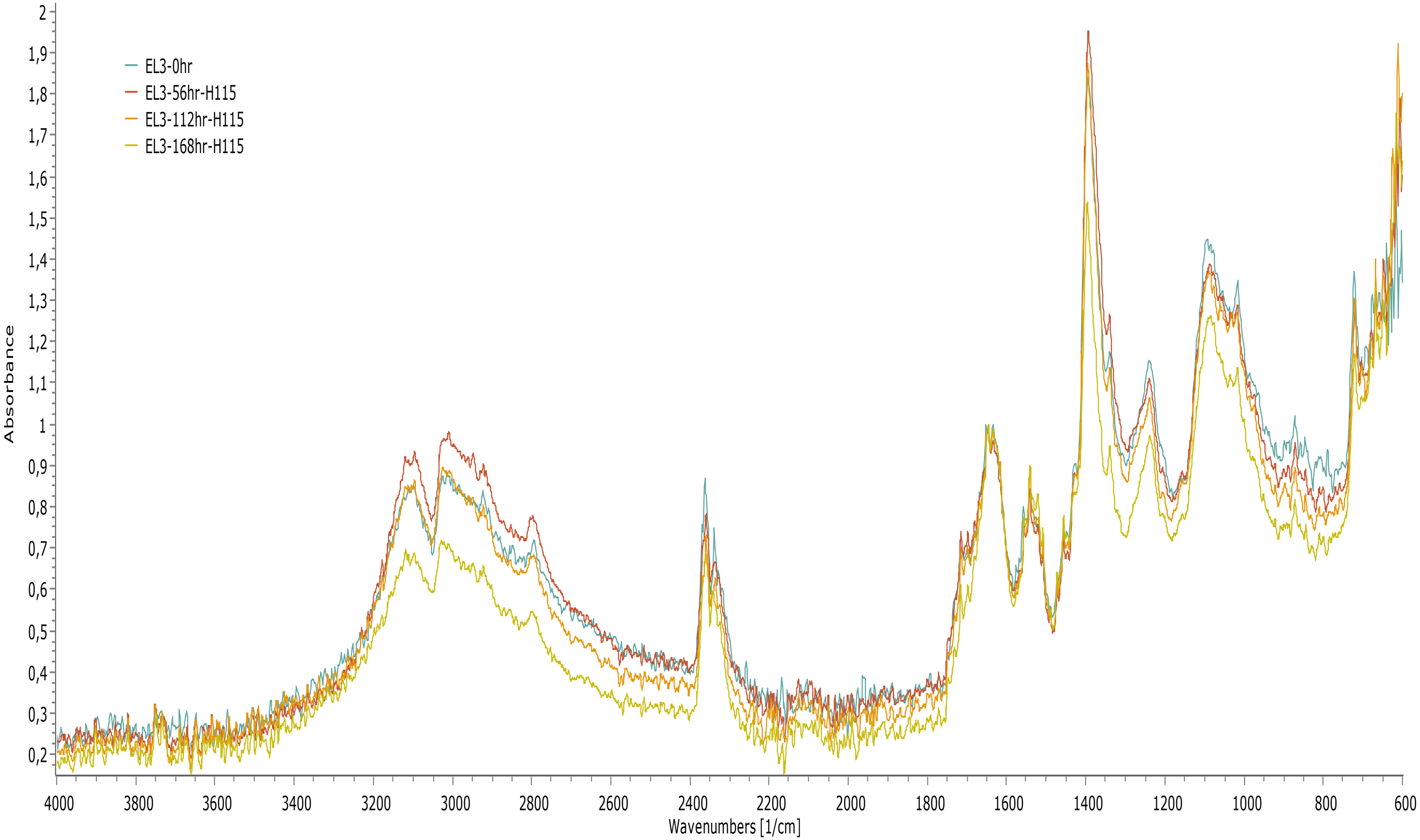


Figure A-35: ATR-FTIR spectrum showing absorbance peaks of EL3 fibrous layer after H115 ageing

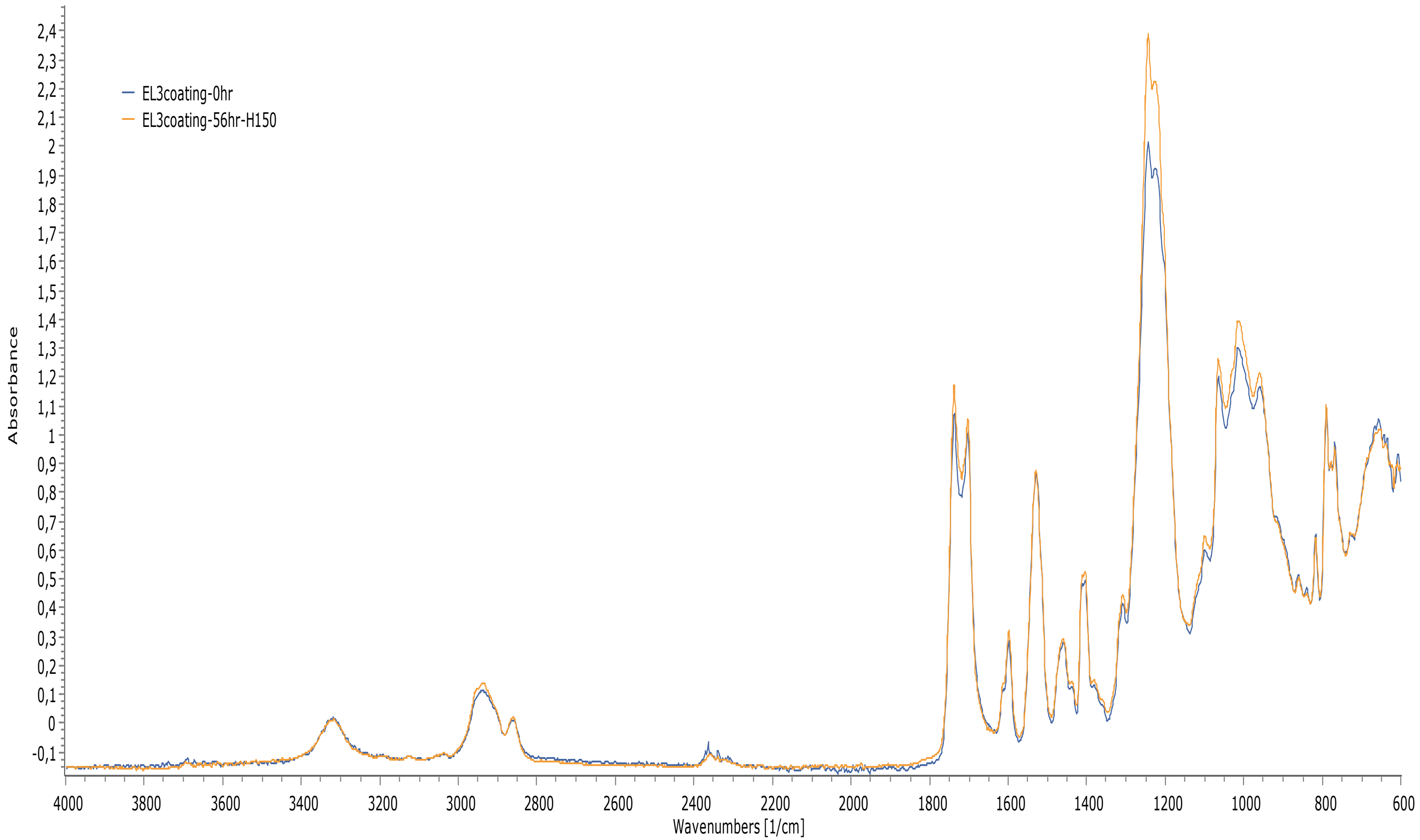


Figure A-36: ATR-FTIR spectrum showing absorbance peaks of EL3 coating after H150 ageing

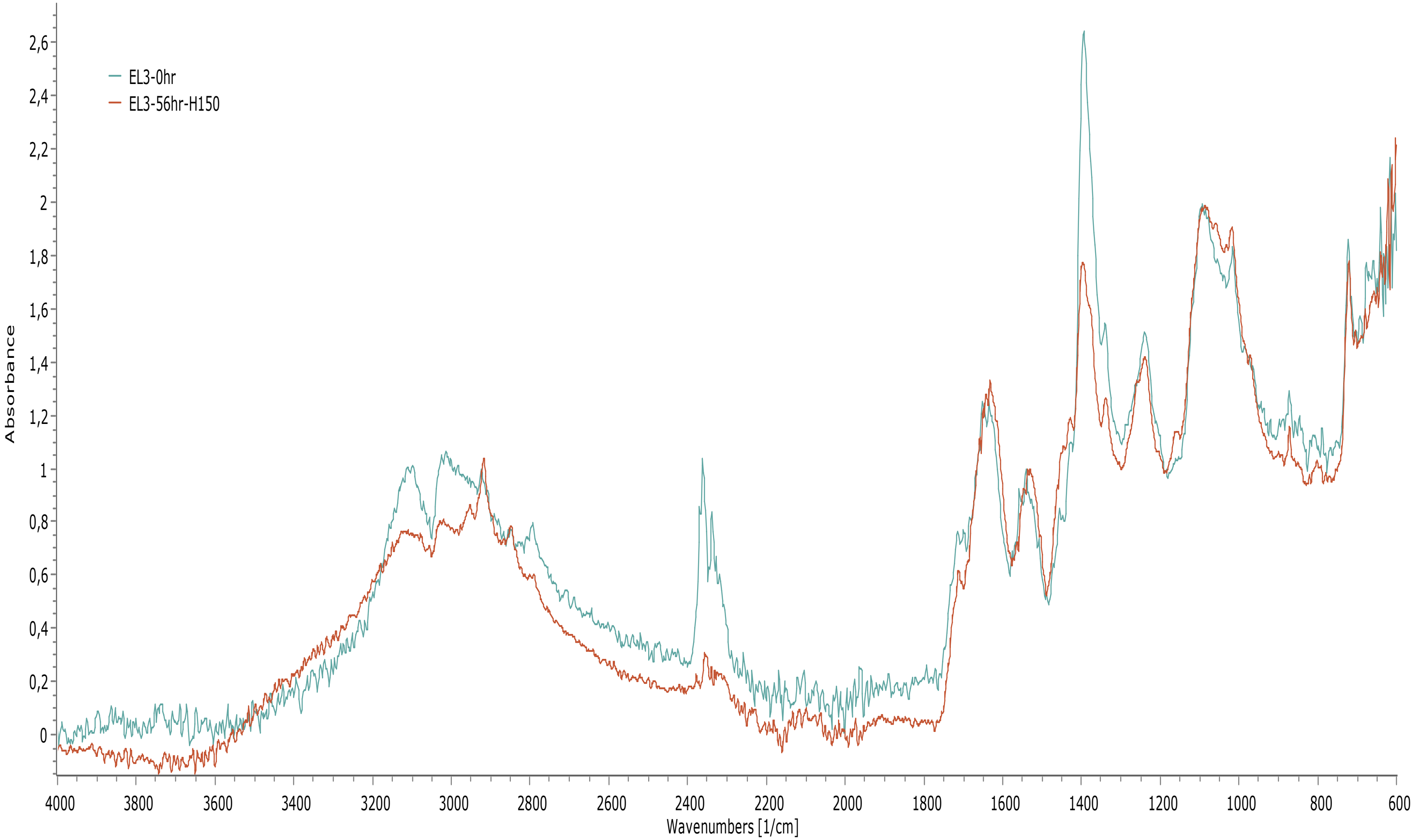


Figure A-37: ATR-FTIR spectrum showing absorbance peaks of EL3 fibrous layer after H150 ageing

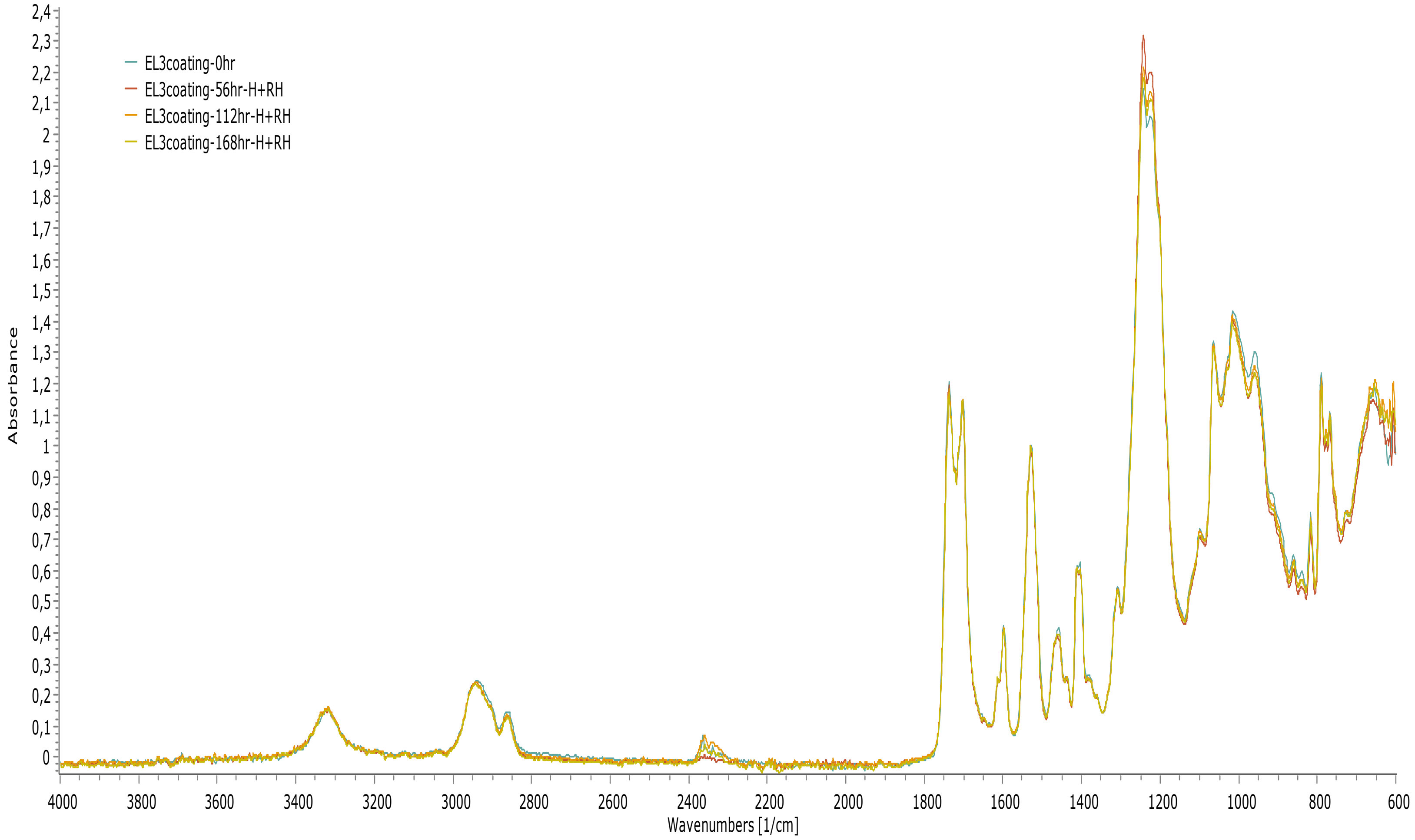


Figure A-38: ATR-FTIR spectrum showing absorbance peaks of EL3 coating after H+RH ageing

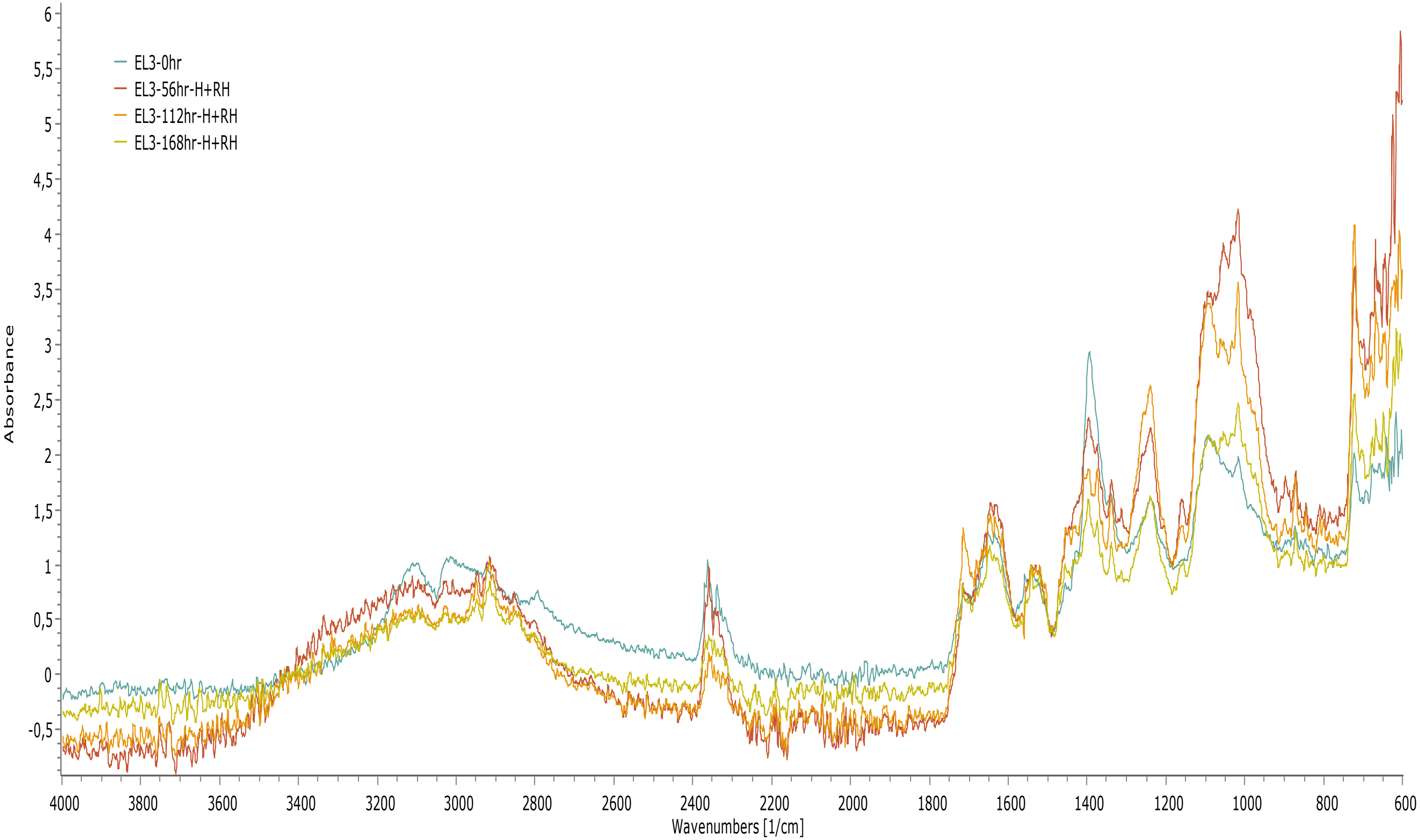


Figure A-39: ATR-FTIR spectrum showing absorbance peaks of EL3 fibrous layer after H+RH ageing

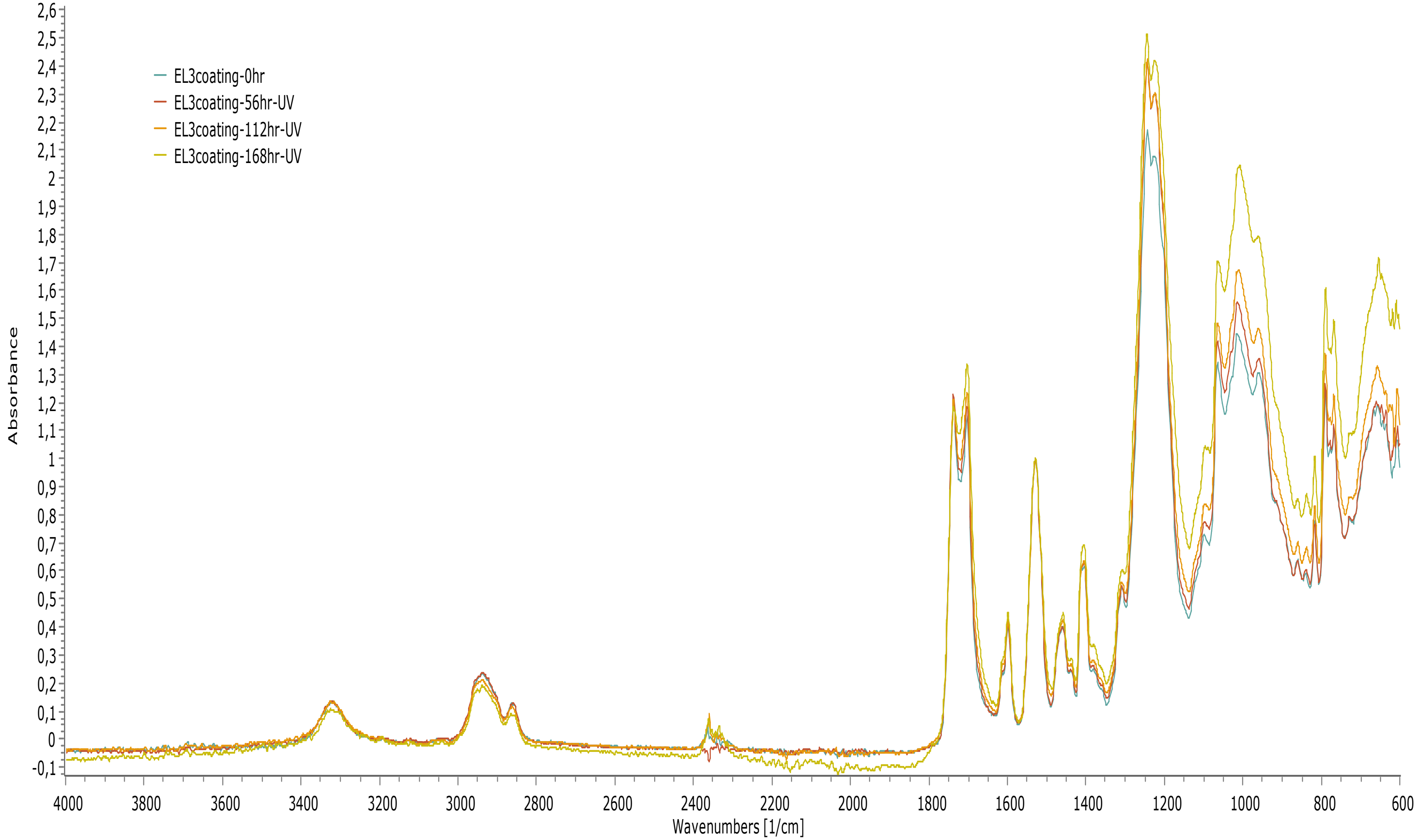


Figure A-40: ATR-FTIR spectrum showing absorbance peaks of EL3 coating after UV ageing

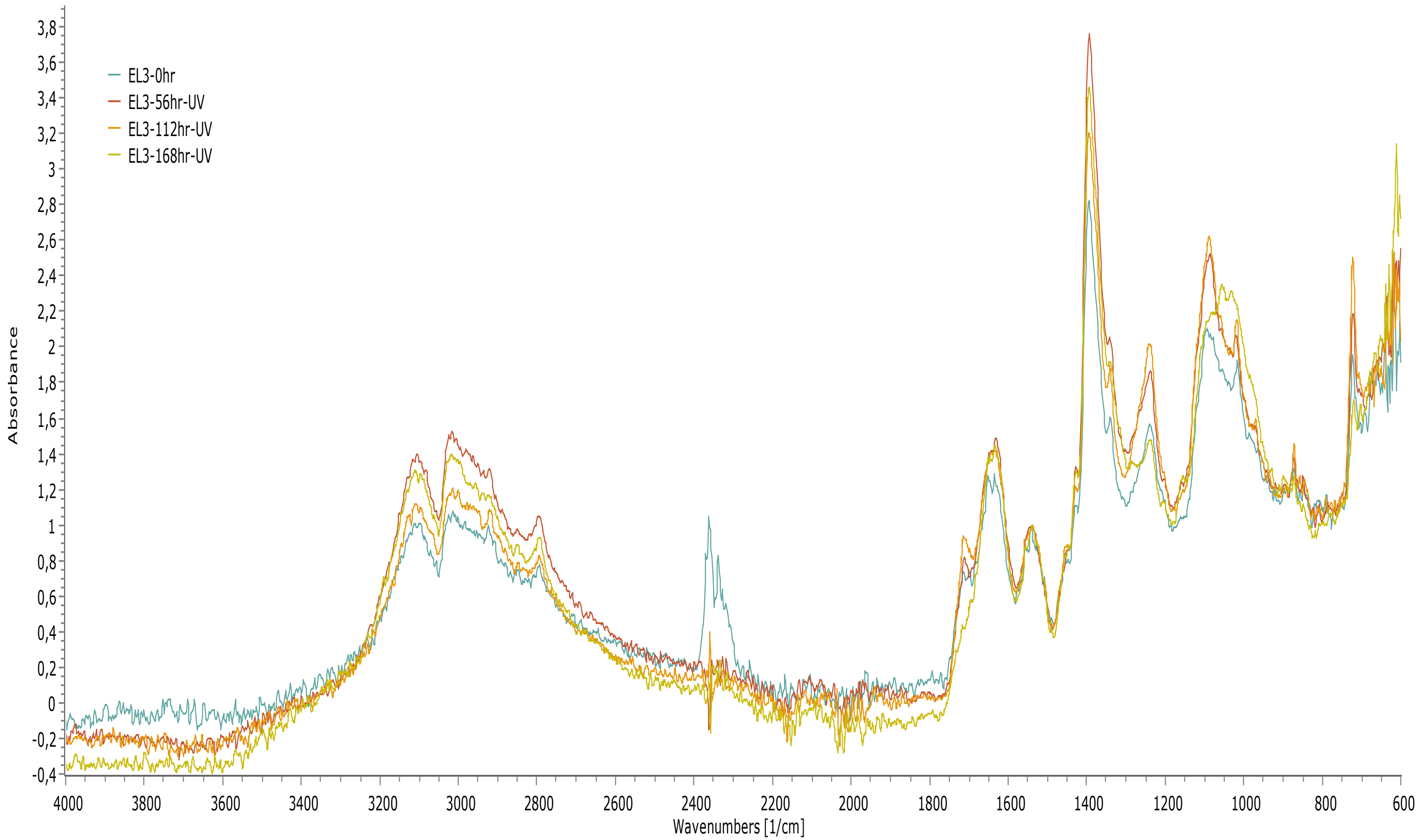


Figure A-41: ATR-FTIR spectrum showing absorbance peaks of EL3 fibrous layer after UV ageing