Liquid repellent finishing in outdoor apparel: chemical management, environmental concerns and performance testing

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The candidate confirms that the work submitted is 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.

Sections of this thesis have been published in the following publication:

1. Hill, P.J., Taylor, M., Goswami, P. & Blackburn, R. S. (2017). Substitution of PFAS chemistry in outdoor apparel and the impact on repellency performance. *Chemosphere,* 181, pp. 500-507.

Hill initiated, planned and carried out the study gathering all materials needed, performing experimental work, data analysis and lead role in authoring the paper. Taylor, Goswami and Blackburn assisted in data analysis, authoring and reviewing.

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Schellenberger and Hill jointly planned the collaborative study, completed experimental work and shared a role in authoring the paper. Levenstam completed laboratory work using the spray test and all other authors assisted in authoring and reviewing of the paper.

“I just knew somehow I could do it. And it was up to me to prove it”
Amy Johnson within the Kendal Mountain Film Festival trailer (2015)

To all the strong-willed, determined and inspirational women in my life.

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Abstract

Liquid repellency is a key textile function for outdoor apparel. Chemistry based on long side-chain fluorinated polymers has been used for repellent textile finishing since the 1950s but in the last two decades has been significantly highlighted for its toxicological potential. This study addresses the move to shorter side-chain fluorinated polymers and non-fluorinated chemistries for repellent finishing specifically addressing the requirements in technical outdoor apparel. In light of the complexities between functionality, legislation and corporate social responsibility, this research has investigated consumer practises and requirements in relation to, and comparison of, the technical performance of long side-chain fluorinated Durable Water Repellents (DWRs), shorter side-chain fluorinated DWRs and non-fluorinated DWRs.

A comparative study on initial repellency functionality showed non-fluorinated DWRs to be inferior in terms of oil repellency but offering similar water repellency. The impact of consumer laundering was studied with a comparison on the influence of differing drying/heat applications. Differences in maintaining liquid repellency functionality of fluorinated and non-fluorinated DWRs, during consumer laundering, have been discussed with surface mechanisms influencing this explained.

This work has identified limitations with the standard spray test method and given modifications to quantify between similar performing repellent fabrics. Calculation of mass increase, calculated after the spray test shower, has been used throughout this work to quantify the wetting of samples. In addition, the use of analytical evaluation by determining the roll-off angle during dynamic wetting has been considered. A comparative study between the spray test and the Bundesmann ran-shower test was carried out but water repellency data differed between the two methods. An extended spray test has been developed to aid discrimination between similarly performing water repellent samples, with a shower time of 60 and 120 minutes recommended.

Adaptations to the Martindale test method simulated abrasion to terrain and adjacent apparel replicating rubbing of the face fabric during consumer end-use. The repeated rubbing created roughness of the fabric face decreasing the repellent functionality.

The relationship between DWRs and thermoregulation has been explored and greater heat loss during rain conditions determined with a build-up of moisture vapour due to a decreased driving force across the outer shell. Further work in this area is strongly recommended.

The main conclusions from this work are to reconsider the use of DWRs and the level of functionality necessary for end-use, the importance of laundering to maintain functionality and the necessity to develop knowledge and communication between brands and consumers. It is hoped that this work has contributed to the ongoing dialogue surrounding chemistry use for liquid repellent textile finishing and will be useful to testing and adoption as, in line with legislation, the move to non-fluorinated DWRs increases.

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Abbreviations

CSR: Corporate social responsibility

D4: Octamethylcyclotetrasiloxane

D5: Decamethylcyclopentasiloxane

DMU: De Montfort University

DWR: Durable Water Repellent

ECF: Electrochemical fluorination

ECHA: European Chemicals Agency

EOG: European Outdoor Group

EU: European Union

FTOHs: Fluorotelomer alcohols

IR: Infrared

LC-MS: Liquid chromatography-mass spectrometry

NGOs: Non-governmental organisations

OECD: Organisation for Economic, Co-operation and Development

PA: Polyamide

PDMS: Polydimethylsiloxane

PEO: Polyethylene oxide

PES: Polyester

PFAAs: Perfluoroalkyl acids

PFASs: Per- and polyfluoroalkyl substances

PFBS: Perfluorobutane sulfonic acid

PFCAs: Perfluoroalkyl carboxylic acids

PFDA: Perfluorodecanoic acid

PFHxA: Perfluorohexanoic acid

PFHxS: Perfluorohexane sulfonic acid

PFNA: Perfluorononanoic acid

PFOA: Perfluorooctanoic acid

PFOS: Perfluorooctanesulfonic acid

PFSAs: Perfluoroalkane sulfonic acids

PFTeA: Perfluorotetradecanoic acid

PFUnDA: Perfluoroundecanoic acid

PTFE: Polytetrafluoroethylene

PU: Polyurethane

REACH: Registration, evaluation, authorisation and restriction of chemicals

RH: Relative humidity

SEM-EDX: Scanning electron microscopy with Energy-dispersive X-ray spectroscopy

ST: Surface thickness

TDIs: Tolerable Daily Intakes

U.S. EPA: U. S. Environmental Protection Agency

UNEP: United Nations Environment Programme

Chapter 1 - Literature review

1.1. Introduction

Mountaineers have been pushing the limits of ‘the possible’ for many decades, exploring mountain ranges and stretching their psychological and physiological boundaries. Without suitable protective clothing and equipment, some of the greatest mountaineering achievements would not have been possible. The involvement of physiologist Griffith Pugh in the 1953 British Everest expedition first highlighted the importance of clothing to physiological performance and health and safety of the mountaineers [1]. He was consulted to assist in the development of equipment and clothing, and his involvement in the expedition played a key part in its success drawing awareness to the importance of developing appropriate clothing.

Clothes are the first line of defence against the elements [2] and outdoor apparel should maintain wearer thermal comfort whilst providing protection from the external environment [3–5]. Wetting of clothing negatively affects insulation and causes accelerated cooling of the wearer [6]. According to Sport England, there are currently 100,000 people participating in mountaineering[*] in the UK on a weekly basis [7]. With these high participation figures, as well as a broad range of outdoor activities being pursued with varying levels of physical exertion, clothing fit for purpose in varying weather conditions is essential for wearer wellbeing. In extreme situations, clothing functionality can be a matter of life and death [8]. In addition, outdoor apparel clothing is not solely purchased by mountaineers, but worn daily by a wide range of consumers.

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[*] Sport England define ‘Mountaineering’ to include indoor climbing, rock climbing, high altitude mountaineering, hill and mountain walking, and bouldering.

As a result, the market of outdoor apparel is consistently growing currently valued at €5.86 billion (with a 7% annual growth) [9].

Liquid repellent finishing of outdoor apparel is a key fabric function causing rain droplets to bead away from the surface rather than lie on and penetrate the outer fabric face. As a chemical wet finishing process, an aqueous polymeric emulsion is applied as a durable water repellent (DWR) to the textile surface. Traditionally, long side-chain fluorinated polymer DWRs have been used, based on per-and polyfluoroalkyl substances (PFASs), since the 1950s imparting a highly durable and stable finish that exhibits a high level of liquid repellency against a range of water and oil-based liquids [10]. With over 100,000 chemicals used in products and processes within our everyday lives, we as consumers can take the functionality they provide for granted [11–13]; of all global chemical production, 25% are used within the textile and clothing industry supply chain [14]. Wet textile chemical processing is a key environmental concern due to the release of potentially hazardous chemicals into watercourses, degradation of chemicals during their lifecycle, and use of unsustainable resources. The chemical class of PFASs has been heavily criticised due to polymer by-products that have been shown to be persistent, bio-accumulative and of concern causing adverse effects within the environment, to wildlife and to human health. Progressively, use of PFAS chemistry is being stringently regulated within the EU and America. Social compliance and environmental issues are at the fore with non-governmental organisations (NGOs) insisting on change and consumers are becoming more informed on sustainability.

Since 2002, 21600 peer-reviewed research articles have been published on PFASs predominantly investigating long-chain PFASs and their precursors [15]. At least 4000 derivatives within the chemical class of PFASs are believed to be on the global market [16]. Used in a wide variety of consumer and industrial products, these include fire-fighting foams, cosmetics, electrical components, cookware and repellent textiles. Due to this, it is a complex subject involving a number of environmental, health and science disciplines as well as corporate social responsibility (CSR). Shorter-chain analogues and non-fluorinated chemistries have been developed as replacements, but their toxicological potential, hazards and risks are yet to be fully understood [15,17]. In addition, their liquid repellent functionality has not been fully evaluated, particularly the longevity of repellency during end-use.

Liquid repellency of textiles can be determined by both analytical assessment and laboratory textile testing. Whilst many test methods have been developed to evaluate liquid repellency, the spray test (BS EN ISO 4920:2012/AATCC 22-2014) is most widely used due to its reproducibility and convenience [18,19]. Conventional evaluation of liquid repellency tests the fabric just after manufacture and determines its future functionality from this assessment. With wetting of clothing, due to insufficient liquid repellency, affecting the thermal comfort of the wearer, it is essential that ‘new’ liquid repellent chemistries are evaluated rigorously for, ultimately, wearer health and safety.

This literature review will establish the context of this research project discussing the use of liquid repellent fabrics specifically in outdoor apparel. This review will discuss the need for liquid repellent clothing for outdoor activities and current test methods to determine this functionality. It will explain the use of PFASs in liquid repellent finishing for outdoor apparel and the extensive criticism, legislation and development in scientific understanding concerning the widespread use of this particular chemical class.

1.1.1 Terminology

PFASs refers to the complete class of per- and polyfluoroalkyl substances. A multitude of terms and acronyms are used within academia and industry when discussing the use of fluorinated polymers and the class of PFASs. ‘PFCs’ is the acronym most widely used but the definition is unclear. The terminology offered by Buck *et al.* [10] has been used throughout this work.

1.2 The development and use of liquid repellent outdoor apparel

Liquid repellency has been a desirable function for decades providing protection to the wearer from the weather and environment. Seal skin and seal or whale intestines were used as repellent clothing whilst remaining breathable (Figure 1.1) [20]. In the 19th century, coating or varnishing fabrics with oils, waxes and resins rendered a waterproof finish predominantly for seafaring garments and equipment [20]. Oiled cotton became the norm in the 1800s but a patent granted in 1823, involving molten rubber being coated between two layers of fabric, revolutionised repellent apparel and would be known as the Macintosh coat [8,20]. Vulcanised rubber was used throughout military outerwear until tightly woven twill gabardine by Thomas Burberry was used within the trench coats of World War I (Figure 1.1) [8]. During World War II, Ventile was introduced, a densely woven cotton fabric of which the interstices between the weave close when in contact with water. This created a barrier to water preventing prolonged personnel exposure to cold water sea conditions and was used widely by the Royal Air Force.

(a) (b)

Military or Naval Catalogues Post Free on request.

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Figure 1.1: Liquid repellent garments have been desirable for centuries: (a) seal or whale intestine used as an outer garment; (b) Burberry trench coat used in World War I [21,22].

Post World War II, expeditions to summit Everest were seen as the regeneration of a nation, showcasing the knowledge and ability of Britain to the world in the form of a new frontier of exploration [23]. The advancement of performance textiles ran alongside an evolving interest in mountaineering. Between the 1920s-1960s, mountains were perceived as symbols of national status, demonstrating the possibilities and skills of a nation [8]. The successful summiting of Everest in 1953 was a heroic event announced at the coronation of Queen Elizabeth II [23]. Despite reservations that scientific research interfered with the purity of man's achievement, advancement and innovation in performance textiles have been fundamental in the pursuit of peaks in extreme and isolating environments, with Griffith Pugh pioneering research on the effect of mountainous environments on human physiology [1]. Innovation in textiles and the progression in mountaineering are closely associated; without the development of synthetic fibres and technical finishing the functionality of outdoor apparel would not be sufficient.

1.2.1 Participation in the outdoors

A growth in participation in outdoor recreational activities has been demonstrated by participatory numbers in outdoor competitions and events, the growth of indoor climbing[†] walls and increase in participation in mountaineering training courses [24]. Hill walking is the most common activity across all ages, with many participating in a combination of outdoor activities [24]. Mountaineers are involved as 'athletes' for brands showcasing their expeditions and initialising development of specific apparel to their needs. With the surge in social media channels, both brands and mountaineers are constantly visible to a large audience of recreational outdoor participants.

Individuals who take part in outdoor sports do so informally, under no obligation to either register or obtain permission to partake and therefore participation cannot be

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[†] Between 2010-2014 there was a 30% growth in indoor climbing walls [24].

definitively quantified. However, nearly 9 million people in the UK are involved in outdoor activities, with over 100,000 people either climbing or hill-walking weekly [7,24,25].

1.2.1.1 Mountaineering

Mountaineering encompasses a number of outdoor sports including hiking, winter hiking, scrambling, traditional climbing and multi-day expeditions. The demands on the mountaineer differ by activity, weather conditions, location and route choice. Clothing provides the mountaineer with protection from the environment whilst aiding regulation of thermal comfort [2]. Committing to a route, means that the mountaineer must dress appropriately for the varied external environmental conditions to be encountered and the changing levels of body heat and moisture generated [2]. Climbing mountains has no obvious purpose besides pushing physicality to limits, addiction and a sense of achievement [26,27]. Amongst the mountaineering community, the psychological aspects and risk can outweigh the physical and physiological concerns. In these situations, clothing becomes a tertiary concern expected to work and function regardless of the wearer’s physiological work, risk and activity.

1.2.1.2 Weather conditions

Britain, as an island, experiences a varied maritime climate with rapidly changing weather. In remote conditions and in the midst of winter temperatures can be sub-zero and conditions barely survivable [28]. Whilst air temperatures may not be at extreme lows, humid air and winds from the Atlantic Ocean with high wind speeds present changeable conditions. Variability in the British weather is due to the different air masses meeting over the country with frequent cloud and high annual rain fall: 1000 mm annual rainfall in England and Wales and over 1600 mm annual rainfall in Scotland [29].

Precipitation is liquid droplets of atmospheric moisture vapour from warm air rising and condensing. When moist air cools, clouds are formed and raindrops are produced from the condensed and accumulating water vapour. Air has a maximum capacity of water vapour it can hold (known as the saturation vapour pressure) and this increases in line with temperature. Warmer air has a greater capacity to contain water vapour and as it cools the saturation vapour pressure is reached with moisture vapour condensing to form clouds and precipitation. Frontal rain is common in the UK where two air masses, of different temperatures, meet and the warmer air cools resulting in clouds and rain droplets. Cloud cover is commonly formed by condensing moist air rising from the Atlantic Ocean; therefore, rainfall is greater on the west of the UK (Figure 1.2) where a large proportion of the mountainous regions are situated.

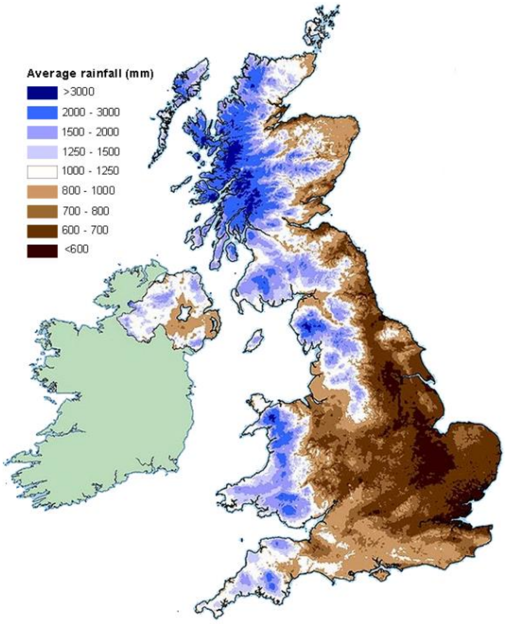

Figure 1.2: Average rainfall across the UK 1981-2000 with greater rainfall across the West and mountainous areas [30].

Greater rainfall coincides with higher ground where there is more cloud cover [28]; moist air is forced upwards meeting colder air and producing cloud with potential precipitation. In addition, ambient temperature decreases with ascent causing warm air to cool as it rises. The topography of the land causes formation of clouds and orographic rain is produced as a result (Figure 1.3). With cloud cover common in mountainous environments there is therefore a high potential for precipitation. Precipitation does not occur at a specific temperature although the type of precipitation is dependent on the ambient temperature in which it falls. Precipitation differs from a light drizzle to torrential downpour and frozen precipitation including snow, ice and hail; all of which can occur in varying degrees of intensity and time periods. In addition, wind can drive the precipitation directionally and at speed. Within a mountainous environment, remoteness and lack of protection/shelter are additional variables to consider and ultimately determine survival should bad weather occur. Rain can affect any participant in outdoor recreation from drizzle to heavy snowfall. Conditions can differ greatly with height gain and, despite best preparation and consultation of weather forecasts, the participant may still be caught out in adverse weather.

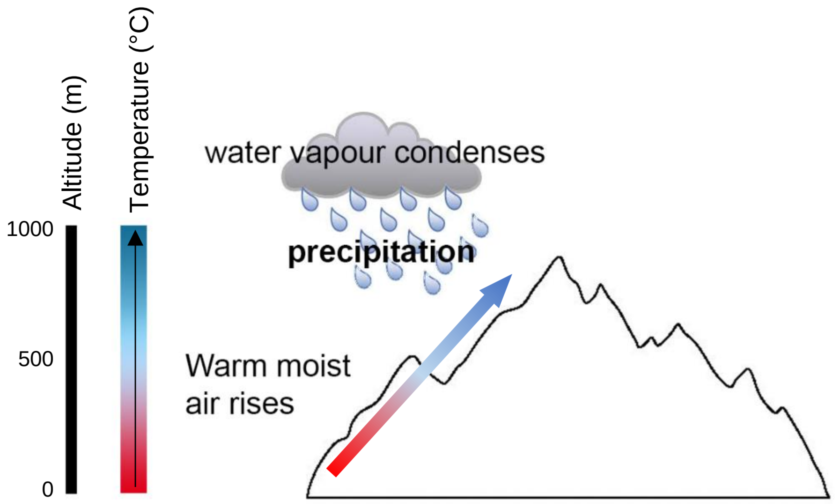

Figure 1.3: Orographic precipitation caused by the formation of the land, common in mountainous environments, adapted from [28,31].

1.2.2 The Clothing system

The interaction between the body, the environment and the clothes worn (clothing system) is a dynamic relationship. Throughout activity, the body has to continue working efficiently with increased body temperature, increased perspiration, increased heart rate and increased respiratory rate. Clothing should provide the wearer with protection whilst maintaining wearer comfort in terms of sensorial comfort and thermophysiological comfort. Layering systems are well accepted as typical in outdoor clothing, being adaptable to a wide range of weathers and maintaining wearer comfort throughout wear. Clothing layers should allow transfer of moisture vapour and body heat through the clothing system and provide protection from environmental conditions, such as wind and rain (Figure 1.4). Between the clothing and the body, a microclimate region is created with its own temperature, humidity and air movement. Clothing layers, for outdoor activity, are normally categorised as base layer, mid layer and outer layer.

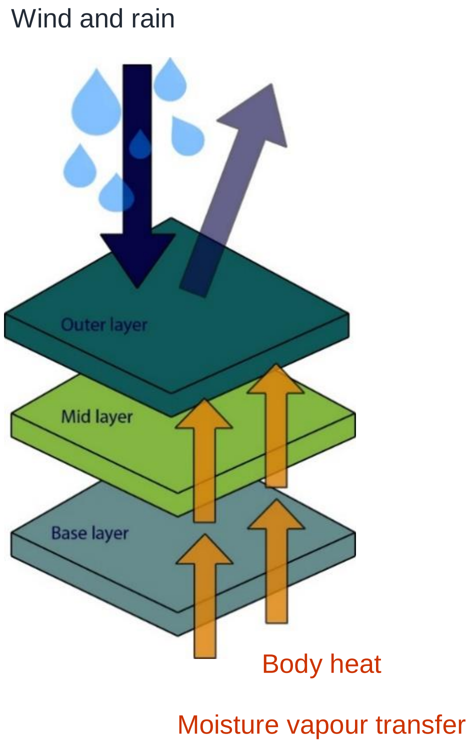

Figure 1.4: The clothing layering system, transfer of body heat and moisture vapour transfer through the layers and protection from environmental conditions.

The base layer is worn next to the skin assisting thermophysiological comfort and sensorial comfort. Whilst, levels of perspiration (or moisture vapour) will differ according to the level of activity and climatic differential, wicking properties are essential to transfer this away from the skin. Traditionally, the mid-layer has been made from polyester or polyamide in a fleece construction. The mid layer is worn over the base layer and its predominant function is to provide insulation whilst allowing transfer of moisture vapour through the clothing system. The outer layer, or ‘shell’ layer, should protect the wearer from the environmental conditions, providing protection from rain or wind, and provide abrasion resistance to the whole clothing system [32]. Additionally, the outer layer of clothing should allow transfer of moisture vapour to/from other layers to dissipate in the environment. Fit and design of the garment are important factors for wearer comfort facilitating movement and appropriate ventilation [33].

1.2.2.1 Waterproof breathable fabrics

Waterproof breathable fabrics are typically made from fabric constructions resisting the penetration of water but allowing the transfer of moisture vapour from the body. This type of fabric can be subdivided:

- *Tightly woven fabric*s – densely woven fabric structures [3]. Ventile (long cotton staple fibres) swells when wetted by water reducing the interstices and pores within the structure minimising movement of water. Tightly woven polyester (PES) or polyamide (PA) means that there are small pores within the fabric imparting inherent liquid repellent properties [3].
- *Microporous membranes or coatings* – thin films of polymer with interconnected holes allowing the transfer of moisture vapour but too small for the penetration of water droplets [3]. Made from polyurethane (PU) or polytetrafluoroethylene (PTFE) this technology is used widely within outer layers, most well-known being branded as GoreTex and eVent.
- *Hydrophilic membranes or coatings* – continuous impermeable membranes which rely on the diffusion gradient for transfer of moisture vapour through the hydrophilic segments [3,34]. Made from hydrophilic polyurethanes or polyesters with polyethylene oxide (PEO), the most well-known branded membrane is Sympatex [34]

Membranes are usually sandwiched between an outer and an inner fabric, although the inner fabric is occasionally omitted.

1.2.2.2 Liquid repellent chemical finish

A liquid repellent finish imparts liquid resistance to the outer fabric face. These are commonly termed as durable water repellents (DWRs). Applied to both the outer fabric face of waterproof breathable fabric constructions and on an abundance of other fabrics within outdoor apparel, the finish provides the initial resistance to water penetration. Liquid repellency within textiles is the resistance of the textile surface to polar and non-polar liquids. Water repellency specifically is the resistance to the absorption, wetting and penetration of water [35,36].

Liquid repellent treated fabrics are used in a number of outdoor apparel where protection from inclement conditions is required. Most associated with repellent jackets and trousers, DWR chemistries are applied to a number of outdoor clothing items to resist water and to prevent staining or blockage of the fabric structure by non-polar liquids/compounds inhibiting the moisture vapour transfer. Liquid repellent fabrics are also used within inner fabrics to prevent seam slippage or impart a better fabric handle, on zips and trims to prevent water penetrating in these areas, and to prevent synthetic or down insulation from getting wet from wicking through the fabric structure. Liquid repellent fabrics are also used on tents, rucksacks and footwear. Consumers subjectively assess the ability of repellent clothing by the ability of water to ‘bead’ (Figure 1.5). This is commonly attributed to the brand of membrane within the garment rather than consumer awareness that a DWR chemistry has been applied. A fabric which wets, or ‘wets out’, shows an insufficient DWR (Figure 1.6).

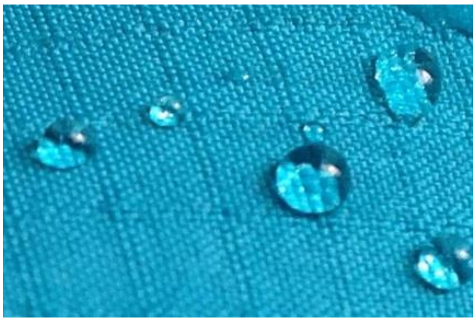

Figure 1.5: Water forms droplets on the fabric surface, referred to as ‘beading’.

Figure 1.6: The outer fabric face is wet by the water.

1.2.2.3 The soft shell and hard shell

The ‘soft-shell’ has evolved as an additional outerwear with a breathable repellent outer layer, excluding any membrane or laminate within the fabric construction [37]. A ‘hard-shell’ garment is marketed as offering full weather protection and includes a membrane or laminate within the fabric construction (Figure 1.7). To all shell garments, a DWR is applied to the outer fabric surface to impart liquid resistance and, within an outdoor environment, prevent the penetration or absorption of precipitation. These garments are worn in inclement conditions (Figure 1.8).

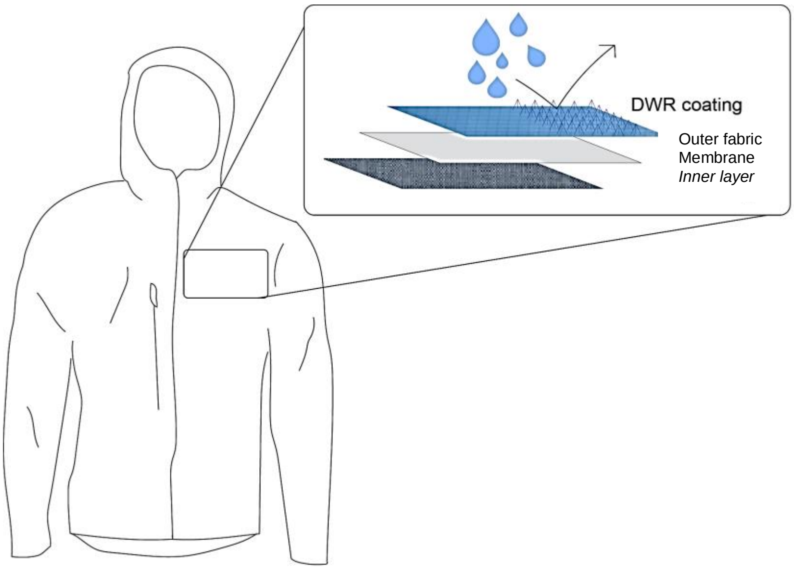

Figure 1.7: The fabric construction of a hard-shell repellent jacket including a membrane and an outer fabric with a DWR coating.

Figure 1.8: Uses of liquid repellent outdoor clothing – (a) winter mountaineering in Scotland in snowy and windy conditions; (b) traversing a route during a snow shower in foggy conditions; (c) rainy weather in which walkers wear both a repellent jacket and repellent trousers to keep dry; (d) climbing a gully in winter conditions where the body and clothing are in direct contact with the snow.

1.2.3 Maintaining thermal comfort

The body's core temperature strives to remain at a thermal equilibrium of 37 ºC [38]. Maintaining this equilibrium, with a fluctuation allowance of ~5 ºC (35-40 ºC), is key to thermoregulation [38,39]. Heat transfer from the body is affected by convection, radiation, conduction and evaporation between the body, clothing and the environment. A balance between production of metabolic heat and heat exchange to the environment is required to maintain thermal balance [3,40]. Heat exchange can be determined by equation 1.1 [33,38,40]:

$$\pm S = M \pm W \pm K \pm C \pm R - E \tag{1. 1}$$

where *S* is heat stored by the body; *M* is the individual's total metabolic heat production; *W* is measurable external work; *K* is heat exchange by conduction; *C* is heat exchange by convection; *R* is heat exchange by radiation and *E* is evaporative heat loss.

This dynamic heat exchange between the individual, clothing and the environment changes under stress of activity and environmental conditions such as wind movement, environmental temperature and air humidity [5,39]. Taking a cold climate as an extreme of mountainous environments, heat loss from a stationery person to the environment will be greater than metabolic heat production leading to a fall in core temperature [40]. However, adding in the variable of heavy exercise may raise the body temperature to 40 ºC [38]. With this, the body will dissipate heat, along the temperature gradient [38]. Maintaining thermal comfort is therefore a balance between activity intensity and accommodating for environmental conditions with appropriate clothing [38,39].

1.2.3.1 Impact of wet environmental conditions on wearer thermal comfort

Due to the significant impact water has on thermal heat exchange, literature discussing the impact of water on a naked body applies to a body in wet clothing [41]. Whilst a small body of literature has explored thermophysiological comfort during wet conditions, to further understand the impact of wet environments and clothing on the body, literature on the effects of water exposure and immersion have also been reviewed. Furthermore, literature focuses on thermophysiological effect of cold conditions; rain as an environment condition is rarely described being difficult to simulate in research studies due to numerous factors and types.

An unexpected change in weather conditions can have major consequences on someone participating in outdoor activities, particularly where shelter or retreat is not possible [42]. A person may be exposed to rain or precipitation that wets clothing and penetrates into other layer contributing to a decrease in body temperature when static. Whilst sub-zero temperatures are commonly associated with the on-set of hypothermia, exposure and immersion in water can have a greater impact on its progression [38]. When fabric is wet or damp it clings to the skin reducing insulative value provided by air layers between clothing layers [43]. Additionally, air between the fibre construction is replaced with water rapidly increasing thermal loss by conduction, and body cooling [33,34]. Since, water conducts heat away from the body at a rate ~24 times faster than air and has a heat capacity 3550 greater than air, thermal conductivity from the body to the clothing, and onwards exchanged to the environment, is increased along with a greater heat capacity within the fabric [6,33,38,41,44,45]. The temperature of the precipitation and the surface area of wet clothing crucially influence the rate of thermal cooling increasing the rate of conduction and convection [38]. Golden *et al.* [46] discuss the fall in core body temperature of an adult wearing outdoor clothing during immersion to 35 ºC and affecting neuromuscular performance, after one hour in 5 ºC water and 3-6 hours in 15 ºC water.

Pugh identified the thermal insulation of clothing in wet and windy conditions to be a tenth of that in dry conditions [47]. In a controlled study over 900 minutes, fall in rectal temperatures and skin temperatures were observed in a windy environment (fall of 5 ºC) with wet clothing and, due to this cold stress, oxygen intake was observed to increase [48]. Participants described severe discomfort and clothing insulation was observed to be 50% greater at rest in wet and cold conditions than during exercise [48]. Confirming these observations, Weller *et al.* [49] observed a fall in rectal temperature over six hours of intermittent walking exercise in wet clothing (6 ºC). Under heavy exercise, six hour work-rest cycles, in cold and wet conditions (5 ºC) peripheral heat loss was observed to increase leading to a fall in core body temperature [50]. In exercise, disruption of the microclimate within the clothing system and insulative air layers will facilitate this additional heat loss [45]. Eventually, this will lead to heat loss being greater than heat production, a decrease in core body temperature and the onset of hypothermia [45].

1.2.4 Consumer end use of liquid repellent outdoor clothing

The market of waterproof breathable textiles is set to rise[‡] as participation increases and there are further demands for functional textiles for a wide-range of activities [51]. Within Europe, the outdoor industry clothing market is worth €2.94 billion (2018) [9]. However, accurate statistics on the production and market of solely liquid repellent apparel cannot be ascertained.

A liquid repellent garment may be worn for a number of outdoor activities, such as hiking, mountaineering and climbing. The garment is likely to come in to contact with rock, which may abrade the fabric, worn with a rucksack where the strapping will sit against the outer fabric, and/or worn with a harness which moves with the wearer and sits against the outer fabric.

[‡] The global market of waterproof breathable textiles is expected to rise, 2015-2024, from $1.43 billion to $2.31 billion (US dollars) [51].

1.2.4.1 Marketing definitions

Literature and marketing of outdoor apparel uses a number of different terms to express the fabric's water repellency. These terms include 'shower-resistant', 'shower proof', 'water-resistant' and 'rainproof' [36]. Additionally, 'waterproof', 'water repellency' and 'water-resistance' are commonly interchangeably used and misinterpreted. These terms encompass a wide range of resistance, from initial resistance to a few drops of water to non-permeability of water, and there remains some ambiguity. Consumers commonly refer to repellent apparel as 'waterproof'.

1.2.4.2 Contact with aqueous and non-polar liquids during end use

During consumer end-use, a liquid repellent garment may come into contact with polar-based liquids and non-polar liquids. These may stain the garment due to the lack of a sufficient DWR or due to pressure overcoming the DWR. During consumer use, these may include commonplace liquids such as coffee, fruit juice, sun-cream and soil. This type of staining is aesthetic and hinders the water repellent functionality due to blocking the fabric interstices and coating the fabric surface with a substance different to that of the DWR.

Body oils are secreted from the skin on to all human body parts largely consisting of sebum, waxy matter, skin cells and dirt or matter from the environment. These oils are transferred to clothing when worn. With sweat production during activity, transfer of secreted fluids to clothing is increased. Both body oils and sweat may stain the fabric and hinder the repellent functionality if the DWR is not adequate. Similarly, transfer of any moisturisers worn or from hand contact may occur.

1.2.4.3 Consumer laundering of liquid repellent clothing

As for other items of clothing, liquid repellent garments are intended to be laundered. Laundering of repellent garments is necessary to restore the DWR and to prevent staining from blocking the fabric interstices. Literature has demonstrated that liquid repellency of textiles decreases after washing but is partially recovered following application of heat [36,52–54]. However, drying and heat application by the consumer, such as tumble drying or ironing, to reactivate the repellent finish is largely unknown. Additionally, there are many unknown variables as to how a liquid repellent garment is laundered by the consumer in terms of washing temperature and use of tumble drying or ironing.

Reproofing is defined as restoring the water resistance, applied during fabric manufacture, of the textile or garment [55]. Due to wear and abrasion the factory-applied repellent finish is thought to degrade, resulting in a lessening of the repellent functionality. Wearers commonly refer to the degradation of the repellent functionality as ‘wetting out’, when the liquid is seen to no longer form droplets and bead away from the surface. Aftercare treatments are purchased by the consumer and used in domestic laundering, or a domestic setting. A re-proofing product is used either as a wash-in formulation, hand wash or washing machine, or as a spray treatment, to be used within the domestic environment. The frequency of using an aftercare product, to revitalise the liquid repellent performance, by the consumer is unknown [56]. There are various formulations, dependant on aftercare brand, and each with instructions on product use; Nikwax is the market leader within the UK.

1.3 Liquid repellency in textiles: application and theory

Chemicals are used within the production of textiles in both wet processes and dry mechanical or physical treatments. There are a number of steps processing fibres to finished items (Figure 1.9). Wet processing occurs during fabric preparation, in colouration, and within finishing treatments [57]. Finishing treatments are the final step of textile production and used to provide, or increase, functionality or to modify the aesthetic [58]. Textile finishing may involve mechanical processes, such as calendaring, steaming and sanding, and chemical processes imparting either aesthetic qualities or adding functional properties to the textile [57,59]. Common finishing treatments are for fabric softening, water repellency, anti-static, anti-microbial finishing, stain release and oil repellency [60]. A chemical solution is applied to the textile by impregnation, soaking or, most commonly, padding on to the textile surface, typically in a continuous roll-to-roll process [59]. Usually, chemical finishes are applied as aqueous dispersions with control of the wet pick-up. Liquid repellent treated fabrics are widely used across the textile and apparel sector. Examples include providing stain resistance to home furnishings, imparting easy-care properties to jeans and suits, and on outerwear jackets providing the wearer with weather protection.

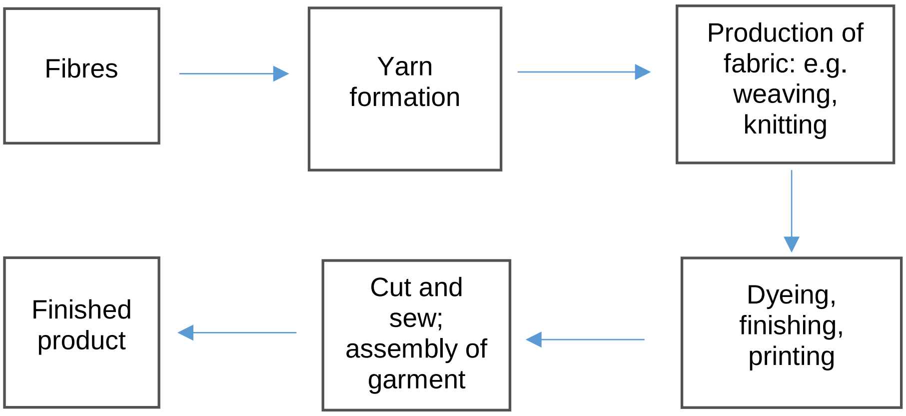

Figure 1.9: Flow chart of textile and apparel production.

1.3.1 Application of a DWR

A textile is treated with a repellent finish or coating to provide liquid resistance properties [61]. The textile is impregnated with a DWR typically in a pad-dry-cure process. Prepared fabric is immersed into an aqueous emulsion bath then put through rollers to remove excess emulsion and control the wet pick up percentage [36,62,63]. Evaporation of the solvent occurs when the fabric is dried, in either heated air or within an oven, and subsequently the fabric is heat-cured at a temperature up to 180 °C (Figure 1.10) [36,62].

Typical curing conditions for apparel fabrics are 160-180 °C for up to 45 seconds; with other conditions differing by textile type and chemical formulation [36]. This is a continuous process with the fabric fed through the entire process. The curing process allows cross-linking between the polymer and textile surface and, therefore, can subsequently affect the optimal level of repellency demonstrated by the textile [62,63]. The aqueous emulsion bath for a fluorinated polymer chemistry will typically consist of 80% water and 20% polymer with 0.5% unbound or unreacted residuals [64]. This emulsion will also contain stabilisers and extenders acting as agents for the reaction between the polymer and textile. The repellent finish is 0.3-0.8% of the total fabric mass; however, this varies for different polymer concentrations and types [59].

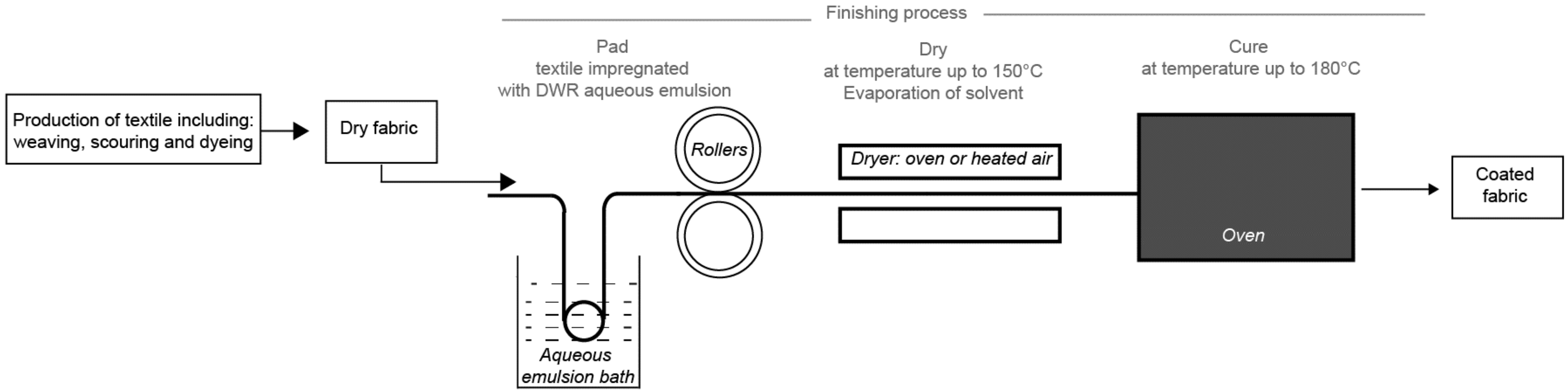

Figure 1.10: Application of a DWR aqueous emulsion to fabric in pad-dry-cure process [10,63,65,66].

1.3.1.1 Contact with aqueous and non-polar liquids during fabric production and garment manufacture

There are several stages during fabric production where a liquid repellent fabric may come into contact with aqueous and non-polar liquids including at heat setting from machinery and from transfer of body oils due to handling at fabric inspection and packaging. In garment production, transfer of oil-based liquids or compounds may occur during sewing with machinery lubricants, as on sewing machine feet, or from sewing auxiliaries. At the same time, hand contact and transfer of body oils during cutting, sewing of the garment, quality inspection and packaging may result in transfer of body oils detrimental to the fabric if the DWR is not sufficient.

1.3.2 Repellency theory

The liquid repellency of a textile fabric is dependent on the wettability of the surface and its resistance to the penetration of a liquid [36]. Wetting is the interaction of a liquid with a surface in terms of adhesion, capillary penetration and spreading [67]. An optimal DWR sees the liquid bead away from the textile surface whereas with an insufficient DWR the liquid will wet the surface (Figure 1.11).

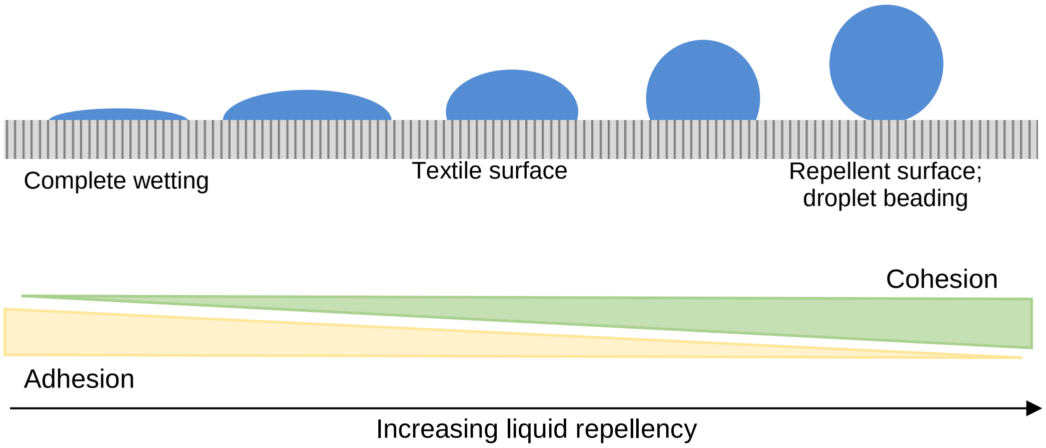

Figure 1.11: Stages of wettability: from complete wetting of the surface to repellent surface, adapted from [68].

The wetting potential is dependent on the adhesive interaction between the liquid, solid surface and the air interface. The degree of wetting depends on the interaction between the molecular properties of a liquid, cohesion forces between molecules, and their interaction with the molecular properties of the surface, known as adhesion (Figure 1.12). Repellency is a result of low adhesion between the liquid and surface. Wetting is due to greater adhesive forces between the surface and the liquid [69].

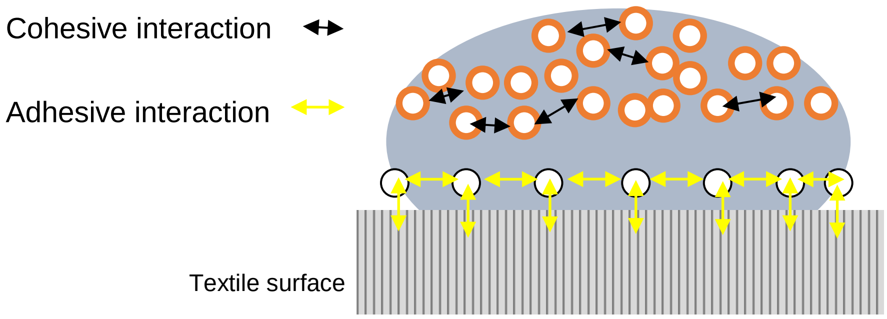

Figure 1.12: Cohesion is the interaction between molecules within the liquid and adhesion is the molecular interaction between the liquid and solid.

A surface with a high surface energy attracts the molecules within a liquid more strongly than they are attracted to each other; likewise a surface with a low surface energy demonstrates a lesser degree of attraction to the liquid’s molecules [70]. This attraction disturbs the balance of energy between the interfaces and causes the liquid to either form a spherical shape upon the surface, spread across the surface or a state in-between [70,71].

Contact angle (θ) is a measurement of the interaction between a liquid and surface within the air interface, or other testing environment. The contact angle quantifies the wettability of a liquid on a surface and the interaction, or energy exchange between the three interfaces: the solid-vapour interface (γ_{SV}); the solid-liquid interface (γ_{SL}); and the liquid-vapour interface (γ_{LV}) (Figure 1.13) [36,72,73]. Young quantified this relationship between the interfaces and contact angle at equilibrium according to equation 1.2 [36,70,72]:

$$Y_{SV} = Y_{SL} + Y_{LV} \cos \theta \qquad (1.2)$$

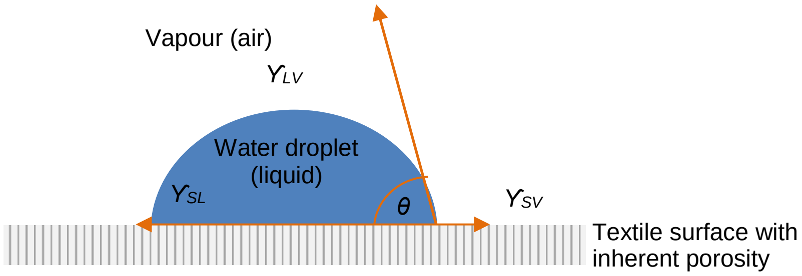

Figure 1.13: Interaction between the three interfaces γ_{SV}, γ_{SL}, and γ_{LV} [74].

Repellency varies depending on the substrate’s surface energy and the surface tension of the liquid being repelled. For a liquid to be repelled, the critical surface energy of the substrate must be lower than the surface tension of the liquid [70]. All textile surfaces given in Table 1.1 will repel water but only a fluorocarbon-based DWR will repel non-polar, such as octane and heptane.

Table 1.1: Surface tension values of common liquids and surface energy values of common textile surfaces (20 °C), adapted from [36,66,72,75,76].

Liquid	**Surface tension (dyn cm^{-1})**	**Textile**	**Surface energy (dyn cm^{-1})**
Water	72.75	Polyamide	46
Olive oil	32	Wool	45
Paraffin oil	31	Polyester	43
Petrol	26	Hydrocarbon finish	31
Octane	22	Silicone finish	24
Heptane	20	Fluorocarbon finish	<15

The surface tension of a liquid is determined by cohesive interactions between the molecules. Surface energy is the interfacial tension of a substrate affecting its adhesion properties. Dupré quantified this interaction further with equation 1.3 [72]:

$$W_{\mathrm{SL}} = \gamma_{\mathrm{S}} + \gamma_{\mathrm{L}} - \gamma_{\mathrm{SL}} \tag{1.3}$$

where W_{SL} is the work of adhesion between the solid-liquid interface, γ_{S} is the energy at the solid interface, γ_{L} is the energy at the liquid interface and γ_{SL} is the combined energy.

However, calculation of contact angle and both equations 1.2 and 1.3 idealise the substrate surface as homogenous and flat which does not exemplify textile surfaces [67,68]. True equilibrium between the interfaces is unattainable with a textile surface. There is a dynamic relationship between the three interfaces and wetting varies with environmental conditions, pressure as wetting continues and is highly dependent on the nature of the surface [36,77].

1.3.2.1 Wetting

The wettability of the solid surface is governed by its chemical composition and macro physical structure, or roughness [78,79]. When a liquid is seen to 'wet out' there has been a decrease in the interfacial energies between the liquid and the substrate [36]. It is this change, in the textile surface's attraction to water, that the wearer determines as a failure of the repellent textile surface. In use, it is possible to overcome the balance between the interfaces by build-up of water droplets or pressure. This can be caused by an individual sitting on a coat, rucksack strapping against the garment or pressure by hard or heavy rain [61]. It can also simply be caused by continuous build-up of droplets that cumulatively create enough pressure to overcome the energy balance and wet the surface.

1.3.2.2 Roughness

In determination of liquid repellency, it is largely assumed that the surface is homogenous (Figure 1.14 a) but a textile surface has inherent roughness and this can further be created by chemical and physical modification [76,77]. Wenzel [77] theorised that on a textured surface there is a greater ‘actual’ surface area on which there is a greater intensity of low surface energy, compared to that on a flat surface.

The thermodynamics of this interaction and the influence of surface roughness on determining the contact angle, between the liquid and solid interfaces has been theorised by Wenzel giving the equation 1.4 [72,80]:

$$\mathrm{r}\cos\theta = \cos\Phi \qquad (1.4)$$

where r is the roughness factor given by the ratio between the true area of the solid plane to the ‘ideal’ apparent plane (Figure 1.14 b), Φ is the true contact angle of the inhomogeneous surface and the ‘ideal’ contact angle θ is determined using Young’s equation (1.2).

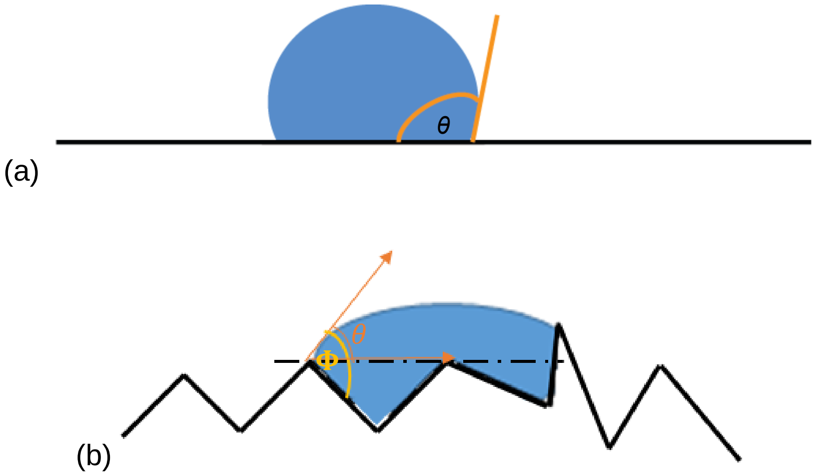

Figure 1.14: Schematic diagrams of (a) a water droplet on an idealised flat surface; (b) The true contact angle Φ and the ‘ideal’ contact angle θ on an inhomogeneous textile surface [68,81].

1.3.3 Evaluating liquid repellency

Both analytical assessment and textile testing methods are used to determine the effectiveness of liquid repellent functionality on textile fabrics [3].

Analytical evaluation: A well-established analytical assessment of quantifying a surface's wettability is quantifying the interaction between the liquid and the substrate through determination of the contact angle. A measurement of the liquid droplet, typically pure water, on the solid substrate within an atmosphere is a static contact angle measurement. The sessile drop method is most commonly used, determined by a contact angle goniometer device, with software for drop shape analysis. A droplet is placed on the textile surface and an image is captured for analysis using the software (Figure 1.15).

However, this analytical assessment can be difficult on textile fabrics that have an inherent macroscopic roughness. This surface can interfere with the interpretation of the baseline, and therefore makes an accurate contact angle determination difficult [82]. An additional problem in assessment of textile surfaces is keeping the fabric taut and flat on the testing platform without over-stretching or using adhesives that could potentially affect the surface interaction.

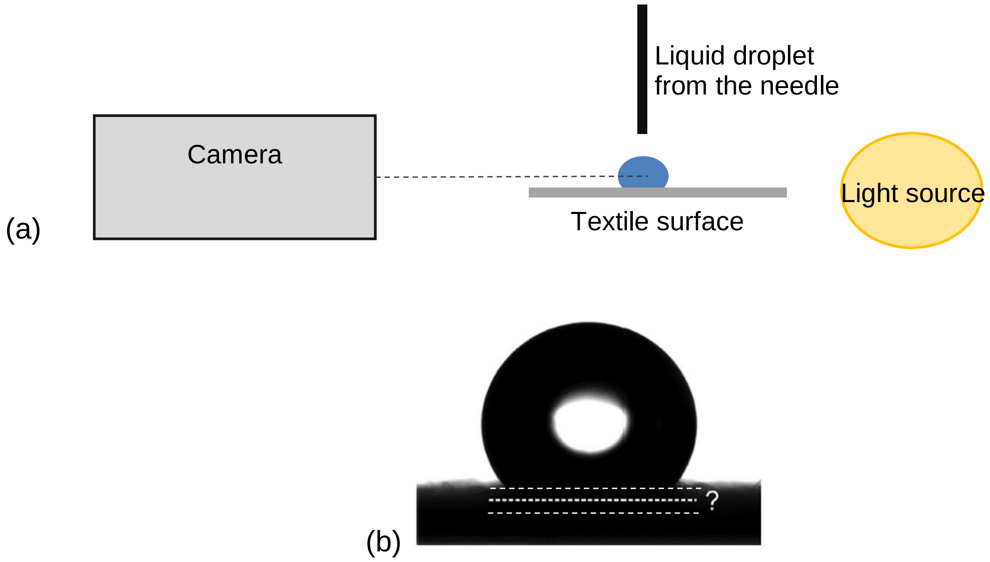

Figure 1.15: (a) Schematic set up of the sessile drop method to determine the contact angle; (b) Droplet (by the sessile drop method) on a textile surface showing the difficulty in accurately determining the baseline [82].

Laboratory test methods: There are several laboratory textile test methods to evaluate the liquid interaction with a textile surface but few are widely used due to availability, desirability and reproducibility. In addition, the tests each have individual test methods, vary in assessment and produce different results which are incomparable to each other [61]. Laboratory test methods to evaluate water repellency fall into three categories: (1) tests simulating exposure to rain by water spray, (2) hydrostatic pressure tests, and (3) immersive tests evaluating the water sorption (Table 1.2) [36]. Most commonly used to evaluate water repellency are the Spray test and the Bundesmann rain-shower tester; both assess the repellency following a spray of water simulating rain exposure.

Table 1.2: Overview of test methods to determine water repellency of a textile surface [18,19,73,83–88].

Test category	Test method	Testing standard	Type of test
(1)	Spray test	BS EN ISO 4920:2012; AATCC 22-2014	Fabric's resistance to surface wetting – simulating rain shower
(1)	Bundesmann rain-shower tester	ISO 9865:1991; BS EN 29865:1993	Resistance of textile fabrics to rain shower by absorption and penetration
(1)	Water resistance penetration test	AATCC 42-2007	Fabric's resistance to impact of water
(1)	Water resistance rain test	AATCC 35-2006	Fabric's resistance to impact of water
(1)	WIRA shower test	BS 5066:1974	Resistance to absorption and penetration under simulated rain shower
(3)	Static immersion	BS 3449: 1990	Absorption of textile fabric when immersed in water
(3)	Wettability of textile fabrics	BS 4554:1970	Resistance to wetting
(2)	Hydrostatic head pressure	BS EN 20811:1992	Resistance to the penetration of water

Field trials, or wearer trials, are frequently carried out by brands to assess the performance of the entire garment and validate findings from laboratory textile testing. Wearer trials are particularly important when evaluating thermal comfort due to wearer movement and generation of heat [88]. Wearer trials can be carried out in a laboratory setting with standardised exercise tests or in the field, which is most common for outdoor apparel due to the mountainous environment.

1.4 Sustainable development in textiles and apparel

Greater than 4000 individual chemicals are used in the textile and apparel industry in an immeasurable number of compounds [89]. From wet processing using colorants, coatings, printing substances and dyes to surface treatments, the complex chemistry behind every day domestic items, apparel, and high performance textiles provides a plethora of functional properties. Advancements in technology, increasing demands of modern life and in pursuit of pushing the ‘possible’ even further a continuous demand on clothing functionality is placed. A wearer expects clothing to work, deliver to the needs of the activity or environment and be at a suitable price.

However, continued manufacture using a plethora of chemicals is no longer sustainable with the recognition of significant impact our chemistry use can have on the earth’s processes and humanity [13,15]. Whilst irreversible impact is acknowledged, recognition and management of chemical use can minimise persistence, widespread mobility and potential impact [90].

Environmental scientists have proposed nine ‘Planetary Boundaries’ (2009) as ‘a safe operating space for humanity’ defining environmental limits in which we can continue to operate without imposing further risk to future generations [17]. These boundaries define conditions to control, or at least minimise, human modification and impact on the global environment [90].

1.4.1 Chemical management

‘The precautionary principle’, has emerged as an approach to chemical use within the ‘Planetary Boundaries’ framework [91]. This concept promotes recognition and restraint of ‘chemical intensification’ which has evolved due to rapid and global production of synthetic chemistry, growth of consumer products and development of global trade in chemicals and waste [90]. Chemicals are prioritised based on their persistence; which is already in practise within the criteria for listing chemicals of concern on the

Stockholm Convention and within the EU's Registration, Evaluation, Authorisation and restriction of chemicals (REACH) [91].

Similarly to the 'precautionary principle', understanding the global hazards, physical and toxicological implications of chemistry use allows plans to be formed to limit risk [92]. The principles of 'Green Chemistry', put together by Anastas and Warner (1998), aim to reduce the use of hazardous substances in chemical production or products [93]. Addressing hazards throughout the life-cycle of the chemical, the twelve principles include: (3) Less hazardous chemistry synthesis; (4) Designing safer chemicals; (5) Safer solvents and auxiliaries; and (10) Design for degradation[§] [93]. This way of working, addresses the use of raw materials through to awareness of the toxicity and biodegradability of products produced and auxiliaries used [92,93].

Whilst understanding and recognising the physiochemical properties highlights a need to change, the reality of modifying existing chemicals can be challenging. The global nature of the textile and apparel supply chain has reduced visibility in chemical use and processes, especially in geographical areas of production where different, or fewer, regulations are in place [60].

1.4.1.1 Textile and apparel supply chain

Globalisation has developed complex supply chains of interconnected companies within the production of textiles and apparel [94]. In a vertical supply chain, schematically represented as a tiered pyramid (Figure 1.16), each stage of textile production is outsourced to a company of that specialism steered by cost-effectiveness. At tier 1, the clothing brand or company states specifications for the

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[§] The twelve 'Green Chemistry' principles are: (1) Prevention; (2) Atom economy; (6) Design for energy efficiency; (7) Use of renewable feedstocks; (8) Reduce derivatives; (9) Catalysis; (11) Real time analysis for pollution prevention; (12) Inherently safer chemistry for accident prevention [93].

garment. Vendors in tier 2 would supply this finished product. Numerous suppliers in tier 3 would provide, or outsource, the fabric and trims. Component suppliers in tier 4 process raw materials and supply these to suppliers.

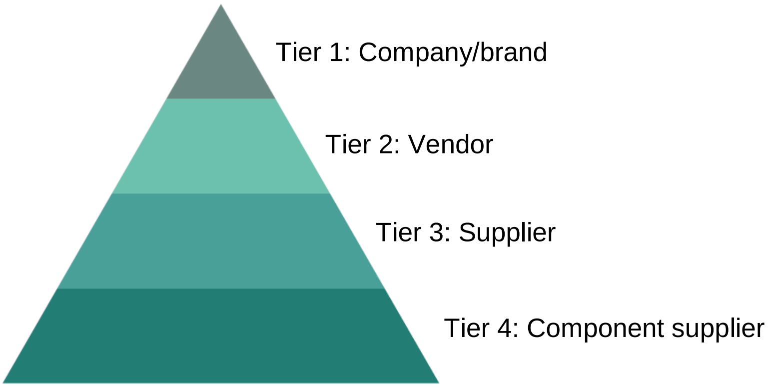


Figure 1.16: Schematic diagram of a tiered textile supply chain.

This supply chain contains a number of production steps completed by a number of global companies as sub-contractors. Within this, transparency on chemical use is limited and chemical compliance is complex due to differing use in global regions [60,89]. Therefore, within a textile supply chain modification of existing chemicals, or nomination of chemicals to be used, is difficult.

1.4.1.2 Supply chain certification

As a measure of environmental impact and an approach to chemical management, within the production of a textile or apparel item, certification systems have been developed to evaluate chemical compliance and to provide assurance of the garment's impact. Most widely recognised certification standards are Oekotex and Bluesign [89,94,95]. These certification schemes are used to give assurance, within the supply chain, on components stating compliance to Restricted Substance Lists (RSL) based on legislation [89]. Datasheets from chemical suppliers may accompany this information.

1.4.2 Per- and polyfluoroalkyl substances (PFASs)

Chemical compounds based on fluorocarbon chemistry provide a wide range of functional, stable properties which are unrivalled by non-fluorinated alternatives [96]. High hydrophobicity and oleophobicity, stability and durability are several of the properties which have fuelled the global dissemination of fluorocarbon chemistry in industrial processes and consumer products. Fluorocarbon compounds and derivatives are relied upon for functionality we daily take for granted [96–99]. Fluorocarbon chemistry, fluorochemicals, fluorinated chemicals or fluorinated substances are synonyms for the generic class of chemistry based on fluorine and carbon. A subset of this are perfluoroalkyl and polyfluoroalkyl substances (PFASs) which are synthetically produced chemicals, where one or more carbon atoms and all hydrogens have been replaced by fluorine; therefore containing a perfluoroalkyl moiety (C_nF_{2n+1}) [10,100]. The chemical class of PFASs includes a number of polymers and non-polymers, including side-chain fluorinated polymers which compromise of a polymeric backbone with branching fluorinated side-chains [10]. The bond between carbon and fluorine (C-F) is the strongest known within organic chemistry [96,101]. This entails a highly stable compound which due to the highly fluorinated chains is inert chemically and thermally and highly durable. The surface energy imparted by a fluorinated polymer is effective at low concentrations and unrivalled by other chemistries [35,102].

1.4.2.1 Synthesis and production

A number of organic compounds are used in the synthesis of PFASs produced by two main manufacturing processes [76,102,103]. In electrochemical fluorination (ECF) the organic substance is reacted with anhydrous hydrogen fluoride by electrolysis, substituting all hydrogen atoms with fluorine to create a mix of linear and branched perfluorinated compounds with varying chain length [10,35,96,104,105]. In telomerisation, perfluorinated iodides are produced with various chain lengths; these intermediates are used in subsequent reactions to synthesise fluorotelomer-based (FTOH) products [10,35,104].

1.4.3 Side-chain fluorinated polymeric DWRs

Repellent chemistries based on side-chain fluorinated polymers are used, widely, for repelling water, oil-based liquids, soils and stains [96]. These fluorinated polymers contain long perfluoroalkyl side-chains, C_nF_{2n+1}, where $n \geq 7$. These polymers are applied to food packaging, to prevent grease and oil penetration, used in cosmetics, ski-waxes, to increase glide, and widely in the textile sector on household textiles, carpets and home furnishings, for resistance of chemical and biological matter in personal protective apparel, for stain resistant clothing and within DWRs for outerwear offering protection from the weather [96].

Fluorotelomer alcohols (FTOHs), originating from the telomerisation production process, are used as intermediate compounds in the production of the aqueous emulsion bath for DWR application (Figure 1.17) [10]. FTOHs, $F(CF_2)_nCH_2CH_2OH$, where n = 6, 8,10,12, have been commonly used based on 8 perfluoroalkyl carbon atoms as 8:2 FTOH [64]. However, a move to 6:2 FTOH has been made as part of the shift to shorter-chain analogues of side-chain fluorinated polymers. Percentage and makeup of residuals, within the aqueous emulsion, will differ amongst fluorinated polymers and production within the market [64].

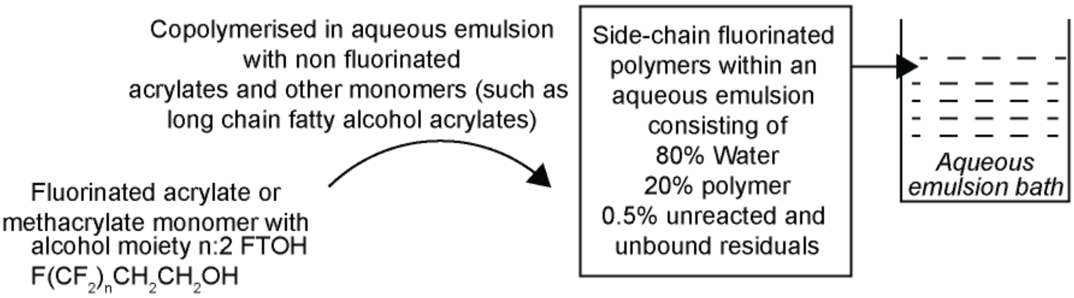


Figure 1.17: Composition of aqueous emulsion bath for DWR application [10,63,65,66].

1.4.3.1 Surface composition in relation to repellent performance

The low surface energy provided by side-chain fluorinated polymers is a unique function to PFASs and is currently unrivalled by other chemistries [106]. A side-chain fluorinated polymer DWR is made up of hydrophobic groups which sit on the outer fabric face and repel against liquids (Figure 1.18). The fluorinated tail with end group $-CF_3$ is connected to the polymer backbone by spacer groups (Figure 1.18). The polymers are cross-linked to the textile surface at the curing stage of application. The structure of the polymer and hydrophobic component support the packing and structure of the hydrophobic components to stand perpendicularly outwardly from the textile surface (Figure 1.18). The high level of hydrophobicity and oleophobicity provided by the side-chain fluorinated polymer DWR is due to the low surface energy provided by both inherent properties of the chemistry and the polymer structure. The extent of liquid repellency is dependent on the orientation, arrangement and packing of the hydrophobic moieties and terminal $–CF_3$ end groups at the surface interface [10,35,69,104,106–108]. The outwardly orientation and close packing of the fluorinated tails creates a surface roughness minimising the liquid’s contact with the fabric face or air pockets within the structure. The creation of this roughened structure and the clustered hydrophobic groups reduces the surface energy of the fabric; a $–CF_3$ surface construction has a surface tension of 6 dyn cm-1 at 20 °C, which repels liquids with a greater surface tension, including polar liquids (e.g. water with surface tension of 73 dyn cm-1 at 20 °C) and non-polar liquids (e.g. octane with surface tension 22 dyn cm-1 at 20 °C) [35,36]. The proximity that the hydrophobic components are packed and their orientation directly impacts on the surface energy [109]. This uniformed structure is dependent on the crystallisation of the side-chains, which decreases with a decrease in carbon chain length [110,111]. With a highly crystalline and ordered formation, there is low mobility of the end-groups giving a durable, rigid surface that is highly repellent [110].

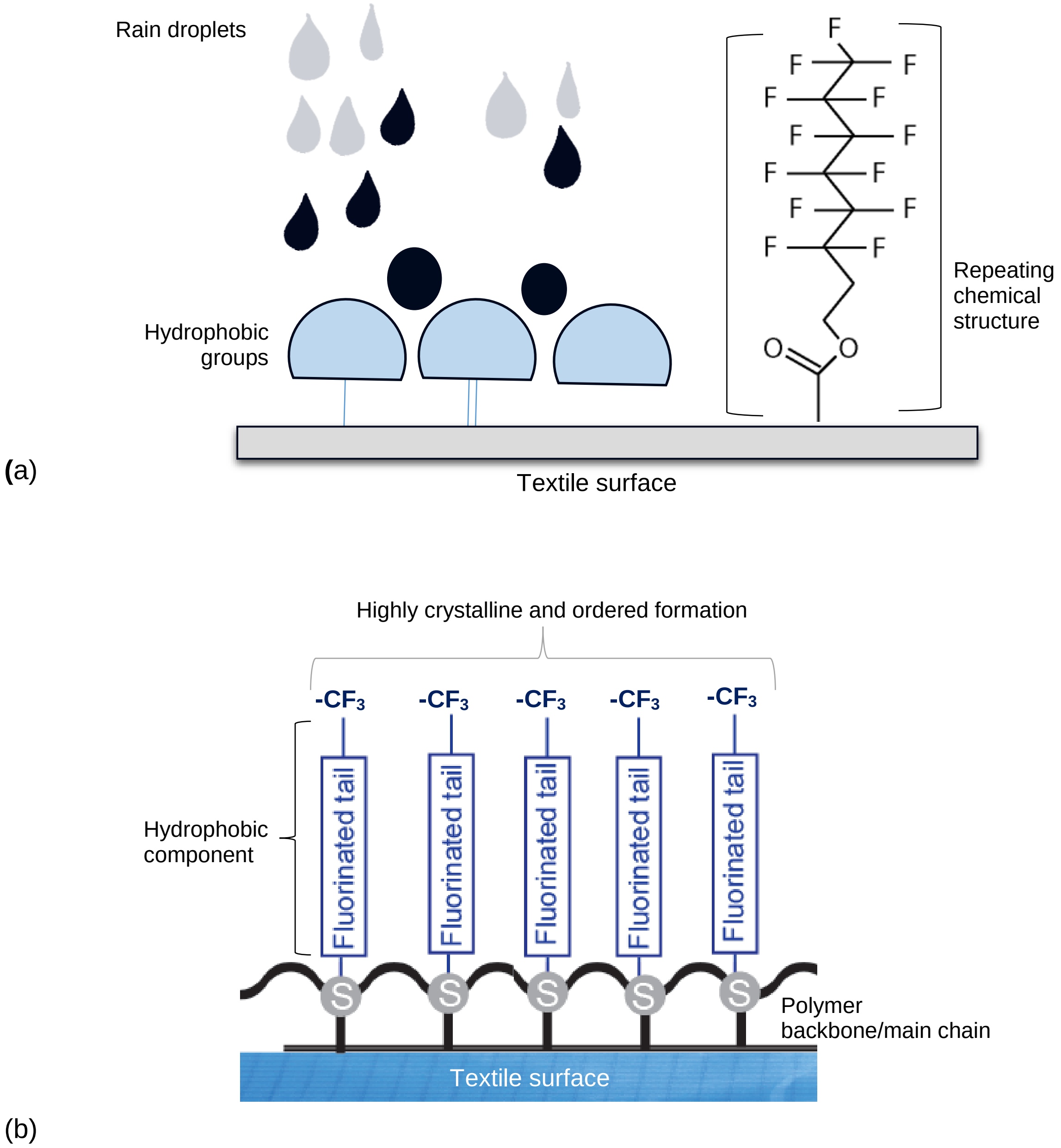


Figure 1.18: (a) Simplified diagram of the hydrophobic groups sitting on the outer fabric face imparting repellence against liquids. This is due to the repeating fluorinated side-chain structure (b) made up of hydrophobic segment with $–CF_3$ end groups, spacer groups (S) and polymer backbone which is cross-linked to the textile surface [110,112].

1.4.3.2 Chain length

The length of the carbon chain within the side-chain fluorinated polymer (C_nF_{2n+1}) DWR directly affects the surface energy imparted onto the fabric surface, and therefore its repellency [10,35,36,69,96,104,107,113]. Surface energy decreases with increasing chain length (Figure 1.19). A greater chain length provides good organisation and efficiency of orientated side-chains and number of $-CF_3$ end groups at the surface interface [69]. 'C8' structures are commonly referred to amongst industry. These are fluorinated polymers containing long perfluoroalkyl chains, C_nF_{2n+1} where n ≥ 7 [112]. The move to shorter-chain analogues is referred to as a shift to 'C6' or 'C4' structures containing shorter perfluoroalkyl chains, C_nF_{2n+1} where n ≥ 5 or n ≥ 3.

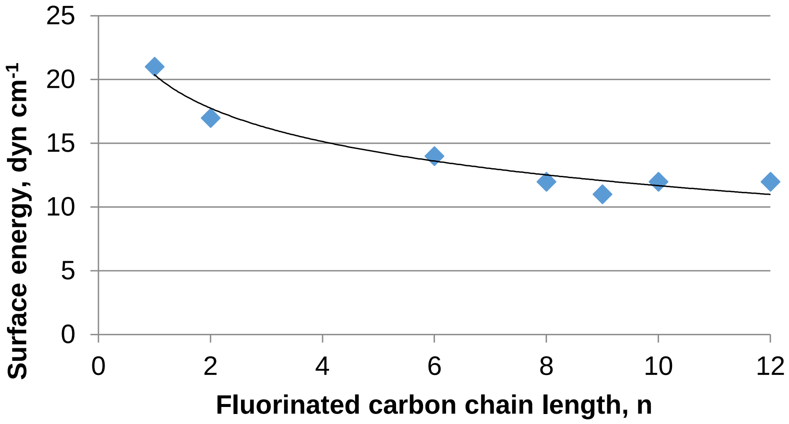


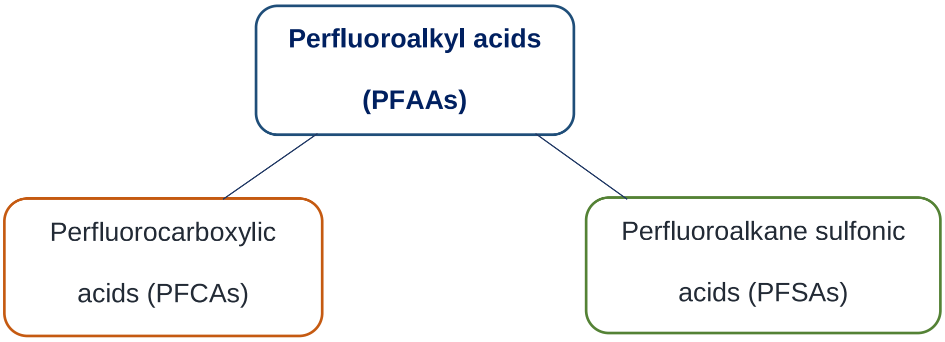
Figure 1.19: The effect of fluorinated carbon chain length on the surface energy, adapted from [36].

1.4.3.3 Polytetrafluoroethylene

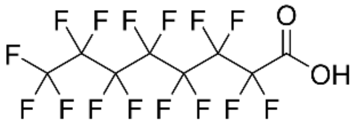
Polytetrafluoroethylene (PTFE) is used as a membrane or laminate within a fabric structure typically in hard-shell garments and is most commonly known under the brand name 'Teflon'. PTFE is a fluoropolymer - a different subset of the chemical class. However, PFOA is used as a processing agent within the production of PTFE. In this case, the manufactured PTFE will therefore contain PFOA as a production residue [114].

1.4.4 Issues and criticism of PFASs

PFASs have been ubiquitously identified within wildlife, humans and found across the world in the environment [96,115]. Of particular concern are long-chain perfluoroalkyl acids (PFAAs) shown to be persistent, bio-accumulative and toxic [116–118]. Of high regulatory interest within the classification of PFAAs are perfluoroalkyl carboxylic acids (PFCAs) with seven or more fluorinated carbons ($C_nF_{2n+1}COOH$; $n \geq 7$), for example perfluorooctanoic acid (PFOA); and perfluoroalkane sulfonic acids (PFSAs) with six or more fluorinated carbons ($C_nF_{2n+1}SO_3H$; $n \geq 6$), for example perfluorooctanesulfonic acid (PFOS) [10,96,119,120] (Figure 1.20). These are direct products of ECF production [10].



PFOA (1)



PFOS (2)

Figure 1.20: The class of PFAAs with sub-classes PFCAs, including PFOA (1), and PFSAs, including PFOS (2) [10,99].

PFAAs have been globally used, exist as manufacturing residuals and potentially on consumer items. The high stability due to the C-F bonding means PFAAs are non-degradable [17,96]. As scientific understanding has increased, a complex toxicological concern has unfolded [121]. A wealth of literature now exists on the ubiquitous and bio-accumulative nature of PFOA and PFOS and associated increased mortality rates, cancers, and toxic effects on liver and immune systems [104,117,122–127]. Bio-accumulation and bio-concentration of PFASs within humans and the food chain are of primary concern [96,128], which increases with increasing chain length; long-chain PFSAs and PFCAs have a higher bio-accumulation potential than their shorter-chain analogues [10,96,128–130]. PFSAs have been acknowledged to have a greater bio-accumulative nature than PFCAs of the same carbon chain length, which is thought to be due to the ability of PFSAs to bind more strongly to human blood proteins [130,131].

1.4.5 Legislation

There has been substantial developments in legislation, as investigative literature has been published and analytical techniques developed. Due to the extensiveness of PFASs as a chemical classification, focus within this work has been made on PFAAs and the legislation and exposure within liquid repellent outdoor apparel. There are over 196 countries with different regulations concerning chemical use within the apparel industry [89]. These differing regulations make it problematic when transporting materials/goods within the global supply chain.

Exploited since the 1950s, there was initially little regulation on the use of PFASs [96,102]. Concern on the use of long-chain PFAS chemistry started in the 1960s, with the detection of organic fluorine within human serum by Taves (1968) [132,133]. The main substitution process away from long-chain PFSAs and PFCAs began in 2000 when the first reports of the ubiquitous occurrence of PFOS within wildlife were published [10,134]. These concerns led to the phase-out of PFOS and related compounds, by 3M, whose key components within the manufacture of their Scotchgard stain products produced perfluorooctane sulfonamide derivatives by ECF with PFOS a resulting product from the intermediate synthesis [10,103,134,135].

The U.S. Environmental Protection Agency (U.S. EPA), in 2006, set out a voluntary phase-out of PFOA in a ‘2010/2015 PFOA Stewardship Program’ [136]. This step was taken after decades of research by chemical manufacturer DuPont into the health issues of PFOA manufacture and use [137]. In addition, the U.S. EPA have issued rules of use concerning the use of PFASs under the Toxic Substances Control Act and evaluated the risk to drinking water [138–140].

The Helsingør statement and Madrid statements from scientists within global academia raised concerns on the impact of PFASs on health, the environment and exposure to fluorinated alternatives, calling for a limit to its use, and requesting a collaborative effort to develop non-fluorinated alternatives [97,141,142].

As an immediate response, the outdoor apparel industry moved to shorter-chain analogues of long side-chain fluorinated polymer DWRs for liquid repellency (in 2014) with non-fluorinated alternatives also being sought [36,119,134]. European legislation on PFCAs and PFSAs has driven this change (Table 1.3). In 2006 the EU imposed a restriction on the use of PFOS [143]; in 2009 PFOS was classified as restricted on The Stockholm Convention's list of Persistent Organic Pollutants (POPs); and in 2015 the European Chemicals Agency (ECHA) adopted a proposal to limit the marketing and use of PFOA European-wide [144,145]. In addition, PFOA has been listed as a POP by The Stockholm Convention, with further information sought to be reviewed for regulation [146].

Table 1.3: European legislation on PFCAs and PFSAs affecting the textile and apparel industry.

Legislation	Date	Region	Reference
PFOS bio-accumulative, persistent and toxic to mammals – Directive 2006/122/ECOF of the European Parliament and Council PFOS cannot be higher than 1µg/m^2 of coated material in textiles – amended in Annex I to Directive 76/769/EEC	2006	EU	[143]
PFOS and its salts added as POPS to Stockholm Convention	2009	EU	[147]
PFOA classified in Annex VI of Regulation (EC) no. 1272/2008	2013	EU	[148]
Germany and Norway submitted proposal for inclusion of PFOA in restriction process under REACH, submitted to ECHA, dossier under Annex XV.	October 2014	EU	[148]
PFOA and PFOA-related substances adopted in REACH regulation. Articles containing PFOA and its salts with concentrations equal to or greater than 25 ppb of PFOA shall not be manufactured nor placed on market.	December 2015	EU	[145,149]
EU published regulation EU 2017/1000 PFOA amending Annex XVII of Regulation (EC) no. 1907/2006	June 2017	EU	[150]

1.4.6 Exposure pathways

Evidence of PFASs emerging as global contaminants has prompted extensive research into reliable determination of the substances using analytical methods. Predominant sources of PFAA exposure to humans are understood to be through dietary intake, water, dust, within air and from consumer products [119,125,128,151–162]. Concentrations of PFSAs and PFCAs have been determined in water, within both outdoor and indoor air, in mammals, aquatic eco-systems, and within humans worldwide [125,163,164]. Dietary intake is widely acknowledged to be the primary route of human exposure with the main dietary pathways considered to be migration from water, soil and food packaging to food products [125,159–162,165,166].

Concern on the global widespread presence, the environmental persistence, and bio-accumulative nature of PFASs, principally perfluoroalkyl acids (PFAAs), has implied continuous release from applications and manufactured products [164,167]. Exposure to the widespread presence of PFAAs is discussed as direct exposure or indirect referring to the breakdown, biotransformation of PFAAs, or precursors [168]. The significance of each exposure route and trends in relation to human exposure remain undefined; and precise understanding on degradation, pathways and PFAS content from products is difficult to determine due to the number of chemical derivatives globally [125,165].

Several non-peer reviewed documents have been published on the use of PFASs, with the aim to develop understanding and facilitate knowledge exchange between the various sectors involved. These include the Organisation for Economic, Co-operation and Development (OECD) and the United Nations Environment Programme (UNEP) on PFASs [99]; the FluoroCouncil working on research and development on behalf of several chemical manufacturers [169]; the Danish Environmental Protection Agency [170–173]; and environmental conservation group Friends of the Earth Norway [174].

A wealth of literature exists on potential routes of human exposure to PFASs. Further literature has been summarised in Table 1.4 although this is by no means the literature in its entirety.

Table 1.4: Further literature discussing exposure pathways to PFASs.

Exposure pathway	Further literature
Food	▪ Transfer of PFOA and PFOS from mother's blood to breastmilk [159,175,176]. ▪ The Food Packaging Forum summarise the chemistry and health implications of food packaging [177]. ▪ Migration from food packaging [98] and non-stick cookware [98,161,162,178]. ▪ Long-range transport of PFASs through aquatic life [178].
Water	▪ Snow samples contaminated by ski wax [179,180]. ▪ Drinking water [181]. ▪ Wastewater treatment plants [164,182–184]. ▪ Geographical studies [185–187]; all of which concluded that determined concentrations of PFASs were low to not pose adverse hazards to humans.
Air and dust	▪ Inhalation within indoor environments [154,160,188–190]. ▪ Assessments of outdoor air in rural and urban environments, Europe, [152,153,191].
Consumer goods	▪ Determination of a diverse pattern of PFCAs in 115 consumer products [158]. ▪ Understanding of exposure pathway [192].

1.4.6.1 Determination of PFAS exposure

The unique physical and chemical properties of PFASs have entailed unique analytical strategies and a large body of development in analytical detection. Liquid chromatography-mass spectrometry (LC-MS) methods have enabled widespread determination of PFASs using analytical means and are now heavily relied upon [162,193–196]. The majority of knowledge on PFASs is owed to LC-MS as a sensitive analytical tool and the reassessment of Tolerable Daily Intakes (TDIs) has only been possible with these developments in analytical analysis [197,198]. A broad range of sample types can be analysed using LC-MS, such as aqueous samples, foodstuffs, biological matter, and consumer products [193,199].

Methods, systems, and parameters of LC-MS for PFAS detection are discussed in detail by Trojanowicz & Koc [193]. Liquid chromatography methods are utilised for determination of PFAS content within consumer products. ISO and ASTM standards have been developed to unify extraction methods, sample preparation and analysis methods. However, there is variability in sampling and assessment methods across literature and challenges with insufficient recoveries during analysis [196,197]. Fragmentation of isomers differs significantly with low fragmentation efficiency and interferences in mass determinations leading to misinterpretation of PFAS product ions [168,197]. One reason for this is that the ECF manufacture of perfluoroalkyl chains result in differing isomer profiles producing branched structures whereas telomerisation manufacture predominantly produces linear structures [197].

1.4.6.2 Consumer items

Consumer items are increasingly being recognised as a potential route to PFAS human exposure but detailed knowledge is limited [157,158,200]. Possible migration from consumer products such as non-stick cookware, carpets, repellent outerwear, inclusive of textile membranes, waterproofing impregnation sprays, food packaging, cleaning products and polishes, and paints [181]. Only limited information is available on the volumes, emissions and specific sources of PFASs, with many derivatives in use.

Significant exposure by residual FTOHs on consumer products have been indicated to contribute to atmospheric contamination [201].This potential to release FTOHs, under suitable environmental conditions, and the potential atmospheric degradation to persistent PFCAs is of primary concern [62,76]. An increasing source of concern is inhalation of indoor dust and air contaminated by PFASs that have migrated from consumer items; perfluorohexanoic acid (PFHxA) has been determined in house dust and associated with release from repellent apparel [162,190].

1.4.6.3 Repellent apparel as an exposure pathway

Exposure of humans and the environment to PFASs from repellent outerwear may occur along the supply chain during manufacture, use and disposal (Figure 1.21) [62,76,119,157,201,202]. Residuals and impurities from the application of the polymeric aqueous dispersion during textile finishing may remain on the garment. Through vapourisation, these unbound residuals can be released directly into the environment and breakdown to PFCAs or PFSAs [64].

A main concern of the European Chemicals Agency is potential PFOA emissions from imported textiles [144]. EU import of PFOA, and its salts, are estimated to be ~40 tons per year [114,146]. It is estimated that textile imports into the EU contain between 1000-10000 tons of PFOA-related substances per year [114,146].

During the use phase, loss of PFASs to the environment may occur by several potential pathways: (i) loss from the fabric by abrasion (either by rubbing on external surfaces such as abrasion caused by rock or other worn apparel), (ii) release into wash water during laundering or reproofing (using wash-in re-proofing products); (iii) from proofing/reproofing sprays *via* air; (iv) atmospheric degradation during use; or (v) from degradation of garment following disposal (Figure 1.21) [162]. Residuals on repellent garments may enter the washing water during laundering, entering the water cycle and contributing to dietary intake of PFASs for humans and wildlife. This loss may also result in a loss in repellent functionality [203].

Kotthoff *et al*. [158] found PFOA, perfluorodecanoic acid (PFDA), and PFOS, with determined concentrations exceeding the 1 µg m^{-2} European limit. A study on behalf of the Norwegian Environmental Agency found concentrations of PFOA on four outdoor clothing items exceeding 1 µg m^{-2} [203], whilst, a study on behalf of the U.S. EPA found that PFOA content within products varied from not detected to 6,750 ng g^{-1} [204].

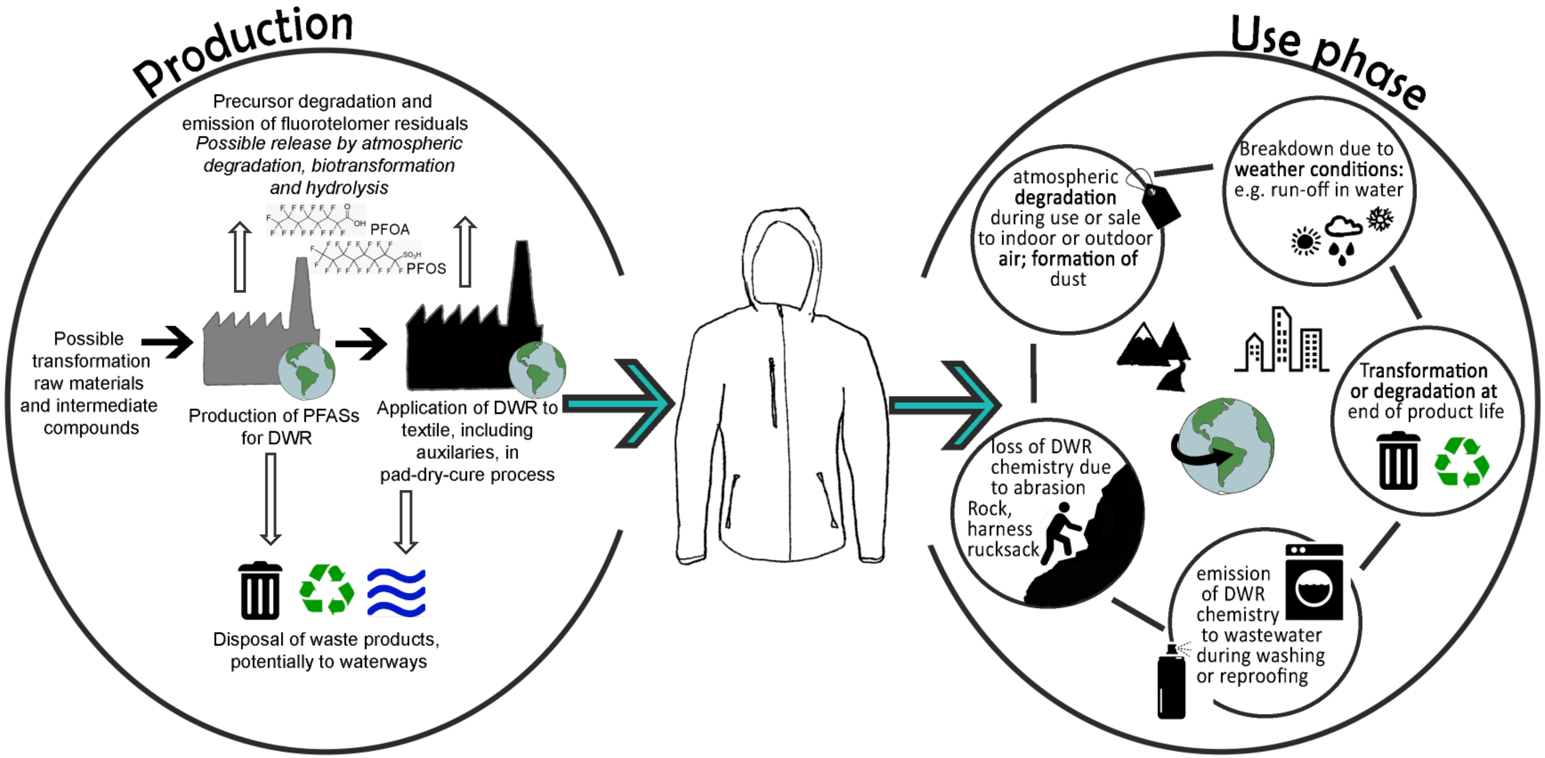


Figure 1.21: Potential pathways of degradation and exposure of PFASs from liquid repellent outerwear apparel during production and end-use [64,119,202].

Berger & Herzke [205] and Schulze & Norin[**] [174] analysed textile samples for PFASs using LC-MS and gas chromatography-mass spectrometry (GC-MS). Using direct extraction from the textile sample, and quantification with internal standards, FTOHs were mainly detected. A study for the German Federal Environment Agency analysed samples from 16 outdoor jackets, hard-shells, soft shells and rain jackets, [202]. PFASs were detected in all samples and FTOHs were determined in the greatest concentrations. This research was later published in 2016 including a reanalysis of the four samples after 3.5 years [62]. An increase in PFOA was detected in three of the four samples as well as a concentration increase of PFDA.

Mawn *et al*. [206] and Washburn *et al*. [192] developed extraction techniques using water, methanol, simulated sweat, and simulated saliva, in order to mimic human skin contact; other work has limited research to extraction samples of outdoor apparel with methanol only [207,208]. As with other PFAS determinations, there are limitations within these methodologies, and discrepancies in blank test spectra suggest contamination within laboratory equipment or within the solvent extraction. Limits of quantification with LC-MS make determination challenging due to the low levels of PFASs that have been found within consumer products [209].

Migration of residuals from the textile surface could occur during the consumer wash. A study on behalf of the Federal Environment Agency in Germany, simulated consumer washing of repellent jackets using a domestic washing machine [202]. Four different jacket samples were washed together in a washing machine, without detergent, and analysis revealed the presence of PFOA, PFHxA, PFDA, perfluorononanoic acid (PFNA), perfluoroundecanoic acid (PFUnDA) and perfluorotetradecanoic acid (PFTeA) within the washing water effluent; PFOA and PFHxA were observed in highest concentrations (Figure 1.22).

[**] This study was a Friends of the Earth Norway publication.

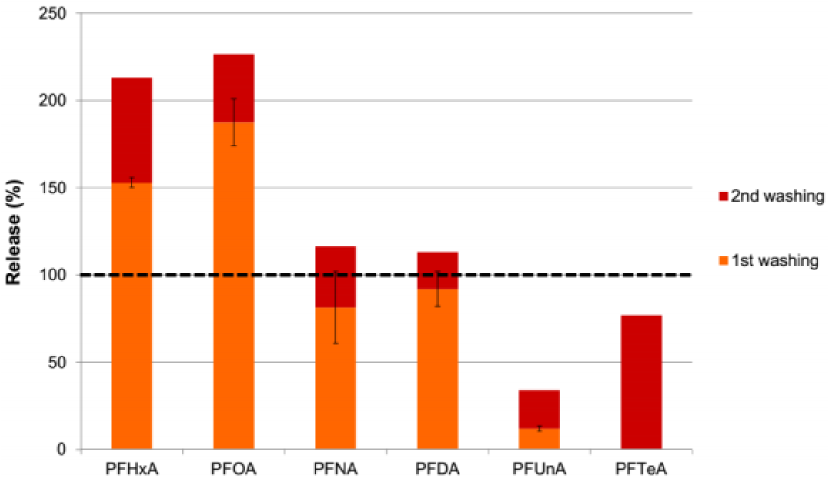


Figure 1.22: Determination of PFAAs within washing wastewater from repellent clothing in Knepper *et al.* [202].

The second wash released a lesser amount of PFCAs. Several PFASs were not quantified due to background contamination; however, it is clearly observed that PFASs are released during the consumer wash into the aquatic life cycle.

Reproofing aftercare products, or waterproofing products, are used within the domestic environment. Used to protect coated textiles and to reapply the water repellent functionality, the polymer solutions are available in either liquid formulation, for wash-in applications in consumer washing machines, and aerosol application for domestic spraying [210]. Re-proofing sprays††, specifically those which are fluorinated polymer based, are readily discussed as source of exposure to PFASs by human inhalation within the domestic environment, and linked to respiratory illnesses [162,210–212]. Fiedler *et al*. [213] analysed ten re-proofing products, including several labelled to contain fluorine and evaluated consumer exposure according to different modelled

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[††] The formulation of re-impregnation sprays contains a propellant gas, a water-repellent agent and a solvent [211,212].

scenarios. 8:2 FTOH and 10:2 FTOH were the dominant compounds determined within the re-impregnating products, with PFOA detected in seven out of nine products.

Overall, it is predominantly FTOHs and PFOA that have been determined from direct extraction of liquid repellent outdoor clothing. A variety of PFAAs were determined in washing water and aftercare products have been reported as a direct source of human exposure to PFAAs. In summary, the main PFAAs that have been determined from liquid repellent outdoor garments are summarised in Figure 1.23.

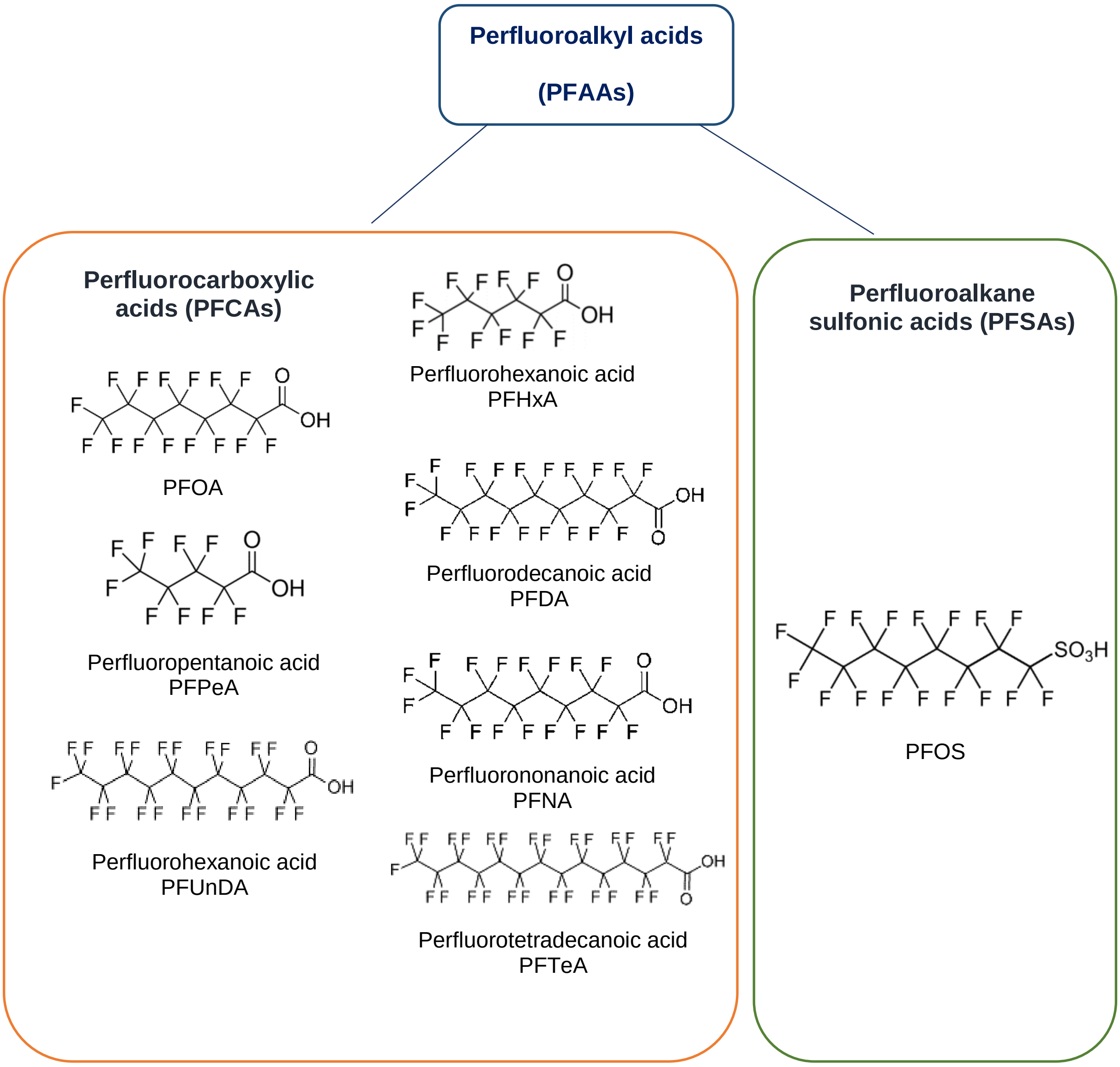

Figure 1.23: PFCAs and PFSAs that have been determined from liquid repellent outdoor garments using a long side-chain fluorinated polymer DWR.

1.4.7 Alternative chemistries for textile liquid repellency

1.4.7.1 Shorter side-chain analogues

DWRs with shorter side-chain fluorinated polymers, perfluoroalkyl moieties (C_6F_{13} or C_4F_9), continue to be used as replacements to long side-chain fluorinated polymers. However, the decrease in chain length and number of perfluoroalkyl moieties increases the surface energy (section 1.4.3.2). The smaller chain length results in a less crystalline structure with less orientation and packing of the end groups [110]. Overall, a lesser degree of liquid repellency is provided with less repellency to polar liquids [112,214].

Academic literature is progressively investigating the potential hazards of shorter side-chain fluorinated polymers. They have been identified as extremely persistent, highly mobile enabling widespread environmental distribution and to have comparable bio-accumulation potential in organisms to long side-chain fluorinated polymers [16,119,128,215]. Their effects are irreversible with the potential to be a planetary boundary threat (section 1.4.1) [119,128]. Shorter-chain analogues show similar characteristics to the long-chain polymers with potential degradation products perfluorohexane sulfonic acid (PFHxS) from 'C6' structures and perfluorobutane sulfonic acid (PFBS) from 'C4' structures (Figure 1.24) [119]. An increasing exposure trend to PFHxS has been observed, and this compound potentially has a similar or longer serum half-life, within mammals that have been tested, to PFOS [134]. Restrictions on shorter side-chain fluorinated polymers are imminent. PFHxS has been recommended to be listed as a POP by The Stockholm Convention, with further information being sought for review on PFHxS and PFBS [216,217]. PFHxS is persistent and bio-accumulative in accordance with Annex XIII of REACH regulation and has been added to the REACH candidate list identified as a substance of very high concern (SVHC) [216,217]. The Norwegian Environment Agency is currently reviewing the inclusion of PFBS within REACH [218].

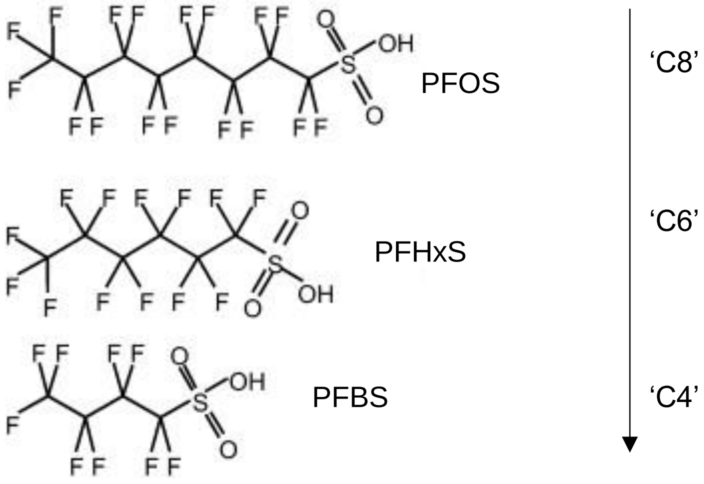

Figure 1.24: Potential degradation products from ‘C6’ analogues and ‘C4’ analogues, PFHxS and PFBS, show similar characteristics to PFOS.

In addition, when shorter side-chain fluorinated polymers are used within DWR applications, a greater concentration of polymer is used in the aqueous emulsion. This leads to a greater amount being coated on to the fabric in compensation to the lesser technical performance [215]. Due to this, brands have reported a whitening of the fabric surface due to the build-up of chemical applied to the surface. It is thought that the concentration of polymer is exceeding that which can be cross-linked to the fabric surface and therefore residual lies on the surface.

1.4.7.2 Non-fluorinated alternatives

Other alternatives to long side-chain fluorinated polymers for DWRs are plentiful, modifying both the surface structure as well as adopting alternative chemistries. However, whilst there are many peer-reviewed papers on alternative repellent surfaces, few have been commercially developed due to durability, cost and adaptation to textile surfaces for mass production. Within industry, alternative DWRs to side-chain fluorinated polymers are commonly referred to as ‘non-fluorinated’, ‘fluorocarbon-free’, ‘PFC-free’ or ‘C0’. DWRs based on the same principles of a hydrophobic component/side-chains linked to a polymer backbone are common [102]. The main groups of non-fluorinated chemistries are those based on hydrocarbons, silicones and hyper-branched chemical structures (Figure 1.25) [119].

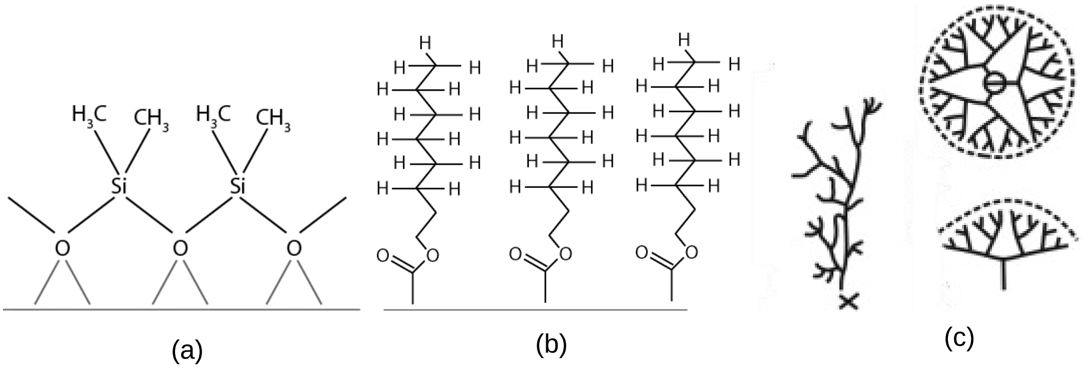

Figure 1.25: Non-fluorinated DWRs based on (a) silicones; (b) hydrocarbons and (c) hyper-branched structures [66,219].

Silicone DWRs refer to siloxane compounds [-Si-O-] with functional groups ($–CH_3$ end groups) [119,220]. Close packing of the side-chains and an outwardly orientation, encouraged by the structural polymer conformation, provide a greater number of end-groups, with low surface energy, at the surface interface. However, siloxane polymers are commonly polydimethylsiloxane (PDMS) with various siloxanes used as intermediate compounds in synthesis. Common building blocks for synthesis are octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) inevitably remaining on the treated textile as manufacturing residuals [119,221]. Following a proposal from Germany, both D4 and D5 are now listed on the candidate list as SVHC within REACH, due to their persistent, bio-accumulative and toxic properties, with additional listing of D4 and D5 as POPs by the Stockholm Convention [221,222]. This is problematic for the future of silicone-based DWRs, subject to concentration limits.

Hydrocarbon-based DWRs are a dense packing of paraffinic groups [119]. They are emulsions of long-chain hydrocarbons, C_nH_{2n+2}, with hydrophobic fatty acid groups, [36,173]. This allows outward direction and orientation of the end-groups. However, the $–CH_3$ end group has an inherently higher surface tension than that of $–CF_3$; thus providing lesser liquid repellency (Table 1.5). This is due to the structural differences between *F*-chains and *H*-chains [223]. Structurally, *F*-chains are larger with a greater cross-section that their hydrocarbon counterparts; additionally they are more rigid due to the helical configuration [223].

Table 1.5: Relationship between surface constitution at the surface interface and surface tension [36,69,103].

Surface constitution	**Surface tension (dyn cm^{-1})**
$-CF_3$	6
$-CF_2H$	15
$-CH_3$	22
$-CH_2$	31

Hyper-branched chemical structures, or dendritic chemistry, are a specific polymer chemistry creating highly branched tree-like units around a core [224]. With this, there is a concentration of functional end groups at the surface-air interface [225]. Dendrimers are regular in their molecular assembly whilst hyper-branched polymers are irregular and can differ by the synthesis approach [226]. Within the polymer, a silicone or hydrocarbon atom will provide inherent low surface energy. However, this non-linear structure prevents crystallisation with less close packing and order of the end-groups.

Biomimetics, defined as designing textile surfaces replicating inherent repellent structures found within nature, has received high interest as one method to find alternative repellent chemistries. The ‘lotus leaf’ is just one example of innovative fabric engineering imitating the hydrophobicity naturally fabricated by a folded, bumpy surface structure of wax nodules creating an hierarchical pattern of surface roughness. The combination of the hydrocarbon wax and surface structure creates a highly repellent surface from which water droplets roll off. Biomimicry is alluded to in the marketing of commercially available non-fluorinated finishes by chemical manufacturers HeiQ (Eco-Dry) and Rudolf (Bionic Finish Eco).

1.4.7.3 Alternative application methods

In addition, academic literature has looked at alternative methods of applying surface chemistry. The most successful is the application of the surface chemistry by plasma but the durability of the finish is problematic [227]. Plasma can be created from different gases to obtain differing surface chemistries and formation of bonds between the gas and substrate [228]; for repellency silicone and fluorine gases are commonly used. On textile surfaces, it has been found that the plasma interacts only with the surface leaving the bulk, and its corresponding properties, untouched.

1.5 Specific criticism towards the outdoor apparel industry

Criticism on repellent finishing using PFASs has had a significant impact on the apparel industry. Specifically within the outdoor apparel sector, workshops were held at annual tradeshows updating information on legislation with evolving pressure for brands to publically disclose their use of long side-chain fluorinated polymer DWRs and substitution process to alternative DWR chemistries. Most notably, Greenpeace have voiced their view on PFASs and published several documents specifically discussing the use of PFASs in outdoor repellent apparel [229–236]. They are the main activist group to have publically criticised the use of chemistry within the apparel industry. Reports published by Greenpeace before 2012 discussed the apparel industry as a whole but there was a noticeable shift to focus on the outdoor apparel industry in 2015 (Figure 1.26). Over the course of this research, the momentum of the Greenpeace criticism and demonstrating has developed rapidly and visibly. Throughout their reports and campaigning, Greenpeace referred to the chemical class as PFCs.

‘Swimming in Chemicals’, published in August 2010, was the first report published by Greenpeace to specifically target the textiles and clothing industry’s use of PFCs [237]. The report discussed the reduced use of hazardous chemicals within America and many European countries but the increase of chemical production and use within China where PFOS manufacture and use is not regulated. Notably, annual production of PFOS fell by a third in the US (2000-2010) but increased fourfold within China between 2004 and 2006 (total production before 2004 was 50 tonnes per year rising to 200 tonnes per year in 2006) [237–239].

Seven of their reports specifically discuss the use of PFCs within outdoor apparel. In 2012, Greenpeace published the ‘Chemistry for Any Weather’ report, followed by a similar study ‘Chemistry for Any Weather- Part II’ report in 2013 [229,230]. These two reports stated to have found hazardous chemicals in jackets and gloves sold by outdoor brands; ‘Chemistry for Any Weather’ called for a phase out of all toxic chemicals by 1 January 2020. These reports were the start of publicity specifically highlighting the use of PFCs in the outdoor apparel industry and set the foundations for an industry focus to substitute to alternative chemistries.

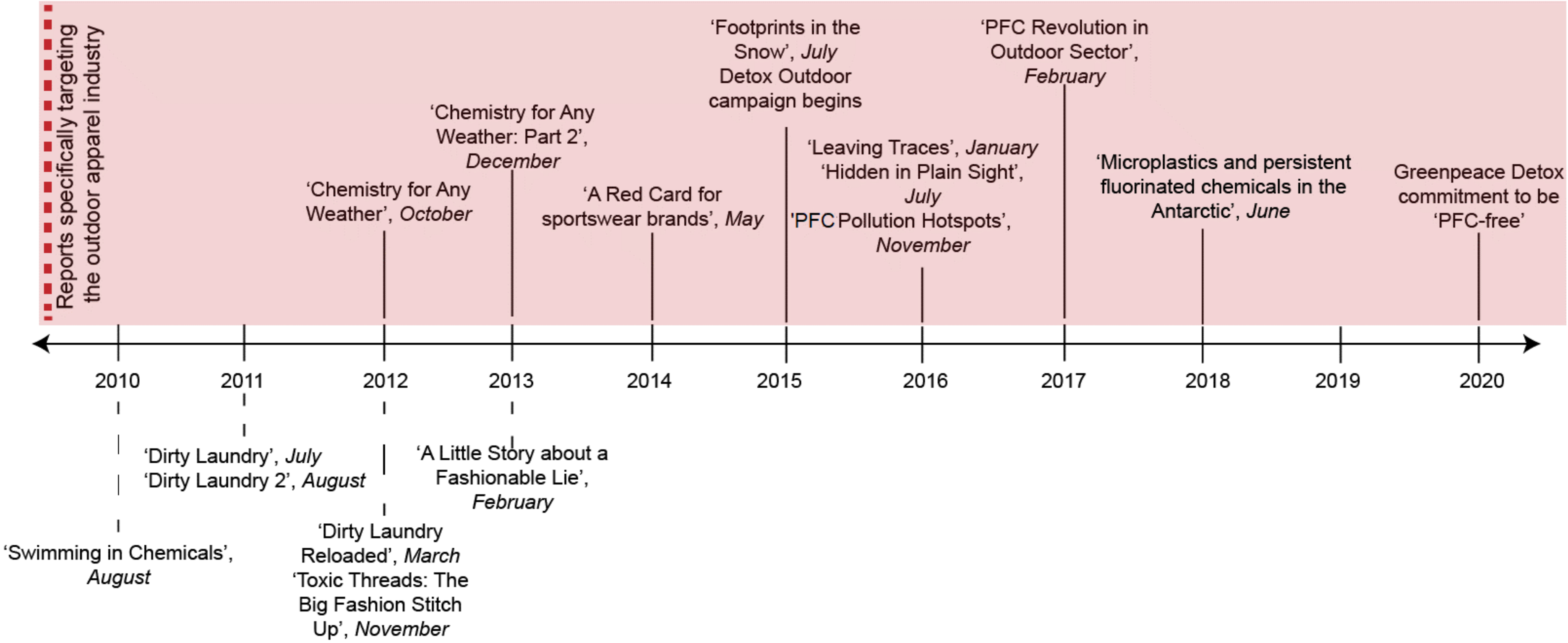

Figure 1.26: Timeline of the Greenpeace reports and campaigns targeting the textile and apparel industry's use of PFASs: the reports targeting specifically the outdoor apparel industry have been highlighted [229–237,240].

In 2015, Greenpeace launched their consumer ‘Detox Outdoor’ campaign coinciding with their ‘Footprints in the Snow’ report, an anticipated report in the wake of Greenpeace news articles on the progress of the sampling expedition to collect water and snow samples for analysis. The ‘Detox Outdoor’ campaign was launched to directly target the outdoor apparel consumer using social media.

The ‘Detox Outdoor’ campaign was accessible to a large consumer audience and directly linked consumer views to the brands through social media interaction. Website visitors were asked to ‘Join the Movement’ and sign-up to the Detox campaign [241]. Throughout the Greenpeace campaign, images were altered to include red trails within mountainous environments symbolising chemistry across mountainous ranges contrasting to the green nature and natural environment (Figure 1.27).

Figure 1.27: Images for the Greenpeace Detox Outdoor consumer campaign [242,243].

In 2015, consumers were asked to directly contact brands about their use of PFCs in outdoor gear by emailing or social media. This encouraged brands to publically discuss their use of DWR chemistry in their product range. The campaign also asked consumers to ask retailers involving other stages of the purchasing chain.

Part of the consumer campaign included voting for products to be tested by Greenpeace: 'Test your Equipment'. Website visitors were asked to select a brand,[‡‡] choose a product category and vote, optionally entering a specific product. The brands to be chosen were American, Canadian, German, Swiss and Swedish; none of the brands were from the UK. The products selected, at this stage, were tested by Greenpeace in the 'Leaving Traces' report [232].

1.5.1 "PFC Revolution" in the Outdoor Sector

This report was released at a press conference during the outdoor industry tradeshow ISPO 2017 and discussed the commitment by Gore concerning the use of PFCs within their membrane technologies [235]. The press conference signalled the end of direct Greenpeace criticism specifically towards the outdoor apparel industry. This was signalled by the Detox outdoor YouTube video thanking consumers for their involvement (Figure 1.28) [244].

Figure 1.28: Screenshot of the YouTube video by Greenpeace thanking consumers for asking brands about their PFC use [244].

The Gore commitment with Greenpeace stated to eliminate 'hazardous PFCs' or those 'to be of environmental concern', from their waterproofing membranes for general

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[‡‡] Eleven brands were specified (The North Face, Patagonia, Mammut, Jack Wolfskin, Salewa, Vaude, Columbia, Arc'teryx, Haglofs, Norrona and Blackyak).

outdoor use, by 2020, and specialised outdoor use, by 2023. An agreed definition of ‘hazardous PFCs’ or those ‘of Environmental Concern’ were agreed between Gore and Greenpeace allowing the manufacture of Gore’s PTFE membranes to continue but changing the manufacturing residuals which could be released during production and use of the product .

1.5.2 Representation of brands

Throughout the reports and publicity from Greenpeace, certain outdoor apparel brands have been targeted more frequently.

Throughout the campaign, The North Face and Mammut have been specifically highlighted within Greenpeace reports and highlighted on the campaign website. Both brands were targeted by Greenpeace campaigners, during 2015-2016. The demonstrations used imagery with toxic connotation directly in front of consumers (Figure 1.29).

Figure 1.29: Greenpeace campaigns targeting the North Face and Mammut: a) Greenpeace image adapting the North Face logo to resemble a toxic chemical tap; Demonstrators covering the North Face sign outside a store in Taipei; and demonstrators at the store entrance [245–247]; b) Imagery used by Greenpeace adapting the Mammut logo to a skeletal mammoth and comparing the brand to a 'Toxic snake' [248,249].

1.5.2.1 Brand commitments

Over the course of this research, outdoor apparel brands were urged to voice their commitments to reduce and eliminate long side-chain fluorinated polymer DWRs and substitute repellent finishes to non-fluorinated DWRs. Several outdoor apparel brands have published information on their websites stating their use of fluorinated DWRs and their timelines to non-fluorinated DWRs (Table 1.6). Despite the pressure to change to non-fluorinated chemistries, substituting chemistries within the supply chain has been a greater challenge often shielded by intellectual property rights and lacking transparency between the supplier, vendor and sub-contractors.

Table 1.6: Outdoor apparel brands highlighted by Greenpeace and their commitments to substituting to non-fluorinated DWRs. Progress/commitments use the original terminology from the brand.

Brand	Progress/Commitments	Reference
Berghaus	Moved from long-chain C8 to shorter-chain C6; PFC free options first available 2016; all DWR to be PFC-free by 2020	[250]
Montane	Moved from long-chain C8 to shorter-chain C6; working to develop non-fluorinated alternatives, PFC-free by 2023	[251]
Mountain Equipment	*No information found online*	
Rab	Moved C8 to C6; search for PFC-free continues, switch from PFC by 2020.	[252]
Gore	Agreement with Greenpeace to eliminate all 'hazardous' PFASs in manufacture - agreed criteria. Aiming to eliminate PFCs of 'Environmental Concern' from consumer laminates by 2023. First prototypes of consumer outdoor products without PFCs of 'Environmental Concern' in 2019 – labelled PFC_{EC}. Altered from pledge in 2017 to eliminate 'PFCs of Environmental Concern' from 85% of consumer laminate products by end of 2020 and from remaining consumer products 2021-23.	[253,254]
The North Face	Spring 2015 - moved C8 to C6. Spring 2017 - 30% fluorinated-free. Aiming to have 100% non-fluorinated DWR used on all apparel by 2020.	[255]
Vaude	95% of Summer 2017 apparel collection are PFC-free; 100% of the 2018 collection are PFC-free. Entire collection to be PFC-free by 2020.	[256]
Jack Wolfskin	95% of apparel collection PFC-free by summer 2018. Entire collection to be PFC-free by 2020.	[257]
Arc'teryx	2014 switched from long-chain C8 to C6; ongoing tests to find suitable PFC-free treatments	[258]
Haglofs	Offer fluorocarbon-free products; aim to be completely fluorocarbon-free by 2020.	[259]
Patagonia	Moved from long-chain C8 to C6; highly invested in finding PFC-free alternatives.	[260]
Mountain Hardwear	Products below EU set PFOS-limit, Jan 2015 Products below EU set PFOA-limit	[261]
Fjallraven	Since 2012, products fluorocarbon-free have been available, since 2015 all products have had 'fluorocarbon-free impregnation'.	[262]
Mammut	PFC free from clothing range by 2022: 'fundamental range by 2018', competence level by 2020, 'professional' by 2022	[263]

1.6 Summary

Liquid repellent outdoor apparel is essential for wearer thermal comfort and protection in inclement conditions. In mountainous environments, functional clothing that is weatherproof is vital where seeking shelter is not always possible, activity levels change frequently and it can be remote, challenging terrain. Adverse environmental conditions can have a detrimental effect on the wearer if a DWR does not adequately prevent the wetting of fabric.

Side-chain fluorinated polymer DWRs impart a high level of repellency to polar and non-polar liquids with good durability. However, legislation and chemical management have steered the need to seek non-fluorinated repellent chemistries. Whilst this substitution process is currently underway, the longevity of these finishes during consumer end-use is yet to be explored and progressively it is being asked whether outdoor apparel is over engineered – what do consumers *actually* require? This research will address this with a focus on consumer end-use and its effect on the longevity of liquid repellent finishes.

Sustainable chemical management is at the forefront of the textile and apparel industry. Despite the magnitude of the concerns raised on the use of PFAS chemistry, there are many unknowns in academic literature and scarce public data is available on the derivatives used, the number of products on the market and steps taken to substitute long side-chain fluorinated polymers [96]. Existing academic literature on PFASs has focused on human exposure pathways, toxicological research and development of analytical methods.

Despite the number of liquid repellent outdoor garments worn and the direct criticism of the industry by Greenpeace, there is little research on the effect that end-use, and consumer variables, have on liquid repellent functionality. This is all the more important considering the move to alternative repellent chemistries, which may have happened with haste overlooking potential chemical and functionality issues.

1.7 Aims and objectives

This research project has specifically focused on the use of liquid repellent chemistry for DWRs in outdoor performance apparel, and the impact that substitution of long SFP (C8) DWR chemistry will have on the consumer. The cross-disciplinary nature of this subject has led to a broader investigation which aims to bridge a knowledge gap between environmental chemistry, commercial application and consumer end-use; to connect the understanding of liquid repellent apparel by academia to that of the outdoor apparel industry, and to contribute to the sustainability of liquid repellent apparel in the future.

The aim of this research is to evaluate the impact that substitution of long side-chain fluorinated (C8) DWR chemistry with alternative chemistries for DWRs for outdoor apparel will have on liquid repellent functionality, maintenance of functionality during consumer use, and suitable evaluation methods to support the adoption of these.

This will be addressed by the following objectives:

1. Survey consumer use of liquid repellent outdoor garments in terms of environments worn within and consumer laundering behaviours;
2. Compare care label and other advice given by brands to consumers for laundering of liquid repellent outdoor garments, particularly with respect to maintaining the liquid repellent functionality;
3. Comparatively characterise and evaluate the performance of fluorinated and non-fluorinated DWR types, on fabrics used within the outdoor apparel industry;
4. Understand potential deterioration of liquid repellency through repeated laundering cycles and the impact of different drying methods;

5. Evaluate the efficacy of laboratory test methods for determining water repellency and their suitability for evaluating the repellency of both fluorinated and non-fluorinated DWR types;
6. Study the durability of fluorinated and non-fluorinated DWRs to abrasion and the impact on liquid repellent functionality;
7. Understand the impact of a DWR, by conducting wearer trials, on regulation of body heat transfer and moisture vapour transfer when worn in wet environmental conditions.

Over the course of this research, there has been a period of change with ongoing legislation on PFASs, publication of reports from NGO activists and research developments in the scope of alternative chemistries. Industry has acknowledged the need to look within their supply chains at chemical use and there has been a progressive shift in awareness of the need for sustainable use of chemistry. Where appropriate, information is dated to acknowledge this pace of change.

The SUPFES research group, working in partnership with Swerea and funded by The Swedish Research Council, have been working within this subject area evaluating the performance and environmental impact of fluorinated and non-fluorinated alternatives. However, their focus is from an Environmental Science perspective not specifically within outdoor textiles and apparel. Jointly, it is hoped that this project and the work completed by SUPFES has added to understanding and awareness of fluorinated polymeric DWRs in textiles and the suitability, risk and management of non-fluorinated alternatives.

Throughout this work, side-chain fluorinated polymer (SFP) DWRs will be referred to as long SFP (C8) DWRs and shorter SFP (C6) DWRs [10]. In Figures, these will be shortened to C8 and C6.

Chapter 2 - Consumer requirements and end-use of liquid repellent outdoor apparel: data collection

2.1 Introduction

As non-fluorinated DWR alternatives continue to be developed and sought, there has, since 2014, been an increased interest in understanding the consumers' knowledge and expectations of liquid repellent outdoor clothing [264,265]. This has been driven by the outdoor apparel industry with the European Outdoor Group (EOG), an umbrella organisation supporting the outdoor industry sector, as a driver.

A typical consumer laundering process for liquid repellent clothing, treated with a DWR, is thought to involve washing, drying and periodically applying an aftercare treatment to reproof the repellent finish (section 1.2.4.3). Wetting of the fabric surface, rather than beading or repellence of water, is a typical indicator to the consumer to use an aftercare treatment in laundering.

Consumers expect garments to be functional and durable [56]. However, ultimately, the laundering processes are chosen independently by the consumer, including the temperature of washing, the type of detergent, the length of wash, application of heat and frequency of laundering [266]. These parameters are determined by the consumer and influenced by their understanding of care symbols and any further information provided [266,267]. Consumer complaints are predominantly associated with deformation, functionality fail or colour change during laundering, in some cases resulting in the consumer discarding the garment [267,268]. Kerr *et al*. [268] discuss the decision, by the consumer, to discard a garment being based not necessarily on the dirtying of a garment but the perceived loss in functionality as a result.

Previous research carried out by the EOG (2014), specifically into consumer laundering practises of liquid repellent clothing, has suggested that the laundering of repellent apparel is commonly misunderstood by consumers, with numerous variables, such as the frequency of laundering and usage of the garment, affecting the revitalisation of the repellent finish [56,264,266]. Other work has found that on average consumers wash their repellent outdoor clothing twice yearly but do not iron nor tumble dry their garment [269]. The study found that aftercare treatments were not applied at all or, in contrast, applied after every wash.

This chapter aims to understand consumer use, expectations and laundering of liquid repellency apparel by addressing objective 1 (section 1.7). This data will be used to inform subsequent laboratory work considering approaches to maintain functionality of non-fluorinated DWRs. A focus will be made on liquid repellent outdoor apparel, namely outerwear jackets.

A consumer behaviour study (2014), in the form of a survey, completed by students at De Montfort University (DMU) on behalf of the EOG[§§] has become a key reference for the outdoor apparel industry and their understanding on consumers knowledge of liquid repellent clothing [264,270]. This research work was the first to study the relationship between the consumer and the brands on the topic of DWRs.

The survey was disseminated to consumers by brand publicity, by the OIA and the EOG. The completion of the survey was incentive led, with a prize draw to win a backpack. The twenty-question survey was completed by 698 respondents [265]. Consumers were questioned about a ‘non-insulated jacket’ and an ‘insulated jacket’ on three topics: purchasing factors and use of the jacket, cleaning and reproofing, and

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[§§] The consumer survey was also supported by collaborative partners the Outdoor Industries Association (OIA), Association of the German Sports Good Industry (BSI) and Zero Discharge to Hazardous Chemicals Group (ZDHC).

briefly on environmental issues [264]. The brand survey was answered by 47 brands and asked which were important properties for these jackets, the recommended washing procedure, the brands instructions to reproof, whether the brand is looking for alternatives to fluorocarbon-based DWRs and how this will influence marketing [264].

The consumer survey concluded that commonly outdoor jackets are used by consumers for casual use and the important factors are durability, water repellency, breathability and wind resistance [264]. Stain repellency was concluded to be fairly important/useful to consumers [271]. The study concluded that the use of re-proofing products by consumers varies greatly [270]. Consumer laundering practise varied widely and the number of washes before using an aftercare product was not consistent amongst respondents [271]. Therefore it was concluded that there is a gap in the dialogue between consumers and brands in informing how to care for water repellent garments [264,270]. Brand instructions to consumers were also seen to vary with 37 brands offering no recommendation on when to reproof their jackets, in terms of wash cycles [264].

2.2 Survey design

An online survey was designed and launched through Bristol surveys, in affiliation with the University of Leeds, enabling a URL link to be disseminated to participants. Ethical approval (LTDESN-032) was granted prior to the research starting.

2.2.1 Sample size

The total number of participants in outdoor recreation cannot be determined due to the nature of participation (section 1.2.1). The total population of the group to be questioned was therefore unknown and a method of convenience sampling was adopted.

2.2.2 Length

The length of the survey was important in relation to the number of completed responses and therefore the survey was split into sections. If a respondent did not own a waterproof jacket then the questions skipped to ‘Completion of survey’ (Figure 2.1).

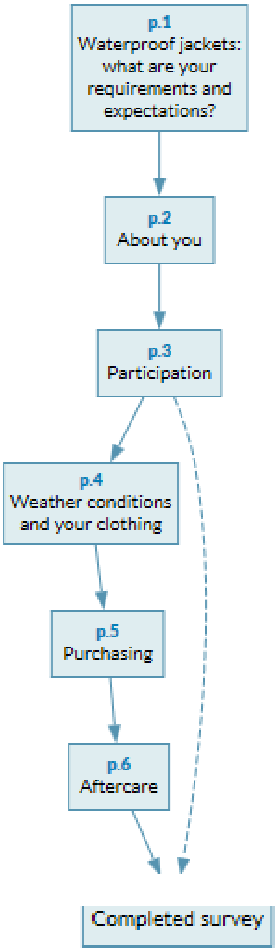

Figure 2.1: A layout map of the online survey.

2.2.3 Dissemination

The dissemination of the DMU and EOG study was predominantly through brands, via online social media and websites. The publicity of this survey was marketed with an incentive.

For this work, the target audience was decided to be consumers that regularly wear liquid repellent clothing for outdoor activities and participate in a range of activities.

Therefore outdoor recreation blogs, websites and social media sites were initially used for promotion of the survey. UK consumers were targeted due to buying habits differing by country according to weather, terrain and availability of brands.

2.2.4 Focus groups and pilot studies

Focus groups were held to assess the validity, and accessibility, of questions proposed to be used within the survey. In March 2015, a focus group was held with 14 members of Leeds University Union's Hiking Club and in April 2015, a second focus group was held with four members of hiking club 'Take a Hike', Leeds. Signed consent was received by participants prior to the group meeting and participation was voluntary. In March 2015, the first pilot study was launched with the aim to verify the contents of the survey, the survey structure and the language used.

2.3 Results and discussion

2.3.1 Focus groups

Focus groups enabled the accessibility of the questions proposed for the survey to be evaluated. These groups were important to evaluate the wording used and length of the survey. Participants were asked to discuss their expectations of liquid repellent apparel, their understanding of a DWR and their laundering practises. Qualitative data collected during these focus groups is included within A.1.

2.3.2 Consumer survey

Both quantitative and qualitative data was collected through the survey.

2.3.2.1 Respondents demographics and participation

The survey ran for 15 months from 15th May 2015 to 19th August 2016 and received a total of 575 responses; survey questions are included within A.2. The demographic data showed that the study had reached a wide UK audience with 526 respondents (91.5%) living within the UK, 35 other respondents from Europe and 14 from other countries worldwide. All age groups were represented with most respondents in the age categories (21-25 years), (31-35 years) and (41-45 years); 72.2% of respondents were male. 83 people (14.4% of respondents) participated in outdoor activities every day (Figure 2.2).

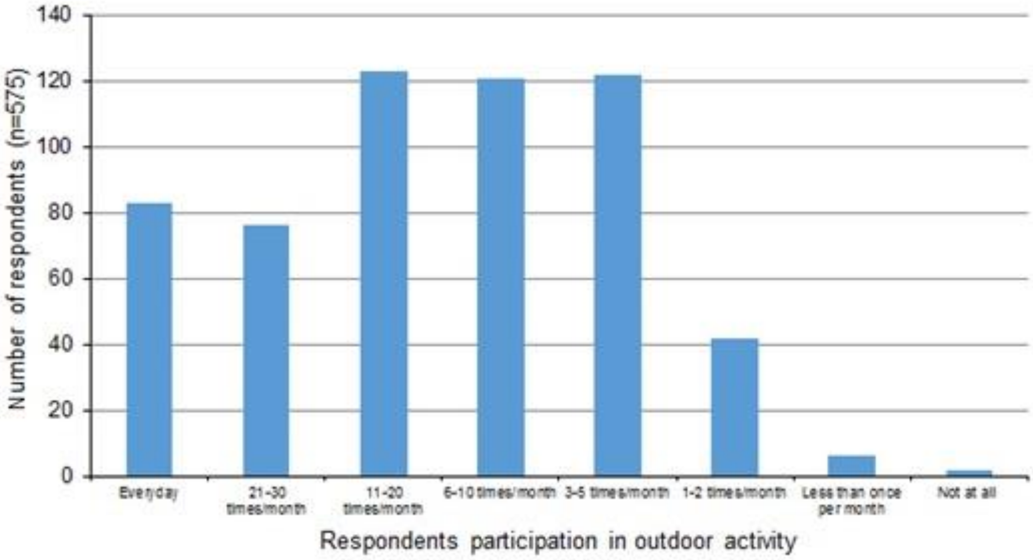

Figure 2.2: Respondents frequency (monthly) of participation in outdoor activities.

Overall, respondents participated frequently in outdoor activities (Figure 2.2). Two respondents did not participate in outdoor recreation at all (0.3%). Most respondents (54.6%) chose ‘walking, hiking, trekking, mountaineering and hill-walking’ as their main recreational activity. 112 respondents (19.5%) considered ‘cycling, running, trail running’ as their main activity and 78 respondents (13.6%) considered ‘climbing, caving and bouldering’ as their main activity. Slightly under half of respondents (47.1%) were members of an outdoor recreation club, society or group. This choice of activity describes the type of environment and terrain in which most respondents take part in outdoor recreational activities.

2.3.2.2 Consumer use

To understand consumer use, questions were asked about the current liquid repellent jacket owned, duration of wearing the jacket (monthly) and other items of apparel worn.

Over 73% of respondents (421) owned two to five repellent jackets with 2.8% owning more than ten jackets. The majority of garments cost between £101 and £200 (40.6%) and most had been owned for 1-2 years (31.6%). On a monthly basis, 43 respondents (7.5%) wore their repellent jacket 0-2 hours, 146 respondents (25.5%) 3-8 hours, 144 respondents (25.1%) 9-15 hours, 118 respondents (20.6%) 16-25 hours, 41 respondents (7.2%) 26-35 hours and 81 respondents (14.1%) more than 36 hours. From this, respondent use of a repellent jacket is high and a key garment to the respondent group.

348 respondents (60.7%) said that they usually wear a rucksack on top of their jacket and 140 respondents (24.4%) said they wear both a rucksack and harness on top of their jacket (Figure 2.3). Whilst the pack load would differ by person and activity, this data highlights areas of the garment which may be abraded by rucksack strapping or harness waist belt and leg loops. This, consequently, may affect the liquid repellent functionality.

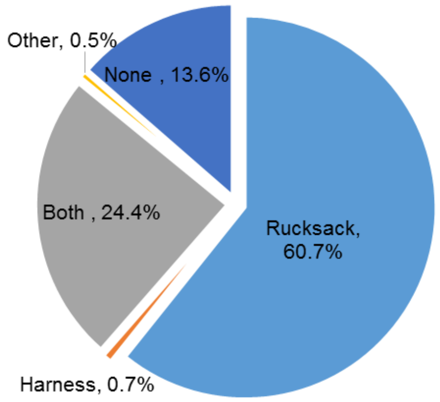

Figure 2.3: The percentage (%) of respondents wearing a rucksack or harness on top of their liquid repellent jacket.

2.3.2.3 Environment

384 respondents (67%) said they participated in outdoor recreational activities in all weathers, including rain and snow, with 268 respondents being outdoors in the rain more than 20 times per year; advocating the need for a high, sustained level of water

repellency on their apparel. 421 respondents were willing to participate in their recreational activities in heavy rain, 307 in heavy snow and 139 in light snow. This highlights the wide range of outdoor mountaineering activities undertaken by respondents and their readiness to participate in adverse weather conditions.

2.3.2.4 Laundering

499 respondents washed their repellent jacket but detergent use varied (Figure 2.4). The two most used washing products were a soap-based product (247 respondents; 43.1%) and non-biological detergent (165 respondents; 28.8%).

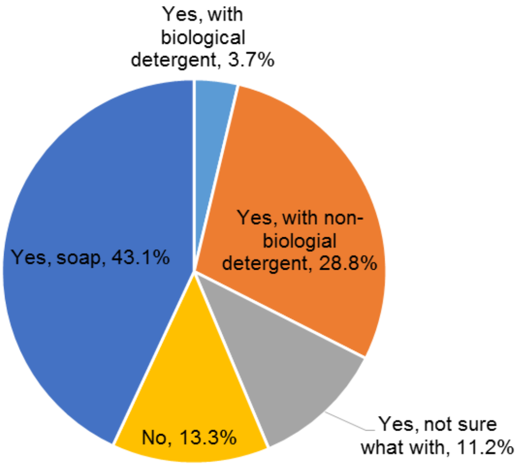

Figure 2.4: Use of detergents by respondents.

Of all the respondents, 203 (44.8%) did not apply any heat, by tumble drying or ironing, during the wash process (Figure 2.5). A small percentage of respondents (6.6%; 30 respondents) said they ironed their repellent jacket. 159 respondents (35.1%) said they tumble dried their jacket and 61 respondents (13.5%) said they sometimes applied heat during drying in the wash process.

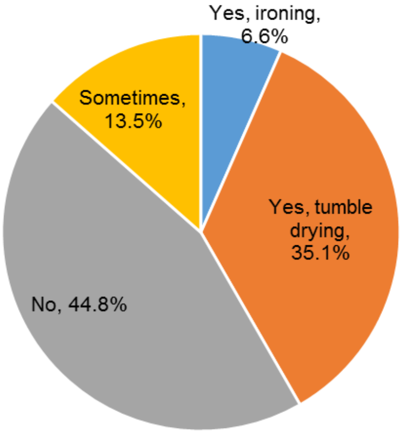

Figure 2.5: Choice of drying or heat application by respondent, during laundering.

Just under half of respondents (286; 49.9%) had asked for further advice on how to care and maintain the repellency of their jacket. This included asking retailers, consulting clothing labels, looking at brand websites, asking friends and through social media. Most respondents (453; 79.1%) said they used a re-proofing product; of these 69.8% (316) followed the instructions on the product precisely using the product a few times a year.

2.3.2.5 Purchasing factors

Respondents ranked purchasing factors by importance. None of the factors were ranked as ‘unimportant’ but respondents, overall, stated water repellency, breathability, fit, durability and wind resistance to be very important. Overall, the majority of respondents (82%) considered water repellency to be the most important factor, compared to a high number of respondents being indifferent to stain resistance (48%) and dirt and oil repellency (42%) (Figure 2.6). Respondents were more concerned with performance factors than appearance. This highlights the primary consumer demand of a liquid repellent garment: protection from the rain and inclement conditions.

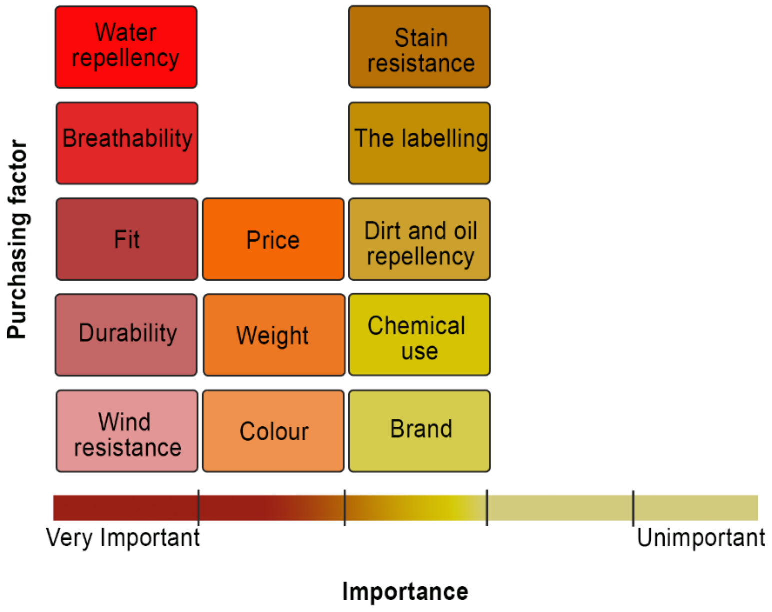

Figure 2.6: Water repellency was the main requirement for survey participants, ranked as ‘very important’ by 82% of respondents.

Respondents selected factors they considered to be important in the ‘environmentally friendly production’ of a repellent garment. The main priorities of consumer environmental considerations in production were ‘functionality to not be lessened’ (310 respondents), product to be ‘ethically sourced’ (255 respondents), a ‘repairable product’ (252 respondents) and ‘non-toxic chemicals’ (242 respondents). This, again, highlights the importance of performance for the consumer and also suggests that social and environmental impact are of concern to the consumer.

2.4 Conclusions

This consumer survey was undertaken for data collection on consumer end-use and laundering practises. In similarity to the previous consumer survey study, by DMU and the EOG, water repellency, durability, breathability and wind resistance were seen by respondents as important factors. Within this study, fit was also rated as important. Within the DMU and EOG study, stain resistance was considered as fairly important/useful but here rated as indifferent by respondents.

Of the data collected, in summary:

- The main recreational activity of respondents was walking and mountaineering.
- Number of jackets owned and time spent, on a monthly basis, participating in outdoor recreation implied that respondents were highly active within outdoor activities and a repellent jacket is a key item of their clothing.
- Most respondents (43.1%) wash their repellent jacket with a soap-based product.
- Heat application during the wash process is varied but just over a third of respondents tumble dry their repellent jackets.
- Most respondents use a re-proofing/aftercare product throughout the year in the wash process.

Data collected within this chapter will be used to inform subsequent laboratory investigation and variables chosen within the experimental design.

Chapter 3 - Evaluation of laundering information from care labelling: data collection

3.1 Introduction

Labelling of clothing is an important communication tool between brands and consumers. Care labels*** offer consumers easily accessible guidance on laundering and information on procedures to maintain their product, in terms of washing, drying, ironing and professional care [272]. Attached to the inside of the garment the care label is intended to help the consumer effectively care for their garment and is a main source of information [267,273]. Swing tags can be used to inform and communicate with the consumer but these are usually removed post-purchase.

In outdoor apparel, issues arise with care labelling due to the clothing typically compromising of multiple fabrics, the finishing treatment, and the associated combination of functionality [268]. A challenge lies in advising consumers on accurate laundering procedures whilst maintaining the performance of the garment and its components [56]. Furthermore, the use of the garment and the conditions it is subjected to during its lifetime affect its performance and cannot be predetermined variables [273]. However, a lack of functionality in a garment can reduce its performance and life-span; reduction in functionality can be seen as a failure of performance with the consumer discarding the item [273].

***There are several mandatory international care labelling systems: United States of America, China, Australia and Japan. At European level, there is not a mandatory care labelling procedure, but if a label is applied it is a legal requirement that the care method is fit for purpose [275,305].

As detailed in the testing standard BS EN ISO 3758-2012 [272], symbols are used to specify five key laundering instructions for washing, bleaching, drying, ironing and dry cleaning; Figure 3.1 shows use of the symbols within a care label. Additional care instructions are included to give further information. Care labelling guidance states that additional wording should be used to provide information on sustaining ‘ordinary use’ [272]. Building on this, the ASTM guide [274] discusses additional wording to be used to ‘refurbish a product without adverse effects’ and restore functionality’ where it may be necessary to convey special instructions not covered by the appropriate care symbol’. However, there are currently no requirements within the EU for labelling at the point of sale nor within the garment, in relation to chemical use, chemical regulations or chemical testing of garments [275].

MESHFODER 100% POLYESTER
■ SI : ZUNANJI DEL 100% POLIAMID S
POLIURETANSKO MEMBRANO
KOSI 100% POLIAMID S POLIURETANSKO MEMBRANO
PODLOGA IZ TRDNEGA MATERIALA 100% POLIAMID
PODLOGA IZ MREŽICE 100% POLIESTER

■ GB : DO NOT BLEACH / LOW TUMBLE DRY / COOL IRON / DO NOT DRY CLEAN / USE NON-BIOLOGICAL WASHING POWDER / DO NOT USE FABRIC SOFTENERS / WASH WITH SIMILAR COLOURS / RINSE THOROUGHLY IN COLD WATER / REMOVE IMMEDIATELY AFTER WASH / STORE IN A COOL, DRY ENVIRONMENT / KEEP AWAY FROM SHARP OBJECTS

Figure 3.1: A diagrammatic care label with common symbols.

To establish the washing variables advised to the consumer, an evaluation of care labels on liquid repellent jackets and online guidance was undertaken as set out in objective 2 (section 1.7). The data collected in this study will be used to inform subsequent laboratory work considering the maintenance and durability of DWRs.

3.2 Analysis of care labels

Quantitative and qualitative data methods were employed to analyse care labelling of repellent outdoor performance jackets. Jackets analysed were men's and women's jackets currently on sale within stores in Leeds, UK (September 2015, March 2016) and Munich, Germany (January/February 2016) and a range of jackets from 17 different brands were assessed, as a sample of those available in stores and on sale. During the research it was found that jackets from the same brand had similar care labels. Therefore, for this research purpose, only one label per brand was selected. Photographs of the care labels were taken. Further to this, information given online by brands for cleaning and reproofing of garments was sought. A literature search was conducted to compare the advice offered by brands online,[†††] on their own websites (September 2015 to March 2016) to care advice given on labels of outer jackets currently on sale. Swing tags were not analysed as these can be easily removed post-purchase. Tabulation charting of the care instructions was completed with systemic categorising to ascertain frequency of instructions, and patterns and trends within communication [276]. Following initial research, this study was segmented into the three areas of laundering associated with maintaining a liquid repellent garment: washing, drying (including ironing) and further care, principally re-proofing.

3.3 Results and discussion

Care instructions were tabulated according to Table 3.1. Only information given on the care label was used in completion of the charting; where information was not given the entry remained blank. Further charting was completed on specific further worded instructions ascertaining the word frequency, in all labels consulted. This enabled an

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[†††] The brand websites were Montane [306], Rab [307], Arc'Teryx [308], Berghaus [309], Sprayway [310], Mountain Equipment [311], The North Face [312], Jack Wolfskin [313], Vaude [314], Mammut [315], Millet [316], Marmot [317], Haglofs [318], Tierra [319], and Gore [320].

analysis on further laundering instructions, the use and type of soap/detergent, and on re-proofer application method.

Table 3.1: Charting headings of care instructions.

Brand	Fabric type	Membrane/ laminate	Wash: type, temperature	Dry: iron or tumble dry, settings	Suggested re-proofer	Soap/ detergent	Further instructions: wash/dry

Each jacket was given an alphabetical reference: A to I were on sale within the UK; J to R were on sale in Germany

3.3.1 Care labels: Washing

The information given on care labels was categorised by washing temperature and further details on alternative laundering methods: ‘hand wash’, ‘dry clean’. Overall, brands advise to wash repellent outerwear at 30 °C and 40 °C. On seven care labels, the guidance advised to machine wash at 30 °C, ten care labels advised to machine wash at 40 °C, and only one care label (H) advised to either hand wash or machine wash; three recommended dry-cleaning on the care label (F, L, R; Table 3.2).

Overall, connections between the fabric composition and the washing instructions could not be ascertained. Both brands L and M with 100% polyester fabric type with a PTFE membrane advised to wash at 30 °C. Brands C, F, P, who all state the use of a GoreTex ePTFE membrane and are partially or 100% polyamide, all advised to machine wash at 40 °C. The DWR chemistry type was not specified on any care labels.

Table 3.2: Washing symbol instructions on care labels.

Sample	Brand	Fabric Type	Membrane/ laminate	Wash Temp (°C)	Hand Wash?	Dry Clean?	Soap/Detergent Recommendation
A	Montane	100% PA	Pertex membrane	40			Nikwax
B	Rab		Pertex membrane	40			
C	Arcteryx	100% PA	GoreTex ePTFE membrane	40			
D	Berghaus	100% PA	PU membrane	30			
E	Sprayway	100% PA		30			Grangers 2 in 1 cleaner, prewash with regular detergent
F	Mountain Equipment	100% PA	GoreTex ePTFE membrane	40		Y	Silicone-free treatment
G	The North Face	100% PES		40	Y		
H	Lowe Alpine	100% PA		40			
I	Jack Wolfskin	50% PA/ 50% PES	Own branded	30			
J	Salewa	67% PA, 33% PES		30			
K	Vaude	100% PES	PU membrane	30			Wash with mild liquid detergent
L	Mammut	100% PES	PTFE membrane	30		Y	Use sportswash detergent (membrane friendly)
M	Millet	100% PES	PTFE membrane	30			
N	Marmot	90% PES 10% elastane		40			Powdered detergent
P	Haglofs	66% PA, 34% ePTFE	GoreTex ePTFE membrane	40			Liquid soap-free detergent
Q	Black Diamond	100% PA		40			
R	Tierra	53% PA, 27% PES 20% PTFE		40		Y	

3.3.1.1 Worded washing instructions

Further worded instructions were provided on several care labels detailing further information in regards to washing (Figure 3.2). The majority of the worded instructions were advising to avoid the use of fabric softeners (15 brands).

Figure 3.2: Word cloud highlighting the frequency of the worded further washing instructions.

Other worded instructions included rinsing twice (C, Q), washing the garment inside out (I, P, R), washing the garment separately (G, J), using warm washing water (G, N, Q), using cold washing water (D) and to not use bleach (N, Q). Overall, there were a variety of further washing instructions offering diverse advice.

3.3.1.2 Soap and detergent recommendations

Seven brands provided guidance on the use of soap or detergent (Table 3.2). Two brands (A, E) recommended the products sold by reproofing brands Nikwax and Grangers. Other brands advice varied; terminology used included ‘silicone-free treatment’ to ‘liquid soap-free detergent’. The clarity of the terminology, here, lies with the consumers’ knowledge and understanding the difference between detergents. Two brands (K, P) directly referred to using liquids; one brand recommended detergent powder (N, Table 3.2).

3.3.2 Online brand information: Washing

An online website gives an opportunity to provide further information than on a product care label. For comparison, the same brands, as were represented in the section on care labels, were consulted. The Gore website was also consulted to compare between brand advice for GoreTex ePTFE membranes and advice from Gore. Only brand A advised to wash at either 30 °C, 40 °C, or to hand wash (Table 3.3). Figure 3.3 gives a grouped frequency of the washing temperature instructions from brand websites, including the GoreTex website. Two brands (J, Q) did not have any laundering instructions on their online websites. Four brands advised to wash at 30 °C; two brands, including GoreTex, advised to wash at 40 °C; brand A advised to wash at either 30 °C or 40 °C; and eleven brands did not give any advice on wash temperature (Figure 3.3). Eleven of the seventeen brands, along with the information on the GoreTex website, stated to follow the care instructions provided on the garment label.

Most brands online guidance recommended to avoid using fabric conditioners and softeners (Figure 3.4). Brand K reasoned this to be due to the potential of fabric softeners to reduce breathability. Three brands (A, C, G) and GoreTex recommended to rinse twice. Brand G reasoned this was to ensure no detergent residue remains. Brands B and E advised to avoid dry-cleaning. Other instructions included washing the garment inside out (L, K, P) and washing on a gentle or delicate cycle (A, B, K).

Table 3.3: Brand instructions for washing from online brand websites. Note that Lowe Alpine (H) ceased to sell clothing in 2015, and Salewa (J) and Black Diamond (Q) provided no instructions on their website.

Sample	**Brand**	**Follow Care Instructions On Label?**	**Wash Temp (°C)**	**Hand Wash**	**Dry Clean**	**Soap/Detergent Recommendation**
A	Montane		30 & 40	Y		Pure soap or specialist cleaner Nikwax. Non-biological detergent.
B	Rab	Y	40	Y		Nikwax Tech Cleaner. Avoid detergents.
C	Arcteryx		40			Free-rinsing soap or non-detergent cleaning agent.
D	Berghaus	Y	30			Soap powder/liquid. For stubborn grease and dirt use non-biological detergent.
E	Sprayway	Y	30	Y		Soap-based Techwash or pure soap flakes. Avoid detergents.
F	Mountain Equipment	Y	--			Do not use ‘modern’ detergents. Pure soap or specialist cleaner.
G	The North Face	Y	--			Liquid detergent rather than powder. Use a soap-based product.
I	Jack Wolfskin	Y	--			Use Jack Wolfskin products.
K	Vaude	Y	--			Mild liquid detergent, preferably a special detergent such as Nikwax Tech Wash.
L	Mammut	Y	--			Liquid detergent
M	Millet		30			Non-aggressive detergent or a special detergent for waterproof materials
N	Marmot	Y	--			Granger’s cleaner or powder. Do not use liquid detergent.
P	Haglofs	Y	--			Use liquid (non-soap based) washing detergent.
R	Tierra	Y	--			-
	GoreTex	Y	40			Liquid detergent

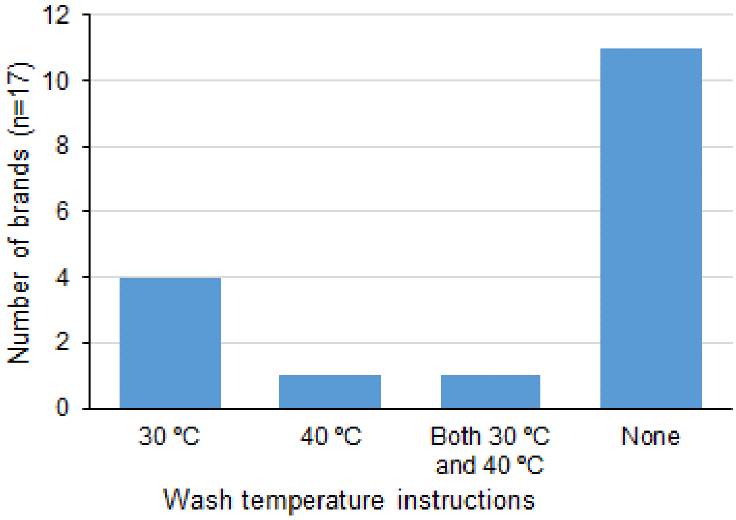


Figure 3.3: Grouped frequency of washing temperature guidance given on brand websites.

Figure 3.4: Word cloud highlighting the frequency of words in further washing instructions on brand websites.

3.3.2.1 Soap and detergent recommendations

Overall, more information was given on online brand websites concerning soap/detergent recommendations than on care labels. However, there was vast variation in the recommendations for soap or detergent product use in online brand information. Additional worded instructions from online information regarding soap/detergent use are shown in Table 3.3. Overall guidance was to use liquid washing products rather than powder washing products (Table 3.4). Five brands (A, D, E, F, G) recommended using pure soap or soap-based products, however, in contradiction, brand P recommended using non-soap detergent. Liquid products were recommended by four brands (G, K, L, P) as well as GoreTex. Brand L reasoned that a washing powder would block the pores of the fabric membrane. Conversely brand N recommended to use washing powder reasoning that liquid detergent clogs pores. Three brands (B, C, E) recommended to not use a detergent; whilst six brands recommended ‘detergent’ (A, G, K, L, M and P). Most unclear was the terminology used by brand M stating to use a ‘non-aggressive detergent’ and Brand F to not use ‘modern’ detergents (Table 3.3). Similar advice on both the care label and brand website was given by brands (A, K, N, P). The advice given by three brands (E, F, L) on the care label differed to that on the brand website. Only brand C advised to rinse the garment twice on both the care label and in online information. Avoiding fabric softener use was the main further instructional advice given on both care labels and in online brand website advice.

Table 3.4: Overall frequency table showing guidance on type of soap/detergent product to use.

	Mild	**Avoid biological/ use non biological detergent**	**Nikwax**	**Liquid**	**Soap**	**Non-detergent, avoid detergents**	**Specialist cleaner**	**Grangers**	**Non-soap**	**Do not use fabric conditioner**	**Do not use fabric softeners**	**Powder**	**Detergent**
Labels (n=17)	2	2	1	3	2	1		1	1	3	13	2	5
Online information	1	1	2	5	4	3	1	1	1	3	6	2	7
GoreTex				1						1	1		1
Total	*3*	*3*	*3*	*8*	*6*	*4*	*1*	*2*	*2*	*6*	*19*	*4*	*12*

3.3.3 Care labels: Drying and heat application

Drying information on care labels was categorised by recommended drying type, ironing or tumble drying, and temperature (Table 3.5). Overall, eleven brands advised to apply a cool iron to the garment and three brands advised to use a medium heat iron (Figure 3.5). Twelve brands advised to tumble dry the garment at a low heat and three brands advised a medium heat (Figure 3.6). None recommended to air dry the garment.

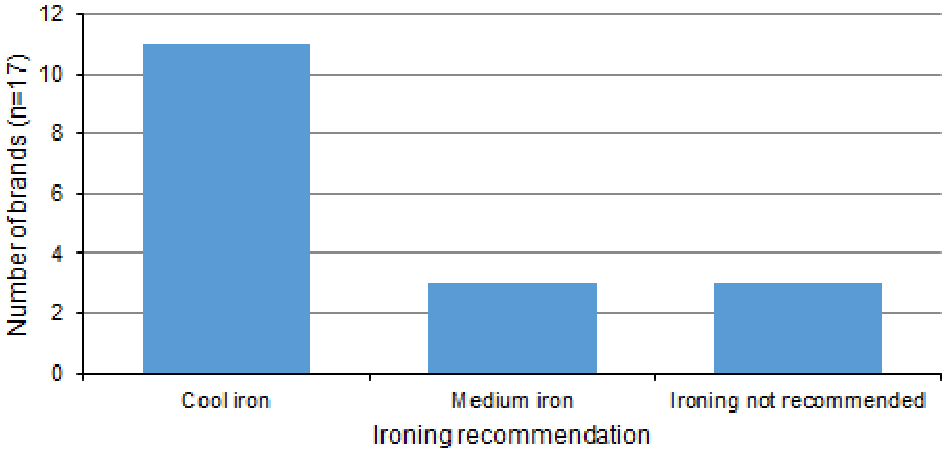


Figure 3.5: Grouped frequency of ironing recommendations on care labels.

Only brand M advised to neither iron nor tumble dry the garment. Brand J advised to not tumble dry the garment while two brands (G, N) advised to not iron the garment. Overall, for garment drying a relationship between the fabric type and DWR could not be established. Worded instructions were given on several of the care labels but gave varied recommendations including to cool iron to restore appearance (B), to use warm steam iron (E) and to avoid use a steam iron (R). One brand (J) advised ironing for ‘ideal functioning’ and one brand (K) advised to iron whilst damp or tumble dry for ‘optimal function’. Brand L was the only brand to specifically recommend a time guideline of tumble drying for 15 minutes.

Table 3.5: Drying instructions on care labels.

Sample	Brand	Fabric Type	Membrane/laminate	Iron	Tumble Dry	Worded Instructions
A	Montane	100% PA	Pertex membrane	Cool	Low Heat	
B	Rab		Pertex mebrane	Cool	Low Heat	To restore appearance, cool iron.
C	Arcteryx	100% PA	GoreTex ePTFE membrane	--		
D	Berghaus	100% PA	PU membrane	Cool	Low Heat	
E	Sprayway	100% PA		Cool	Low Heat	Warm steam iron, light tumble dry only.
F	Mountain Equipment	100% PA	GoreTex ePTFE membrane	Medium	Medium Heat	Tumble dry/iron or silicone free treatment to reactivate water repellency. Tumble dry medium temperature.
G	The North Face	100% PES		Do not	Low Heat	Tumble dry at low heat, do not iron.
H	Lowe Alpine	100% PA		Cool	Low Heat	
I	Jack Wolfskin	50% PA/ 50% PES	Own branded	Cool	Low Heat	Close all zips and fasteners. Do not iron print.
J	Salewa	67% PA, 33% PES		Cool	Do not	Do not tumble dry. Iron at max sole plate temperature of 110◦C. Iron right side only. Ironing recommended for ideal functioning.
K	Vaude	100% PES	PU membrane	Cool	Low Heat	Ironing while damp or tumble drying recommended for optimal function.
L	Mammut	100% PES	PTFE membrane	Cool	Low Heat	Approx. 15 minutes tumble dry time for optimum function.
M	Millet	100% PES	PTFE membrane	Do not	Do not	
N	Marmot	90% PES 10% elastane		Do not	Low Heat	Do not iron, tumble dry low.
P	Haglofs	66% PA, 34% ePTFE	GoreTex ePTFE membrane	Cool	Low Heat	
Q	Black Diamond	100% PA		Cool	Low Heat	Permanent press. Tumble dry normal low heat. Iron low. Do not steam.
R	Tierra	53% PA, 27% PES 20% PTFE		Medium	Medium Heat	

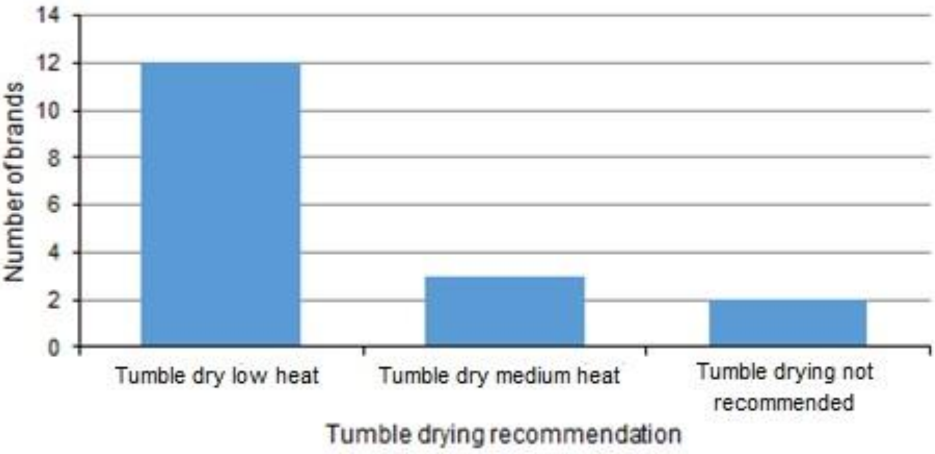


Figure 3.6: Grouped frequency of tumble drying recommendations on care labels

3.3.4 Online brand information: Drying and heat application

Online brand websites provided space for further information on recommended drying procedures (Table 3.6). Twelve brands recommended to tumble dry and four brands recommended ironing. Five brands (E, F, I, L and N) discussed applying heat to restore the repellent functionality and maintain DWR. Similarly, the GoreTex website advised to tumble dry or iron to reactivate the repellent finish.

Table 3.6: Brand instructions for drying from online brand websites. Note that Lowe Alpine (H) ceased to sell clothing in 2015, and Salewa (J) and Black Diamond (Q) provided no instructions on their website.

Sample	Brand	Follow Care Instructions On Label?	Iron	Tumble Dry	Soap/Detergent Recommendation
A	Montane		Only eVent	Y	
B	Rab	Y		Y	Avoid ironing. Hang dry or tumble dry.
C	Arcteryx			Y	
D	Berghaus	Y		Y	
E	Sprayway	Y		Y	Avoid ironing as this may damage the garment. Hand dry or tumble dry on a low temperature. Tumble drying helps maintain the DWR.
F	Mountain Equipment	Y			Let garment drip-dry. DWR can be reactivated by applying heat, if reproofing product not effective cool iron or tumble dry.
G	The North Face	Y			Dry in tumble dryer, cool setting or use iron, cool setting
I	Jack Wolfskin	Y	Y	Y	Iron or tumble-dry after each wash to restore repellency.
K	Vaude	Y		Y	Tumble dry only when stated on label.
L	Mammut	Y		Y	Leave the garment to dry completely. The DWR of water-repellent products can be re-energised after washing by giving them a heat treatment. Tumble-dry your product for approximately 5 minutes or iron it carefully
M	Millet			Y	Drying should be done in the open air or in a tumble dryer at low temperature
N	Marmot	Y		Y	Tumble dry to restore DWR.
P	Haglofs	Y	Y	Y	GoreTex must be exposed to heat after every wash. Tumble dry inside out.
R	Tierra	Y			
	GoreTex	Y	Y	Y	Line or tumble dry on warm gentle cycle. Once dry, tumble dry for 20 minutes to reactivate DWR. If unable to tumble dry, iron on gentle/warm/no steam.

3.4 Conclusions

This study has highlighted differences between advice on maintenance of repellent apparel between care labels and brand websites, and amongst brands. Whilst care label information will differ between products, this study gives an overview on advice given by brands and shows little consistency between care advice given by brands on care labels. Advice is varied with confusing information on washing and reproofing of liquid repellent garments.

Information between that given on care labels and on the brand website of the same brand was not comparable. As one example, brand P advised on both the care label and online information to wash inside out, brands I and R advised to do so on the care label, and brands L and K advised to in online information.

Whilst care labelling advice advised to wash at 40 °C, online information advised to wash at 30 °C. The wash temperature guidance on the GoreTex website agrees with the advice given by brands for jackets containing a GoreTex ePTFE membrane. None of the online brands stated that the wash temperature depended on the fabric type. Tumble drying and ironing were frequently recommended. However, there was less advice on ironing on brand websites compared to care labels. Within online information, brands did not always give advice on the heat setting of ironing or tumble drying. Several of the care labels and online information discussed heat application to restore the DWR although this advice differed in terms of time, for example brand L online stated to tumble dry for 5 minutes but for 15 minutes on the care label. Specific DWR chemistry was not specified and therefore it is unknown if specific recommended practises relate to specific chemistry types.

This study, together with Chapter 2, will inform subsequent work evaluating the effect of laundering on the durability of the DWR.

Chapter 4 - Characterisation and evaluation of liquid repellency between fluorinated and non-fluorinated DWR chemistries for outdoor apparel

4.1 Introduction

Within the outdoor apparel industry, substitution of long SFP (C8) DWR chemistry with non-fluorinated alternatives is largely driven by legislation, NGO campaigns and European policy (section 1.4.5). Substitution with shorter SFP DWR chemistry has taken place with shorter fluorinated chain lengths, such as C6 or C4 analogues. However, there is increasing concern on the persistent and bio-accumulative potential of these short-chain analogues, which have the capability to degrade to short-chain perfluoroalkyl carboxylic acids (PFCAs) or perfluoroalkane sulfonic acids (PFSAs) (section 1.4.7.1) [134,277]. There is an ongoing challenge to find an alternative chemistry and/or physical modifications to provide equivalent liquid repellent functionality to that given by PFAS chemistry.

Non-fluorinated chemistries used for DWRs are based on silicone chemistries, hydrocarbon chemistries and dendritic structures (section 1.4.7.2). Whilst knowledge on degradation routes, exposure trends and analytical techniques remains central to research on the generic chemical class of PFASs, there is sparse comparative literature on the repellent functionality of SFP DWR chemistry and alternative non-fluorinated DWR chemistry in outdoor apparel; one non-peer-reviewed study exists [278]. This functionality is highly important to the end-use of the fabric and therefore development of successful equivalent surface chemistries.

Herein, a comparative study in relation to objective 3 (section 1.7) was undertaken as an initial benchmark to provide an independent evaluation of functionality between the repellent finishes; aiming to communicate the variation in functionality between long SFP (C8) DWRs, shorter SFP (C6) DWRs and non-fluorinated DWRs within outdoor apparel fabrics. This study also allowed evaluation of the spray test as an assessment of water repellency. Fabrics sought for this study were in current use by outdoor apparel brands or being considered by brands as a replacement to long SFP DWRs.

4.2 Experimental

4.2.1 Materials

Fabrics used for outdoor repellent apparel were kindly supplied by European brands to support the project. These were representative of the fabrics currently commercially in use for repellent outerwear apparel, rather than adaptations or in-house treated. Fabrics used were therefore illustrative of the outdoor apparel industry directly relevant to consumer use.

All samples were woven with the majority either 100% polyester (PES) or polyamide (PA) fibre content, some samples contained a laminate or membrane. The fabrics display a range of commercially used fibre and fabric types, within outdoor apparel.

According to manufacturer details three of the fabrics were finished with long SFP (C8) DWRs, nine fabrics were finished with shorter SFP (C6) DWRs, nine fabrics were finished with non-fluorinated chemistry, and two fabrics were untreated. In total, twenty-three fabrics were tested. Supplier information stated that six of the non-fluorinated samples were treated with a DWR based on hydrocarbon hyper-branched polymers (dendrimers). Whilst information supplied with the fabrics was limited, further details are given within A.3.

4.2.2 Characterisation

The fabrics suppled to this study were assigned a sample identification letter (*A*-*Z*) and characterised using the following methods.

Mass and thickness: Three samples were cut from three different areas of each fabric using a James Heal sample cutter (100 cm^2). Each sample was weighed to three decimal places (Ohaus Adventurer balance) and the average mass for each fabric sample, in grams per metre squared (gsm), was calculated.

Thickness of the test fabrics was measured using the FAST-1 Compression Tester at two fixed loads: 2g cm^{-2} and 100g cm^{-2} over a 10 cm^2 area of the fabric [279]. The Surface Thickness (ST) was calculated as the difference between these two measurements, in millimetres.

Characterisation of fabric structure: Fabric structure including yarn count was characterised using a piece glass. The number of layers within the fabric, fabric structure, fibre type and yarn type were determined for both the face fabric and, where applicable, backing fabrics. Details, where given, supplied by the brand were included.

Characterisation of the DWR: Information on the DWR type was not always specified with supply of the fabric. Details that were supplied are included within A.3.

Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) is a widely used surface analytical technique and was used as a semi-quantitative surface characterisation method to indicate the elemental composition of the DWR finish. For the non-fluorinated DWR samples, EDX analysis was used to indicate the type of chemistry used (for example hydrocarbon-based chemistry, silicone-based chemistry). Similarly, the fluorinated finishes were analysed to indicate the fluorine content on the fabric surface, and to allow comparison between this and the fabrics functionality.

Two specimens (size ~ 1 cm^2) were taken from different places of each fabric sample and mounted separately on to stubs. Since imaging was not required in the analysis, samples were not coated.

SEM-EDX (Jeol JSM 6610LV coupled to an Oxford Instrument INCA X-Max 80 EDS) was used for semi-quantitative elemental analysis of the fabric sample surface, at a magnification x50, accelerating voltage 20kV, spot size 50, working distance ~10 nm and aperture of 2. The mass percentage of the elements detected was recorded and the average mass percentage of each element calculated from the two repeat specimens. The error was calculated as an average from the instrumental error of the two specimens.

4.2.3 Evaluating liquid repellency

To determine the repellent functionality, the resistance to both polar and non-polar liquids was evaluated.

4.2.3.1 Water repellency

A specimen measuring 165 x 165 mm (27225 mm^2 in area) was used. All samples were conditioned at 20 ± 2°C, 65 ± 5% relative humidity (RH) for 24 hours before testing.

Spray test: AATCC 22-2014 [18] (equivalent to BS EN ISO 4920:2012 [19]) is a widely used test method to determine the resistance of a fabric to surface wetting by water. The scope of the test is to determine the resistance of a fabric sample to surface wetting by evaluation of the wetted specimen against a descriptive pictorial rating scale [19,280].

The spray test consists of a funnel, spray nozzle and mount for the fabric sample (Figure 4.1). The testing apparatus consists of a specimen holder at 45° which is 150 mm from a spray nozzle through which the water flows (Figure 4.1). The conditioned fabric sample is mounted within the circular hoop and placed on the support. 250 mL of filtered water is poured through the funnel onto the fabric sample to produce a water flow of 25-30 seconds. When the spray has ceased, the sample holder is removed and tapped once vertically, smartly against a solid surface; it is rotated by 180° and tapped smartly again, according to AATCC 22-2014.

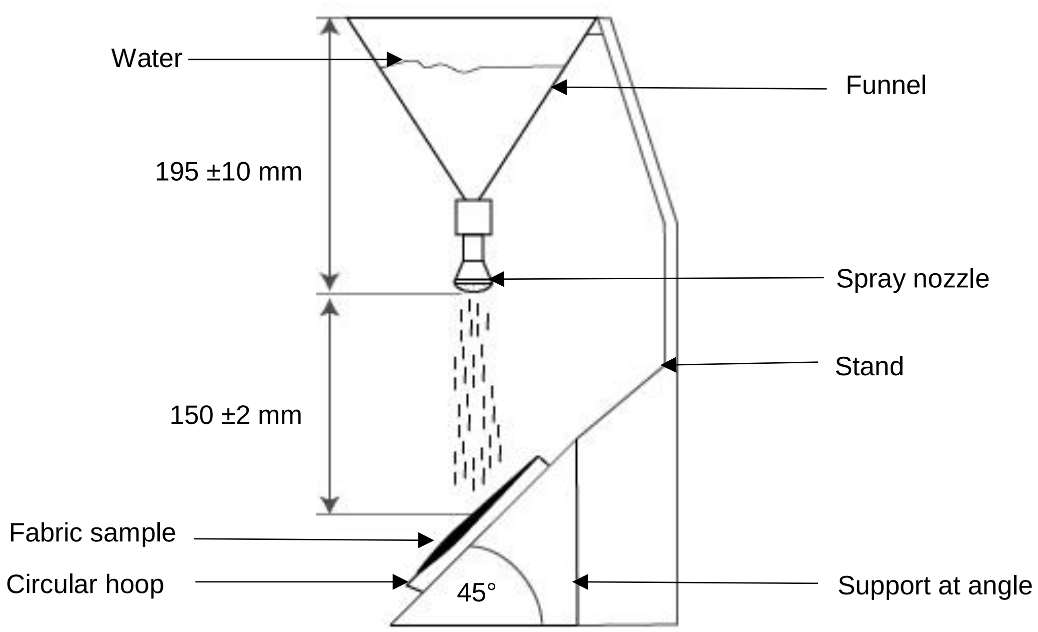


Figure 4.1: Diagrammatic view of the spray test apparatus, showing set up and water spray on to the sample, adapted from [18,19,57,83].

A subjective assessment is made, by the assessor, using the photographic scale and descriptive statements included within the standard testing method according to the appearance of the water on the fabric surface (Figure 4.2). BS EN ISO 4920:2012 scale rates the fabric 0-5, where 0 is complete wetting of the entire sample fabric face, and 5 is no wetting or sticking of water to the fabric face (Figure 4.2). The AATCC scale rates the fabric 0-100, where 0 is complete wetting and 100 is no wetting or sticking (Figure 4.2). Within the standards, the rating scales of both the ISO and AATCC standard are cross-referenced. Samples were tested using a James Heal spray test. The procedure set out in the standard was followed using three different specimens. These were cut from separate places of the fabric sample length with, in modification of the testing standard, 5 repeat tests on each. The specimen was allowed to dry fully between repeat tests.

(a)

100 no sticking or wetting of the specimen

90 slight random sticking or wetting of the specimen face

80 wetting of specimen face at spray points

70 partial wetting of the specimen beyond the spray points

50 complete wetting of the entire specimen face beyond the spray points

0 complete wetting of the entire face of the specimen

(b)

Figure 4.2: (a) the photographic scale included within the testing standard for assessment of samples; (b) the descriptive rating scale included within the testing standard, corresponding to the photographic scale.

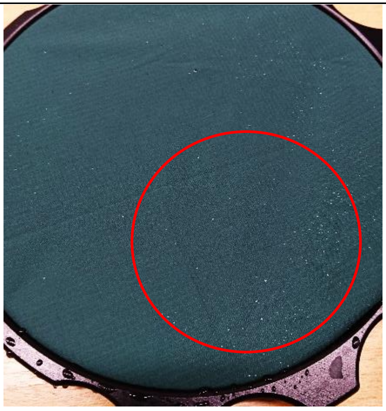
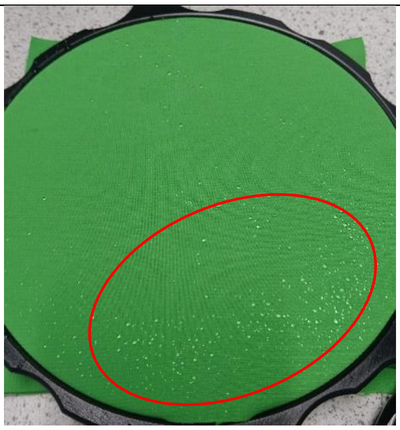
4.2.3.2 Intermediate ratings and modified AATCC-22 rating scale

The AATCC test method allows intermediate ratings of 50 or higher allowing greater discrimination between similarly performing fabric test samples [18]. During this research, it was found that assessment by this method was a widely adopted procedure by outdoor apparel brands and manufacturers, as well as textile testing companies.

A rating of 100 is when there is no sticking or wetting of the specimen fabric face. However, during initial testing, it was observed that there is always some sticking to the fabric surface, albeit very small droplets. It was therefore determined that a rating of 100 was unfeasible and a rating of 97.5 would be given where very few droplets sticking the surface were seen (Table 4.1).

During initial testing, it was acknowledged that a large majority of the fabric samples were rated either 90 or 97.5. It was acknowledged that ‘slight random sticking or wetting of the specimen face' can be interpreted in various ways. For this reason it was decided to include a rating of 95 (Table 4.1) to discriminate further between samples of similar water repellency. Likewise, it was decided to use intermediate ratings of 85, 75 and 60 throughout laboratory testing. For each sample, five repeats were measured using the modified rating scale. The mode value of the spray rating assigned was calculated for each fabric.

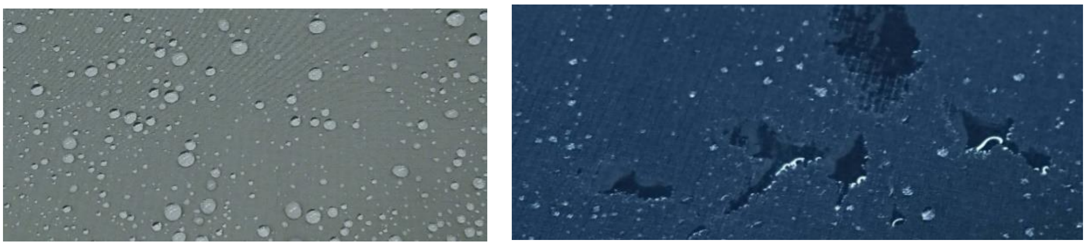
Table 4.1: Modified AATCC-22 scale: Intermediate spray ratings (scale 90-97.5).

Spray rating	Wetting of the fabric face	Descriptive rating
97.5		Very little sticking of water droplets to the surface. Droplets are small and sparse.
95		Sticking of water droplets to the fabric face. Droplets sit on top of the surface and are randomly distributed across the fabric surface.
90		Random sticking of water droplets to the majority of the fabric face, including areas which lie flat across the surface or show signs of wetting the fabric.

4.2.3.3 Calculation of water adherence

In addition to assigning a spray rating a calculation of the water adherence to the fabric surface after the spray test shower was calculated. In unpublished research, measuring the mass of the fabric sample before and after the spray test shower has been discussed as an additional measurement to discriminate between fabrics with a similar spray rating [281].

Water adherence refers to the water remaining on the fabric surface at the end of the spray shower. Water adherence is defined as the water sticking to, lying on, or wetting, through absorption by capillary action, into the outer fabric surface (Figure 4.3).



(a) (b)

Figure 4.3: Images showing water adherence – (a) water droplets sticking to and lying upon the fabric surface; (b) water droplets lying across the fabric surface and wetting the surface.

The mass of each dry and conditioned fabric sample was measured using a Precisa 310C-3010D balance (g) and noted to two decimal places. The spray test method was used and a rating assigned. At the end of testing, the sample was carefully removed from the fabric holder, to avoid any wetting or movement of droplets on the fabric surface. The mass of the fabric sample after testing was measured.

The percentage difference between the initial mass of the fabric (m_i) and the mass after testing (m_t) was calculated as a water adherence mass increase, m_A (%), using the mean value of measurements of the five repeat test measurements calculated according to equation 4.1:

$$m_A\ (\%) = \frac{Mt - Mi}{Mi} \times 100 \qquad (4.1)$$

4.2.3.4 Calculation of mass increase

Due to differences in the fabric constructions between the sample fabrics used, and in addition to calculation of water adherence, mass increase, in g, (Δm) was calculated. This calculation allowed comparisons between the uptake of water following the spray test and to focus on wetting of the fabric surface, and within the fabric bulk should this occur. This was calculated as an average value from the three repeat specimens, with five repeat testings of each, according to equation 4.2:

$$\Delta m\ (\text{g}) = Mt - Mi \qquad (4.2)$$

4.2.3.5 Aqueous and oil repellency

Aqueous liquid repellency - Water/alcohol test: The BS ISO test method 23232:2009 for aqueous repellency determines the resistance of a fabric to staining by water/alcohol-based liquids using standard test liquids [282]. Comparable everyday liquids include wine, coffee and fruit juice. Using the grading system within the standard, the resistance to aqueous liquids is evaluated using eight grades of water and isopropyl alcohol solutions (with surface tension values between 24.0-59.0 dyn cm^{-1}, at 25°C; Table 4.2). Droplets are placed on to the surface of the substrate and their interaction with the surface observed. The test is used to assess the interaction between the surface energy of the fabric and surface tension of the liquid. The test specimens were conditioned, for a minimum of four hours, and placed on a flat horizontal surface. It was ensured that the sample was flat; any creases or flaws within the fabric were avoided. The test liquids were mixed according to the composition

(Table 4.2) by volume using distilled water and the isopropyl alcohol (Sigma Aldrich). Using 60 mL dropping bottles, the test liquids were placed in sequential order on the laboratory bench and droplets of each test liquid were sequentially placed on the specimen, on two different locations of the sample at least 1 cm apart.

Table 4.2: BS ISO 23232:2009 Standard test liquids: Aqueous solution repellency grade number, composition and surface tension [282].

Aqueous solution repellency grade	Test liquid composition	Surface tension at 25°C (dyn cm^{-1})
8	40:60 Water:isopropyl alcohol (v/v)	24.0
7	50:50 Water:isopropyl alcohol (v/v)	24.5
6	60:40 Water:isopropyl alcohol (v/v)	25.4
5	70:30 Water:isopropyl alcohol (v/v)	27.5
4	80:20 Water:isopropyl alcohol (v/v)	33.0
3	90:10 Water:isopropyl alcohol (v/v)	42.0
2	95:5 Water:isopropyl alcohol (v/v)	50.0
1	98:2 Water:isopropyl alcohol (v/v)	59.0
0	None	-

The droplets were observed for penetration into the fabric surface, wicking (movement through the fibres) and absorption. A grade number was assigned to each test specimen by comparison to the grading example given within the test standard (Figure 4.4). A 'pass' is associated with droplets (A) and (B) where the fabric surface has a low surface tension. Where the droplet observed resembled droplet (A) (Figure 4.4) with no penetration or absorption observed, the next higher grade solution was used and the method repeated. With a 'borderline pass', droplet (B) (Figure 4.4), darkening could be seen around the droplet. The final assessment grade was expressed by subtracting 0.5 from the number of the borderline pass liquid. A 'fail' was associated with droplets (C) and (D) (Figure 4.4). In this case, the next lower grade solution was tested upon the fabric. A grade was assigned to the substrate as the highest-numbered test liquid which was not absorbed nor penetrated, or wet, the substrate surface.

Two specimens were evaluated for each sample and a grade assigned if in agreement. Where necessary, a third specimen was evaluated and the third grade reported if in agreement to either of the first two determinations or, if in disagreement, a median grade was reported.

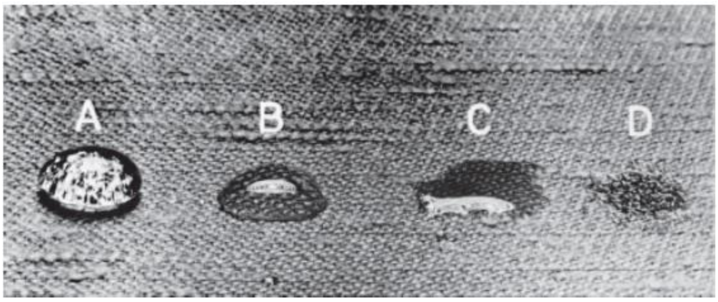


Figure 4.4: Grading example given within BS ISO 23232:2009. (A) Pass; clear rounded drop, (B) Borderline pass; rounded drop with partial darkening, (C) Fail: wicking or wetting seen; (D) Fail: complete wetting [282].

Oil repellency - Hydrocarbon resistance test: The BS EN ISO test method 14419:2010 determines the resistance of a fabric to oil-based staining (oleophobicity), for example food products, body oils and oil-based compounds [283]. It uses eight test liquids of selected hydrocarbons to indicate the fabric's surface energy. It follows a similar procedure and evaluation method to the Aqueous liquid repellency test (BS ISO 23232:2009).

The eight hydrocarbon test liquids (Table 4.3) were used (Sigma Aldrich), at a purity >98%, with surface tension values between 19.8-31.5 dyn cm^{-1} (25°C). Test liquid 2 was prepared using a composition of 65:35 white mineral oil: hexadecane by volume. The test specimens were conditioned for a minimum of four hours prior to testing. Taking one test specimen at a time, the samples were placed on a flat surface within the laboratory. Creases, folds or flaws within the sample were avoided. Using dropping bottles, with 2 mL tip, the test liquids were lined sequentially on the laboratory bench. Sequentially, the test liquids were placed on to the fabric surface and the droplets were observed for penetration, absorption and wicking. Droplets were placed on to the sample in two different locations, spaced at least 1 cm apart.

Table 4.3: BS EN ISO 14419:2010 Standard test liquids: Hydrocarbon resistance test - repellency grade number, composition and surface tension [282].

Oil repellency grade	Test liquid composition	Surface tension at 25°C (dyn cm^{-1})
8	Heptane	19.8
7	Octane	21.4
6	Decane	23.5
5	Dodecane	24.7
4	Tetradecane	26.4
3	Hexadecane	27.3
2	65:23 white mineral oil: hexadecane	29.6
1	White mineral oil	31.5
0	None	-

The interaction of the test liquid on to the surface was observed and assessed in comparison to the grading example, which is the same image given within BS ISO 23232:2008 (Figure 4.4). The grading matches that of the aqueous repellency test. If there was a variance between the first two grades assigned then a third test was carried out. The reported grade was the third determination if in agreement to either of the first two determinations, or if in disagreement the median grade was reported.

4.3 Results and discussion

4.3.1 Characterisation

Twenty-three fabrics were supplied and evaluated within this study. Full characterisation, including mass and thickness, is given within A.3; fabric samples are grouped according to their DWR type.

One fabric type was supplied with a long SFP (C8) DWR (sample *C*), shorter SFP (C6) DWR (sample *M*), non-fluorinated DWR (sample *V*) and as an untreated fabric (sample

Y). This enabled direct comparison between the DWR types without the variables of the fabric characteristics.

The majority of the fabrics were plain weave apart from samples *B*, *C*, *M*, *Q* and *V* which were twill.

SEM-EDX was used to indicate the elemental composition of each fabric's repellent finish. Elemental composition was recorded by mass percentage. Two specimens of each fabric sample were analysed and average values calculated from the data (Table 4.4).

From the supplier information, twelve samples were allegedly finished with either long SFP (C8) DWRs or shorter SFP (C6) DWRs, however, no fluorine content was detected on samples *C*, *K*, or *M*. For sample *C*, this was surprising given that the fabric was specifically supplied to the project as a long SFP (C8) DWR finished fabric. During analysis, it was seen that some elements were detected within the analysis frames but not culminating as peaks in the detection – this was particularly seen in analysis of samples *K* and *M* with the element fluorine. Fluorine, throughout analysis, was detected a low levels, at times hardly above the background noise levels of the analysis program, and it was thought that detection below 0.74% would not be seen. Carbon and oxygen were detected on all non-fluorinated DWR fabric samples suggesting a hydrocarbon-based surface chemistry; neither fluorine nor silicone were detected on any non-fluorinated DWR samples. Detection of titanium is thought to originate as titanium dioxide associated with fabric whitening.

While EDX is a surface analysis technique it is thought that several elements of the fabric bulk were detected. Detection of silicone was at a maximum value of 0.35% and is thought to be from the fabric bulk. Similarly, neither the detection of sulphur nor chlorine can be related to specific features of the fabrics. Detection of these elements may be from within the fabric bulk. Aluminium and sodium were detected on sample *Y* at 0.07%; similarly are thought to be from the fabric bulk or manufacturing residuals.

Overall, EDX detection of chemical elements fluorine, sulphur, silicone and chlorine was at relatively low mass percentages. EDX analysis has allowed identification of the major constituents and indicated the use of hydrocarbon-based DWRs on all non-fluorinated fabric samples. However, it needs to be acknowledged as a semi-quantitative method as a standardless quantitative analysis.

Table 4.4: SEM-EDX analysis of all fabric samples. Elemental content shown in mass percentage (%) of elements carbon (C), oxygen (O), fluorine (F), titanium (Ti), sulphur (S), silicone (Si), and chlorine (Cl) - magnification x50.

DWR type	**Sample id**	**C (%)**	**O (%)**	**F (%)**	**Ti (%)**	**S (%)**	**Si (%)**	**Cl (%)**
Long SFP (C8) DWR	***A***	74.2±0.9	22.6±0.8	2.05±0.44	0.78±0.09	0.19±0.05	n.d.	0.23±0.05
	B	73.4±0.7	23.7±0.6	2.11±0.36	0.58±0.06	0.18±0.04	n.d.	n.d.
	C	59.9±0.5	38.9±0.5	n.d.*	1.21±0.08	n.d.	n.d.	n.d.
Shorter SFP (C6) DWR	***D***	73.8±1.0	22.4±0.9	2.77±0.56	0.84±0.11	0.22±0.51	n.d.	n.d.
	E	75.0±0.6	22.7±0.6	1.38±0.29	0.35±0.06	0.16±0.04	0.12±0.03	0.34±0.04
	F	74.7±0.7	22.6±0.6	2.01±0.36	n.d.	0.22±0.05	0.28±0.05	0.19±0.05
	G	76.2±0.5	21.0±0.5	1.62±0.25	0.85±0.06	0.20±0.04	0.10±0.03	0.13±0.03
	H	77.8±0.5	21.1±0.5	0.74±0.20	0.20±0.09	0.17±0.04	0.14±0.03	0.23±0.04
	J	72.7±0.8	19.7±0.7	5.53±0.46	0.83±0.08	0.52±0.10	0.28±0.05	0.48±0.06
	K	75.0±0.7	24.1±0.7	n.d.	0.57±0.07	0.17±0.04	n.d.	0.19±0.05
	L	74.3±0.8	23.7±0.8	1.43±0.41	0.60±0.08	n.d.	n.d.	n.d.
	M	61.0±0.4	37.8±0.4	n.d.	1.16±0.06	n.d.	n.d.	0.11±0.02
Non-fluorinated	***N***	73.4±0.9	25.2±0.9	n.d.	1.48±0.13	n.d.	n.d.	n.d.
	O	72.6±0.7	26.8±0.7	n.d.	0.59±0.09	n.d.	n.d.	n.d.
	P	72.8±1.0	25.9±1.0	n.d.	1.30±0.14	n.d.	n.d.	n.d.
	Q	72.4±1.2	25.6±1.2	n.d.	2.01±0.20	n.d.	n.d.	n.d.
	R	65.8±0.8	33.4±0.8	n.d.	0.73±0.11	n.d.	n.d.	n.d.
	S	60.2±0.9	39.4±0.9	n.d.	0.44±0.12	n.d.	n.d.	n.d.
	T	72.8±1.4	24.5±1.4	n.d.	2.73±0.25	n.d.	n.d.	n.d.
	U	72.1±1.2	26.4±1.2	n.d.	1.47±0.19	n.d.	n.d.	n.d.
	V	58.5±0.9	39.5±0.9	n.d.	1.99±0.16	n.d.	n.d.	n.d.
Untreated	***Y****	59.6±0.18	39.3±0.18	n.d.	1.01±0.02	n.d.	n.d.	n.d.
	Z	75.2±0.2	24.5±0.2	n.d.	0.12±0.02	0.11±0.01	n.d.	n.d.

Detection limit to parts per thousand (1 x 10^{-3}). Two specimens were evaluated from each sample. Error calculated as an average of instrumental error from two repeat specimens.

* sodium (Na) and Aluminium (Al) were detected on analysis of sample *Y* at a very low weight percentage of 0.07%.

4.3.2 Evaluating repellency

4.3.2.1 Water repellency

All the samples were evaluated using the modified spray rating scale (discussed in section 4.2.3.2). The mode of the spray rating was calculated from the three specimens of each fabric sample (Figure 4.5).

All treated fabric samples were assigned a spray rating of 90 or above, showing a good level of resistance to surface wetting. Overall, the long SFP (C8) DWR fabric samples were rated at either 95 or 97.5. Shorter SFP (C6) DWR fabric samples were rated either 95 or 97.5, with the exception of two shorter SFP (C6) DWR examples (samples *G* and *H*), which were rated 90. For sample *H*, this may be due to the low fluorine content. In comparison, non-fluorinated DWR fabric samples were generally rated at 90, although two samples (samples *O* and *V*) were rated 95.

Untreated fabrics (sample *Y* and *Z*) were completely wet by the water spray with movement of water by capillary action through the fibres, wicking, within the fabric structure and penetration of water through the fabric; Samples *Y* and *Z* was assigned a spray rating of 0.

In elemental analysis, fluorine was detected at low levels on two of the long SFP (C8) DWR fabrics – samples *A* and *B* – but not detected on sample *C*. This was surprising given its high level of repellency (Figure 4.5) and the information given by the brand on the fabric, with samples *M, V* and *Y* supplied by the same brand with different DWRs. It is therefore thought that the fluorine content of sample *C* was below the limits of detection. Similarly, fluorine was not detected on samples *M* and *K* but they demonstrated comparative levels of water repellency to other shorter SFP (C6) DWR fabric samples, and therefore it was thought that the fluorine content was below limits of detection.

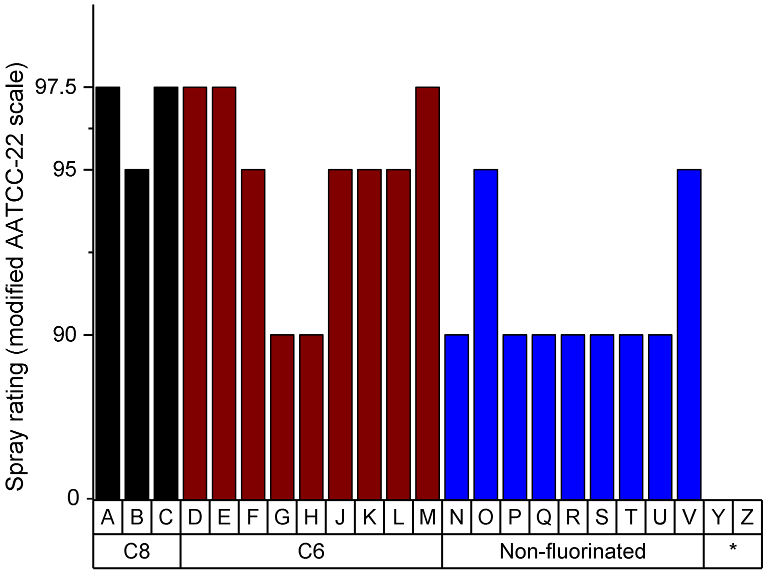


Figure 4.5: Spray rating of samples. Samples categorised by sample id and DWR type; * Untreated fabrics.

Water adherence was also calculated as an average value from the three specimens with five repeats of each (Figure 4.6). The long SFP (C8) DWR fabric samples, samples *A*, *B*, and *C*, all had $m_A < 2\%$ following the spray test shower, with a low standard deviation ranging between 0.23-0.72% for all samples. This suggests a highly uniform repellent finish on the fabric samples. Shorter SFP (C6) DWR fabric samples which were assigned a spray rating of 97.5 had a low m_A, whilst the two fabric samples assigned a spray rating of 90 had a much greater m_A (sample *G* 27.5% and sample *H* 30.9%) and greater standard deviation between measurements (sample *G* 6.51% and sample *H* 5.24%). This was due to the greater adherence of water droplets to the surface with absorption into the fabric bulk and suggests a non-uniform surface finish.

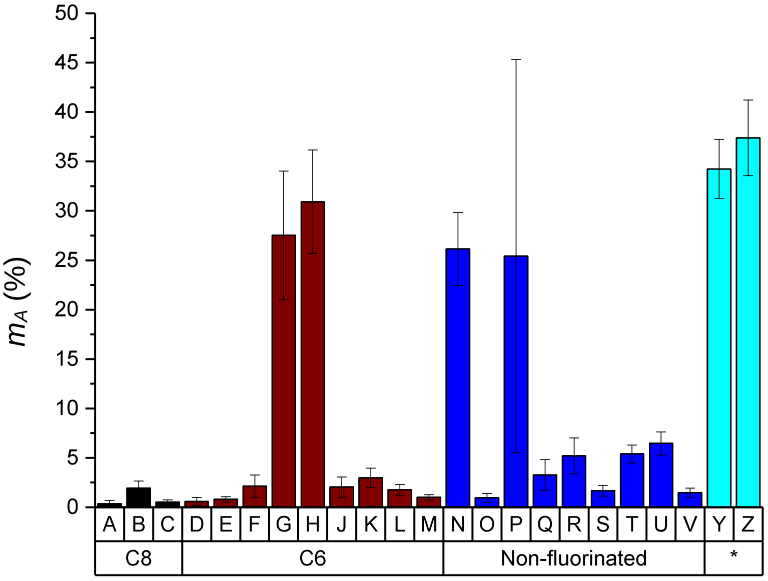


Figure 4.6: Water adherence (m_A, %) of samples. Samples categorised by sample id and DWR type; * Untreated fabrics. Error bars show standard deviation.

There was variation in the water adherence measurements for non-fluorinated DWR fabric samples, following the spray test shower (Figure 4.6). Those assigned a spray rating of 95 had a low m_A; out of those assigned a spray rating of 90 samples *N* and *P* had a greater m_A with significant standard deviation between repeat measurements (sample *N* 26.1% increase and sample *P* 25.4% increase). These two samples were assigned a spray rating of 90, but m_A was much greater than the other non-fluorinated DWR samples also assigned a spray rating of 90. Untreated samples *Y* and *Z* had the highest m_A and water uptake in line with the assignment of spray rating 0, signifying complete wetting of the sample face.

The long SFP (C8) DWR samples, *A, B* and *C,* had $\Delta m < 0.06$ g (Figure 4.7). Shorter SFP (C6) DWR samples which were assigned a spray rating of 95 or above had a low Δm; comparable to the m_A calculations, samples *G* and *H* were assigned spray ratings of 90 and had a greater Δm (sample *G* 0.33 g and sample *H* 0.36 g).

There was variation in the measurements for the non-fluorinated DWR samples (Figure 4.7). Samples *O* and *V* had low Δ*m* correlating with their assigned spray ratings of 95. As in m_A calculations, sample *N* had a greater Δ*m* (0.84 g). Standard deviation between calculations for sample *P* was much greater than other samples. As expected, untreated fabric samples *Y* and *Z* had the greatest Δ*m* of 1.39 g and 0.96 g respectively.

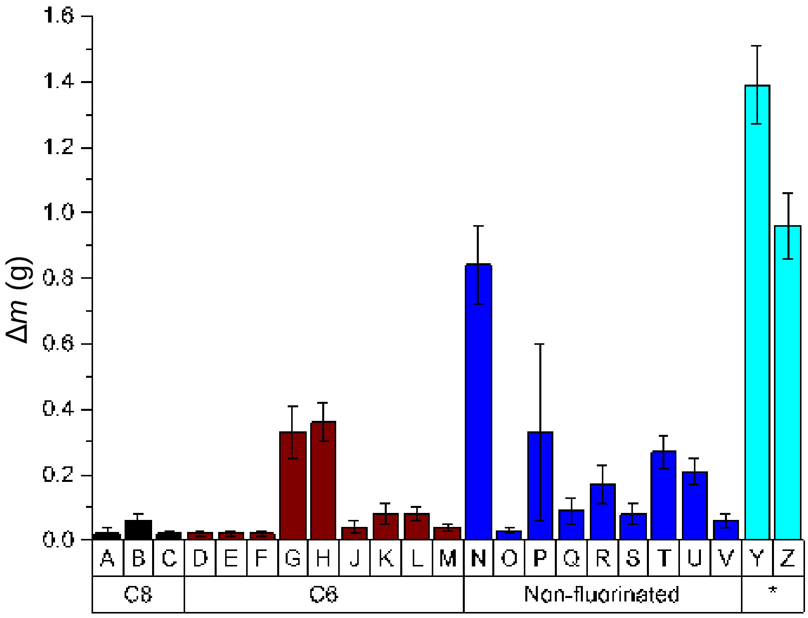


Figure 4.7: Mass increase (Δ*m*). Samples categorised by sample id and DWR type; * Untreated fabrics. Error bars show standard deviation.

Directly comparing long SFP (C8) DWR sample *C* and shorter SFP (C6) DWR sample *M* were both assigned a spray rating of 97.5; the non-fluorinated DWR fabric sample *V* was assigned a rating of 95.

Long SFP (C8) DWR sample *C* demonstrated a lower Δ*m* (0.02 g) than shorter SFP (C6) DWR sample *M* (0.04 g) and non-fluorinated DWR sample *V (*0.06 g).

A one-way between-groups analysis of variance (ANOVA) was conducted on Δ*m* data from fabric samples *C*, *M* and *V* (A.4) to determine if there was a statistical difference between the DWR types. There was a statistical significant difference at the confidence level of 95% between the three fabric samples and therefore DWR type. However, post-hoc Tukey HSD test indicated that only long SFP (C8) DWR sample *C* was significantly different from non-fluorinated sample *V* ($p<0.05$). A box and whisker plot of the data shows this difference between DWR types (Figure 4.8).

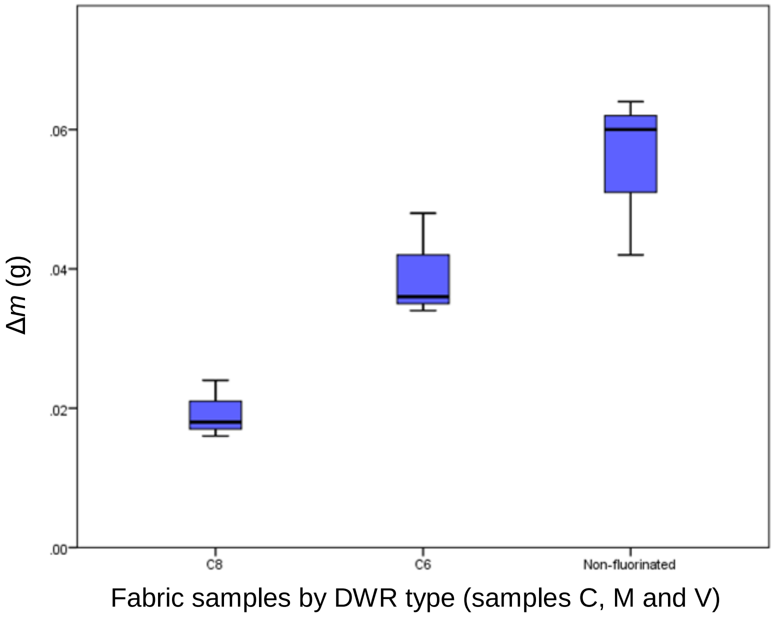


Figure 4.8: Box plot of Δm for fabric samples *C* (long SFP (C8) DWR), *M* (shorter SFP (C6) DWR) and *V* (non-fluorinated DWR). The length of the box is the interquartile range with the whiskers the lower bound and upper bound with the 95% confidence level. The line across the box represents the median value of the data sets.

4.3.2.2 Aqueous and oil repellency

Long SFP (C8) DWR sample *A* showed the greatest level of repellency to aqueous staining [282] (Figure 4.9) with a rating of 6.5 out of a maximum of 8 denoting a surface energy of ~24.9 dyn cm^{-1}. Shorter SFP (C6) DWR samples varied from 2.5-5.0, and non-fluorinated DWR samples varied from 2.5-4.0. This was expected as the surface energy is known to be lower with a reduction of fluorocarbon chain length and presence of fluorine (section 1.4.3.2). Sample *H*, a shorter SFP (C6) DWR sample, and sample *P*, a non-fluorinated sample, were given the lowest rating of 2.5, denoting a surface energy of ~46 dyn cm^{-1}. The untreated fabric samples *Y* and *Z* showed no resistance to aqueous staining.

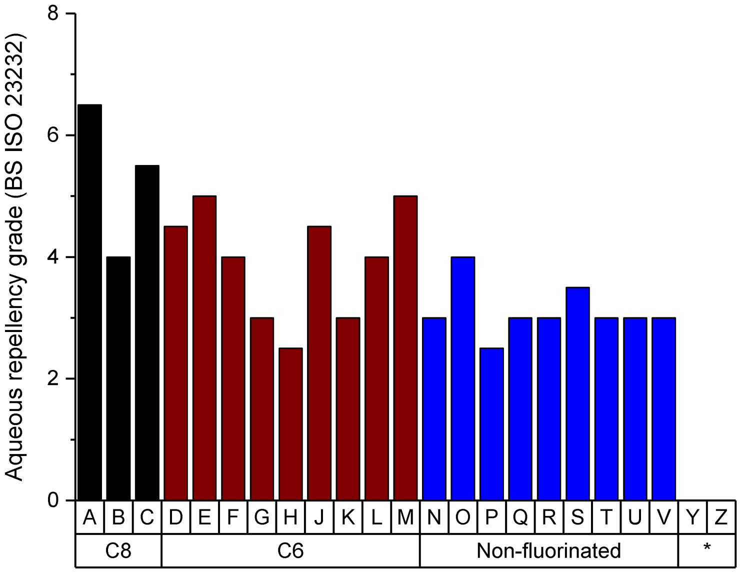


Figure 4.9: Resistance of samples to aqueous-based staining given as a grade number. Samples categorised by sample id and DWR type; * Untreated fabrics.,

All non-fluorinated DWR fabric samples demonstrated no resistance to oil-based (hydrocarbon) liquids (Figure 4.10) which was expected, demonstrating the key differences between repellent functionality provided by side-chain fluorinated polymer chemistry and repellency provided by non-fluorinated alternative chemistries. The greatest level of repellency to oil-based liquids was demonstrated by long SFP (C8) DWR fabric sample *C* with a rating of 5.5 denoting a surface energy of ~24.1 dyn cm^{-1}. Variation between shorter SFP (C6) DWR fabric samples was seen, with ratings ranging from 1.0-2.5. Shorter SFP (C6) DWR fabric sample *H* demonstrated no repellency to oil-based liquids, which may be associated with the absence of fluorine in elemental detection. As expected, untreated fabric samples *Y* and Z demonstrated no resistance to oil-based liquids.

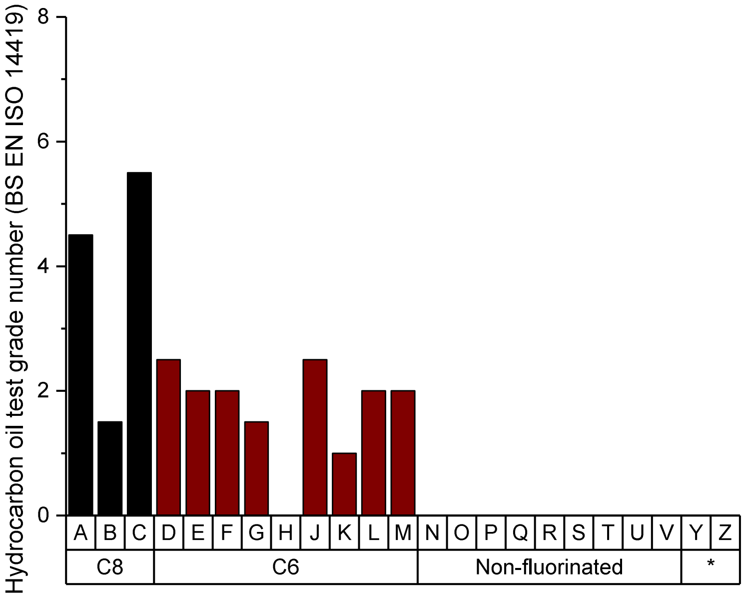


Figure 4.10: Resistance of repellent fabric samples to oil-based staining given as a grade number. Samples categorised by sample id and DWR type; * Untreated fabrics.

The grade given to sample *B* was surprisingly lower than the other long SFP (C8) DWR fabrics; however this was consistent with all other repellency tests. Information given on supply of the fabric stated it was finished with a long SFP (C8) DWR and in EDX analysis fluorine was detected on the surface. This may highlight differences between DWR applications, potential degradation of the surface chemistry or differences between chemical suppliers and formulations.

In terms of aqueous-based staining, sample *C* was graded 5.5 denoting a surface energy of ~26.5 dyn cm^{-1}, sample *M* was graded 5.0 denoting a surface energy of ~27.5 dyn cm^{-1}, sample *V* was graded 3.0 denoting a surface energy of 42.0 and, as expected sample *Y* was graded 0. The decrease in aqueous repellency between samples *C* and *M* was expected with the decrease in fluorocarbon chain length.

As expected, the long SFP (C8) DWR sample C demonstrated a high level of resistance to oil-based staining (graded 5.5, surface energy of ~24.1 dyn cm^{-1}) compared to the shorter SFP (C6) DWR sample *M* (graded 2.0, surface energy of

~29.6 dyn cm^{-1}). Both the non-fluorinated sample *V* and untreated sample *Y* demonstrated no resistance to oil-based staining.

4.4 Conclusions

This work has demonstrated that a DWR is required to provide a level of water repellency to woven apparel fabrics, exemplified by the untreated fabric samples showing no resistance to surface wetting by water, with associated high water adherence and absorption. EDX was employed as a semi-quantitative method to assess the type of repellent finish; analysis detected fluorine content in several of the long SFP (C8) DWR and shorter SFP (C6) DWR fabric samples, potentially showing presence of PFASs. Whilst EDX analysis needs to be acknowledged as a standard-less analysis, it has clearly shown differences in elemental content between fluorinated and non-fluorinated DWR fabric samples, and demonstrated that all non-fluorinated DWR samples to be based on hydrocarbon chemistry. Information supplied with seven of the non-fluorinated finishes stated a hyper-branched hydrocarbon polymer surface chemistry. Multiple hyper-branched (tree-like) alkyl end-groups provide the function of aqueous repellency, but have a lower repellence to oil staining (hydrocarbon test liquids). Fluorine was not detected on any non-fluorinated samples. Limits of detection, however, meant that definite connections between elemental composition and functionality could not be made.

The availability of fabrics to the study meant that there were variables in the fibre type and fabric construction; however this practise-led aspect is replicating commercial fabrics and the scope of consumer use. The majority of the fabrics were plain weave or twill weave (as detailed in A.3), and the testing procedures focus on the surface properties rather than the fabric bulk, and influence of fabric layers nor inclusion of a membrane. Samples *C*, *M*, *V* and *Y* have allowed a direct comparison, with the sole variable being the repellent finish: long SFP (C8) DWR, shorter SFP (C6) DWR, non-fluorinated finish and untreated fabric.

An aim of this study was to evaluate the spray test method and its reproducibility. Additions to the rating scale depicted in AATCC-22 were made with intermediate ratings to further discriminate between similar fabrics. This modified AATCC-22 rating scale shall be used in subsequent work.

Water repellency ratings were similar across the range of fabrics tested (excluding the untreated fabric); all demonstrating a high level of resistance to wetting, with only random sticking or minor wetting of the fabric face observed. Measurements showed that several non-fluorinated DWR fabric samples provide similar water repellency to long SFP (C8) DWRs or shorter SFP (C6) DWRs; all fabric samples demonstrated a resistance to wetting of a spray rating '90' or above. m_A calculations allowed a quantifiable assessment of each fabrics resistance to water. This has previously been calculated in non-peer reviewed literature [281]. A low m_A is related to a high spray rating. In addition, Δm was calculated identifying a clearer relationship between the surface repellency chemistry and water interaction.

Using standard test method BS ISO 23232, some resistance to aqueous-based staining by non-fluorinated DWR fabrics was observed, surface energies of each non-fluorinated fabric ranging between 46.0-33.0 dyn cm^{-1}; this can be associated with repellence of commonplace polar liquids such as wine, coffee and fruit juice. Standard test method BS EN ISO 14419 was used to evaluate the fabric's resistance to oil-based liquids (oleophobicity) corresponding to non-polar liquids used within daily life such as cooking oil, butter, petrol, and sun cream. As expected, non-fluorinated DWR fabrics demonstrated no oil repellency, therefore no resistance to these commonplace liquids and were clearly inferior in this property to long SFP (C8) DWR finished fabrics; two of which demonstrated good oil-resistance (sample *A* grade 4.5 and sample *C* grade 5.5).

Surface energies reported in literature (Table 1.1 and Table 1.5) do not equate to the surface energies determined within this study. The surface energies of a fluorocarbon repellent chemistry and hydrocarbon repellent chemistry, as reported in literature, are 15 dyn cm^{-1} and 31 dyn cm^{-1} respectively [36,66,72,75,76]. However, the lowest surface energy determined within this study for a fluorocarbon repellent chemistry is 24.1 dyn cm^{-1} and 33.0 dyn cm^{-1} for a hydrocarbon repellent chemistry. This is due to the chemistry as an aqueous emulsion, differences in emulsion composition and the interaction with the fabric structure.

As highlighted as a primary requirement by consumers (Chapter 2), water repellency is a priority function required in outdoor clothing and it could be argued that the use of side-chain fluorinated polymer chemistry for such garments is therefore over-engineering, providing oil repellency that is in excess of consumer requirements. However, as discussed in section 1.2.4.2., contamination from body oils is likely to occur when garments are worn impeding the DWR and staining may compromise functionality. Additionally, contact with oil and aqueous compounds during garment manufacture will occur, section 1.3.1.1. Therefore, a level of aqueous and oil repellency is therefore required and should be considered on a case-by-case basis along with further investigation on the durability of non-fluorinated repellent DWR chemistries.

Chapter 5 - Effect of consumer laundering on liquid repellent functionality

5.1 Introduction

Liquid repellency provided by fluorinated side-chain polymers is dependent on the orientation of the side-chains, packing, composition and ordered arrangement of -CF_3 end groups [284]. Side-chain fluorinated moieties orientated outwardly perpendicular from the textile surface provide low surface energy (section 1.4.3) [109,112]. Previous research has demonstrated the re-orientation of fluorinated side-chains and the ordered formation of –CF_3 end-groups during washing and heat application [52–54,268,284,285]; this observed phenomena has been theorised to be the re-orientation of the side-chains following heat application restoring the low surface energy.

Studies of these phenomena have varied in the method of heat application, from heat press to oven, and temperature (150 °C [52,53] and 100 °C [112]). Schellenberger *et al*. [112] studied the durability of long-chain, short-chain and non-fluorinated DWR chemistries in separated wash loads to ‘avoid contamination’; tumble drying was repeated after every wash (up to ten washes), but only after ten washes were fabric samples placed in an oven at 100 °C for 10 minutes as an application of heat. Water repellency was seen to increase following this heat treatment, suggesting the re-orientation of the hydrophobic moieties, both of a fluorinated DWR and a non-fluorinated hyper-branched polymer, restoring low surface energy. The heat treatment by Schellenberger *et al.* [112] does not exemplify the consumer’s heat application/treatment in a domestic environment, which would most often be by tumble drying or ironing. Whilst consumer laundering practises vary, a comparison between the different types of domestic drying/heat application and their effect on reviving the liquid repellent functionality has not yet been undertaken. In addition, the effect of heat application on non-fluorinated repellent chemistries is still unclear. Ultimately, consumer laundering practices could lead to longer term use by the consumer if liquid repellency of the garment is maintained.

Maintaining the repellent functionality of liquid repellent fabrics requires cleaning and re-proofing, but is dependent on the type of chemical repellent finish [268]. As non-fluorinated repellent chemistries enter commercial use, it is unknown how they will interact with laundering practices, drying and application of heat. With consumer expectation of a garment to be liquid repellent throughout use, it is important to maintain the repellent functionality through end-use and give guidance on appropriate care procedures. Maintaining the fabric repellent functionality will contribute to extending the lifespan of the garment reducing potential disposal. Therefore, a study evaluating the laundering impact on liquid repellent functionality of outdoor apparel repellent fabrics was undertaken, addressing objective 4 (section 1.7). Within this, the effect of laundering and drying/heat application of non-fluorinated DWR fabrics and fluorinated DWR fabrics was compared.

5.2 Experimental

5.2.1 Materials

Fabrics selected to be used for this study were samples *A* and *C,* long SFP (C8) DWR, samples *F, J* and *M,* shorter SFP (C6) DWR, and samples *P, T* and *V,* non-fluorinated DWR (fabric characterisation in A.3). These fabric samples were chosen as *C, M* and *V* are the same fibre type (PES) and fabric construction with a hydrophilic membrane; only the DWR differing. Samples *C, F, J, P* and *T* were chosen as a representative group of fluorinated and non-fluorinated fabrics made from the same fibre type (PA), with similarities between their structures and due to their availability to the project. Samples *F* (shorter SFP (C6) DWR) and *P* (non-fluorinated) are both tightly woven fabrics; samples *A, J* and *T* are woven fabrics of a similar structure with two to three layers in the fabric structure. Nine specimens of each fabric sample were cut so that three repeat specimens of each could be air dried, tumble dried or ironed. Specimen size was 165 x 165 mm (27225 mm^2 in area).

5.2.2 Laundering method

A domestic laundering process was simulated using a domestic washing machine and mixed fabric loads. Samples were subjected to a series of washing iterations. With each wash the same procedure of washing, drying and, where applicable, heat application was repeated. The water repellency, aqueous repellency and oil repellency were evaluated after one, three, five and ten washes. A maximum of 10 washes and these testing intervals were chosen after preliminary trials evaluating the liquid repellency after every wash cycle. At 10 washes, the liquid repellency had deteriorated sufficiently to evaluate a trend. Two sets of samples were washed, one with liquid soapflakes and one without any laundry/detergent product.

5.2.2.1 Washing

A 30 °C wash programme was selected (Miele W Classic washing machine) at a spin speed of 1200 rpm lasting 2 hours 29 minutes. Fabric ballast (100% woven polycotton) was used to equalise the mass of each wash load to 1 kg. Following the review of care labels (Chapter 3), 30 °C wash chosen as the most common and recommended practice, particularly in light of mainstream advertising communicating that washing at lower temperatures is just as effective.

Detergent: Following data collection on consumer use, liquid soapflakes were chosen as the washing soap best simulating domestic washing practice. They are commercially available and were purchased locally. Soapflakes were used at a liquor ratio of 40 mL: 1 kg wash load, as advised on the packaging. At each wash the liquid was inserted into the soap drawer, the measuring cylinder rinsed with 25 mL water and the residual inserted into the drawer. Two sets of samples (one with liquid soapflakes and one without any laundry product) were washed to determine the influence of soapflakes on liquid repellency.

5.2.2.2 Drying and application of heat

Following each wash, all samples were promptly removed from the machine. Three specimens of each sample were air dried at room temperature for at least 5 hours. Three other specimens were air dried at room temperature for at least 5 hours and then ironed six times across the fabric sample, lasting for at least 10 seconds using a domestic steam iron, with stainless steel plate, at 135-190 °C (measurement range taken during movement across the sample using a Jenway thermometer, model 2003 with thermocouple attachment; A.5). Three other specimens were tumble dried in a domestic machine (White Knight 44AW) for 40 minutes. Samples were mixed in each tumble dry load and fabric ballast was used to equalise the mass of each load to 500 g. The temperature within the drum was measured using three DS1923 iButton hygrochron logger sensors recording at 10 second intervals and an average calculated (A.5). Over the 40 minute cycle, the temperature ranged from 22.6-62.3 ºC and was above 50 ºC for a predominant portion of the cycle, from 13-32.5 minutes, before cooling to finish at 32.1 °C. The same specimens were subjected to the same drying and heat application throughout the study.

5.2.3 Evaluating repellency

The liquid repellency to water, aqueous-based and oil-based liquids was evaluated.

5.2.3.1 Water repellency

AATCC 22-2014 [18] was used to determine the resistance of the fabric to surface wetting and evaluate its water repellency. The same apparatus, test method and modified rating scale was used as described in section 4.2.3.2. The mode of the spray rating was taken from three repeat specimens; where this was not possible the median was reported. As calculated in section 4.3.2.1, mass increase, Δm, was calculated after evaluation by the spray test.

5.2.3.2 Aqueous and oil repellency

Aqueous liquid repellency was evaluated using BS ISO 23232:2009 [282] using eight grades of water and isopropyl alcohol solutions. Resistance to oil-based liquids was evaluated using BS EN ISO 14419:2010 [283]. Both tests used the grading scale within the testing standard as detailed in section 4.2.3.5. The grade number in agreement from two testings was recorded, with a third test if necessary (procedure and grading detailed in section 4.2.3.5). Prior to testing, the samples were conditioned for at least 24 h at 20 ± 2 °C, 65 ± 5% RH. After testing, the samples were re-washed in an iterative process, as stated in section 5.2.2.

5.3 Results and discussion

Table 5.1 shows the samples tested and their drying conditions. Due to the hydrophilic membrane in samples *C*, *M* and *V,* they rolled up during the wash and, at times, this meant that the whole surface area of the sample was not accessible to the heat within the tumble drier.

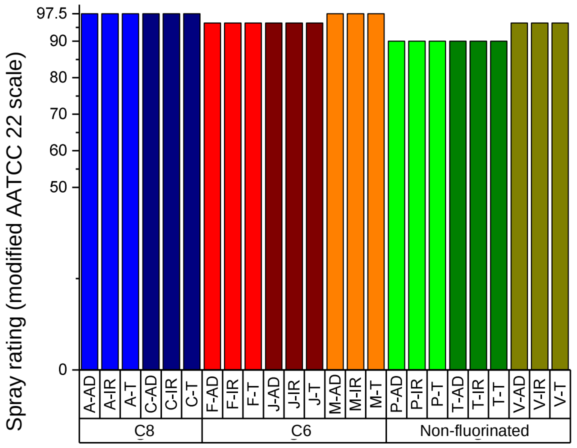
Table 5.1: DWR type and sample ID with drying/heat application. Three drying methods were applied: air dried (AD); tumble dried (T); ironed (IR).

DWR type	**Sample ID**	**Drying/heat application**
Long SFP (C8) DWR	*A*	*AD*
		IR
		T
	C	*AD*
		IR
		T
Shorter SFP (C6) DWR)	*F*	*AD*
		IR
		T
	J	*AD*
		IR
		T
	M	*AD*
		IR
		T
Non-fluorinated DWR	*P*	*AD*
		IR
		T
	T	*AD*
		IR
		T
	V	*AD*
		IR
		T

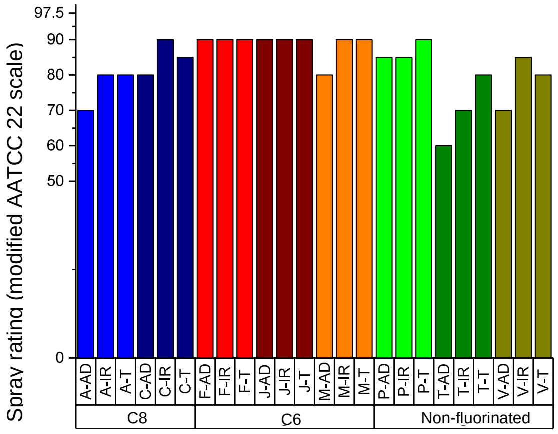
5.3.1 Evaluating repellency

The samples were evaluated after one wash cycle, three wash cycles, five wash cycles and ten wash cycles. The spray ratings assigned to the fabric samples after ten washes were lower than the initial rating (Figure 5.1).

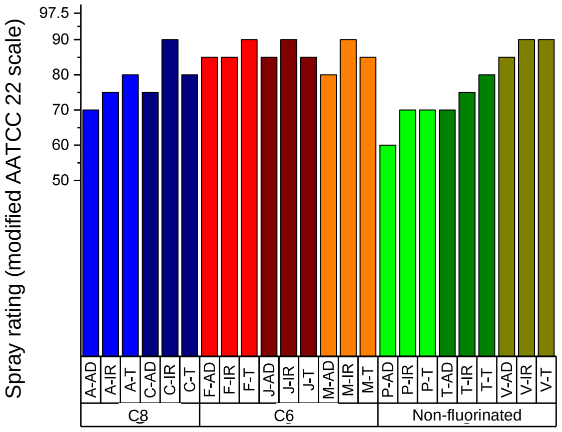
After ten wash cycles, both with and without liquid soapflakes, the water repellency of all samples tested had decreased and this was visible following evaluation by the spray test (Figure 5.2). There was decreased water repellency on both long SFP (C8) DWR samples and shorter SFP (C6) DWR samples apart from samples *A-T*, *C-IR*, *F-T* and *J-IR.* When washed without soapflakes, sample *T* demonstrated a large decrease in spray rating after ten washes, apart from when tumble dried *T-T.* Samples *A* and *V* demonstrated a greater decrease in spray rating when air dried compared to when tumble dried or ironed. When washed with soapflakes, the water repellency of sample *P* notably decreased after ten wash cycles compared to when washed without soapflakes.



Initial spray ratings



Spray ratings after ten wash cycles <u>without</u> liquid soapflakes



Spray ratings after ten wash cycles <u>with</u> liquid soapflakes

Figure 5.1: Spray ratings, according to modified AATCC 22 scale (section 4.2.3.2), initially, after ten wash cycles without liquid soapflakes and after ten wash cycles with liquid soapflakes. For sample codes see Table 5.1.

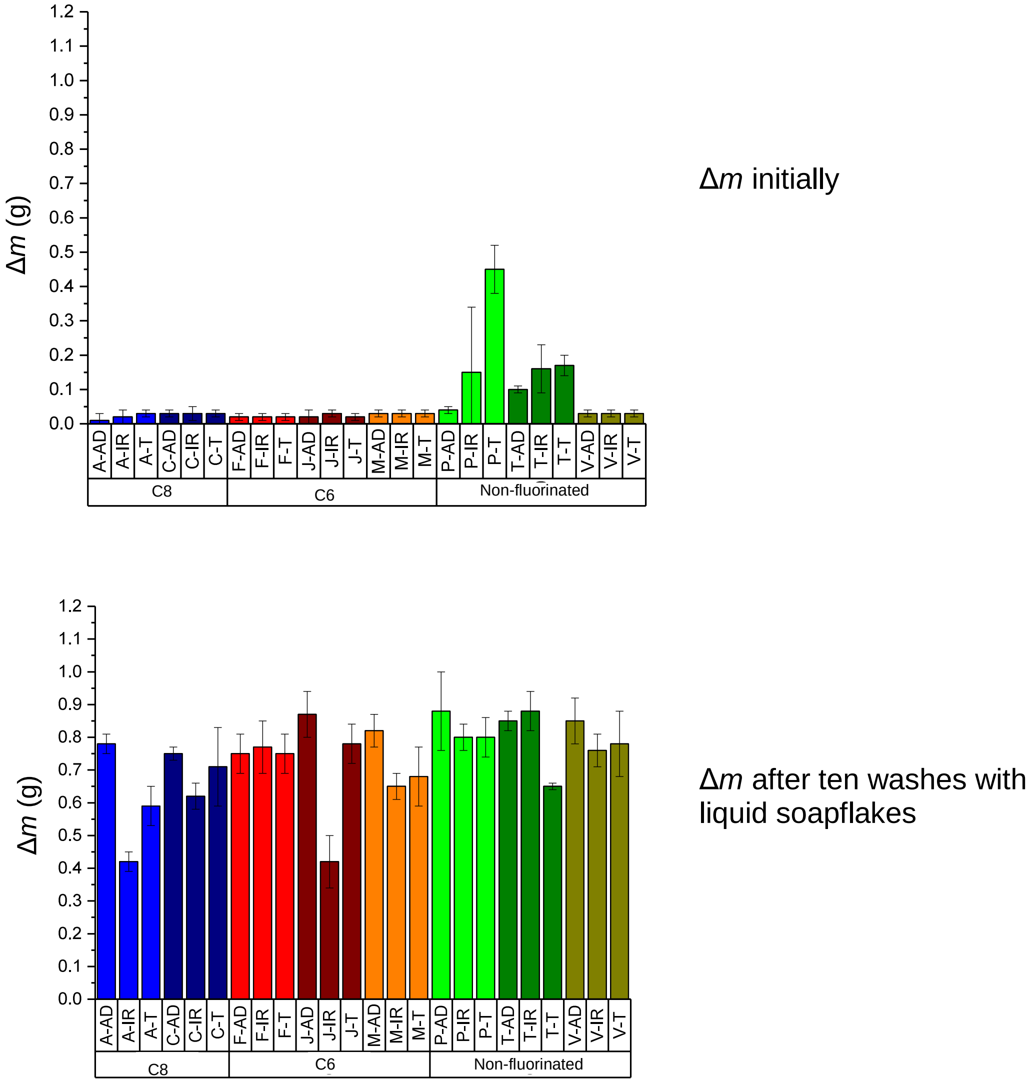
Sample ID *C -AD* *C-IR* *C-T*

Sample ID *M-AD* *M-IR* *M-T*

Sample ID *V-AD* *V-IR* *V-T*

Figure 5.2: Photos of the samples taken after evaluation with the spray test at ten wash cycles (with liquid soapflakes). Increased sticking of water and wetting shows reduced repellency. Red circles have been added to highlight these areas. For sample codes see Table 5.1.

Mass increase, Δ*m,* was calculated to determine the surface wetting and uptake of water. Over the ten wash cycles, the surface wetting of all the fabric samples increased, with a Δ*m* of at least 0.4 g after ten wash cycles (Figure 5.3). Overall, the non-fluorinated samples had a greater Δ*m* after ten wash cycles than the long SFP (C8) DWR samples (Figure 5.3). However, the wettability of samples *A-AD, C-AD* and *C-T* was greater than the wettability of sample *T-T.* A mixed between-within subjects repeated measures ANOVA demonstrated statistical significance difference in Δ*m* between wash cycles and DWR type ($p<0.005$) (A.6.1).


Δ*m* initially

Δ*m* after ten washes with liquid soapflakes

Figure 5.3: Mass increase, Δ*m*, initially and after ten washes with liquid soapflakes. For sample codes see Table 5.1. Error bars show standard deviation.

5.3.1.1 The impact of using liquid soapflakes

Using liquid soapflakes within the wash increased the wettability of the long SFP (C8) DWR samples and the shorter SFP (C6) DWR samples. All long SFP (C8) DWR samples demonstrated a greater Δ*m* after ten washes with liquid soapflakes than after ten washes without liquid soapflakes (Figure 5.3; Figure 5.4). For example, sample *A-T* had a Δ*m* following spray test of 0.59 g with soapflakes compared to 0.46 g washed without soapflakes. This increase in wettability of long SFP (C8) DWR samples when washed with soapflakes was seen after one wash cycle and increased steadily over subsequent wash cycles. Without liquid soapflakes, the wettability increased at a slower rate over wash cycles 1-3. All shorter SFP (C6) DWR samples, apart from samples *J-AD* and *M-AD,* demonstrated a greater wettability after ten washes with soapflakes than without soapflakes. Sample *F* showed this difference substantially with over 0.30 g difference between the two wash loads, after ten wash cycles: *F-AD* Δ*m* of 0.44 g without soapflakes and 0.75 g with soapflakes, *F-T* Δ*m* of 0.40 g without soapflakes and 0.75 g with soapflakes; *F-IR* Δ*m* of 0.42 g without soapflakes and 0.77 g with soapflakes.

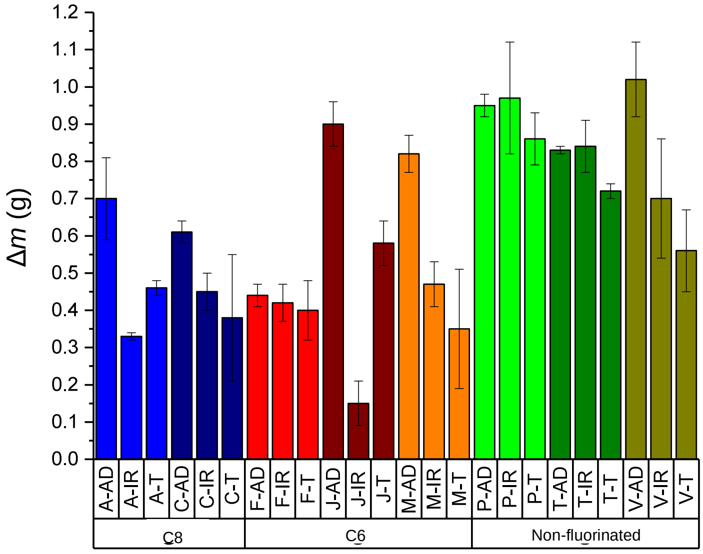


Figure 5.4: Δ*m* after ten washes washed without liquid soapflakes. For sample codes see Table 5.1. Error bars show standard deviation.

Overall the impact of soapflakes on non-fluorinated DWR samples after ten washes varied. The wettability of sample *V* was more consistent when washed with soapflakes compared to without soapflakes (Figure 5.3; Figure 5.4) shown by the error bars of standard deviation. When washed without soapflakes, a high Δ*m* was seen at five wash cycles, *V-AD* and *V-T* 1.37 g and 1.59 g respectively, but this reduced after ten wash cycles.

The difference demonstrated between the wettability of fluorinated DWR fabrics washed with and without liquid soapflakes is due to soap residue on the fabric surface from the wash [286]. Liquid soapflakes are an anionic surfactant consisting of amphiphilic molecules with a hydrophilic head and long hydrocarbon tail (Figure 5.5). Residues of the soap molecules on a fluorinated surface would leave hydrocarbon groups on the textile surface (Figure 5.6) [286]. This would intermingle areas of low surface energy, provided by the fluorinated surface, with areas of a higher surface energy, provided by the hydrocarbon surfactant. The latter areas would be less repellent and therefore would be more prone to wetting by water. In addition, the parallel arrangement would expose the hydrophilic head of the hydrocarbon surfactant attracting water [287]. With this, water can wet the surface and wick into the fabric structure. This has been demonstrated by the long SFP (C8) DWR samples and shorter SFP (C6) DWR samples in this study where a soap hydrocarbon residual has led to a surface which wets more greatly than when washed without soapflakes. When in contact with water, the soap residuals would lower the surface tension of the water increasing the wetting and spreading properties. An additional wash-off step could provide further evidence to this.

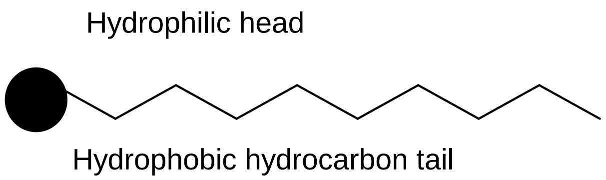


Figure 5.5: Schematic structure of a soap amphiphilic molecule with long hydrocarbon tail.

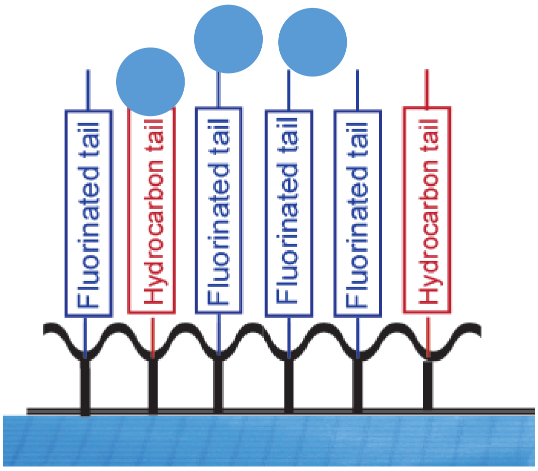


Figure 5.6: Soap residuals (hydrocarbon groups) on a fluorinated repellent textile surface would create areas of hydrocarbon tail groups amongst fluorinated tail groups. The former would be less repellent allowing wetting by water.

Soap residuals on the non-fluorinated DWR fabric surfaces would similarly add areas of hydrocarbon surfactants; in contact with the surface may be hydrophobic tail groups or the hydrophilic segment of the residual. All of the non-fluorinated DWR samples tested in this section of the study are assumed to be treated with a hydrocarbon-based DWR in dendritic structures (section 4.3.1, A.3). The addition of the hydrocarbon surfactant to these would not create a surface of diverse surface energies, but could add a hydrocarbon tail amongst other hydrocarbon tail groups. As demonstrated by the wettability of the samples tested, this has little impact on the repellency of the textile surface. In one case (sample *V)* the use of soapflakes has potentially added uniformity to the surface, demonstrated by the difference in Δm between washing with soapflakes and without soapflakes across ten wash cycles (Figure 5.3 ; Figure 5.4).

5.3.1.2 The effect of drying/heat application

The samples were air dried, tumble dried or ironed after every wash simulating consumer laundering practice. Air drying long SFP (C8) DWR samples increased the wettability, and therefore reduced the water repellency, compared to tumble drying or ironing (Figure 5.7).

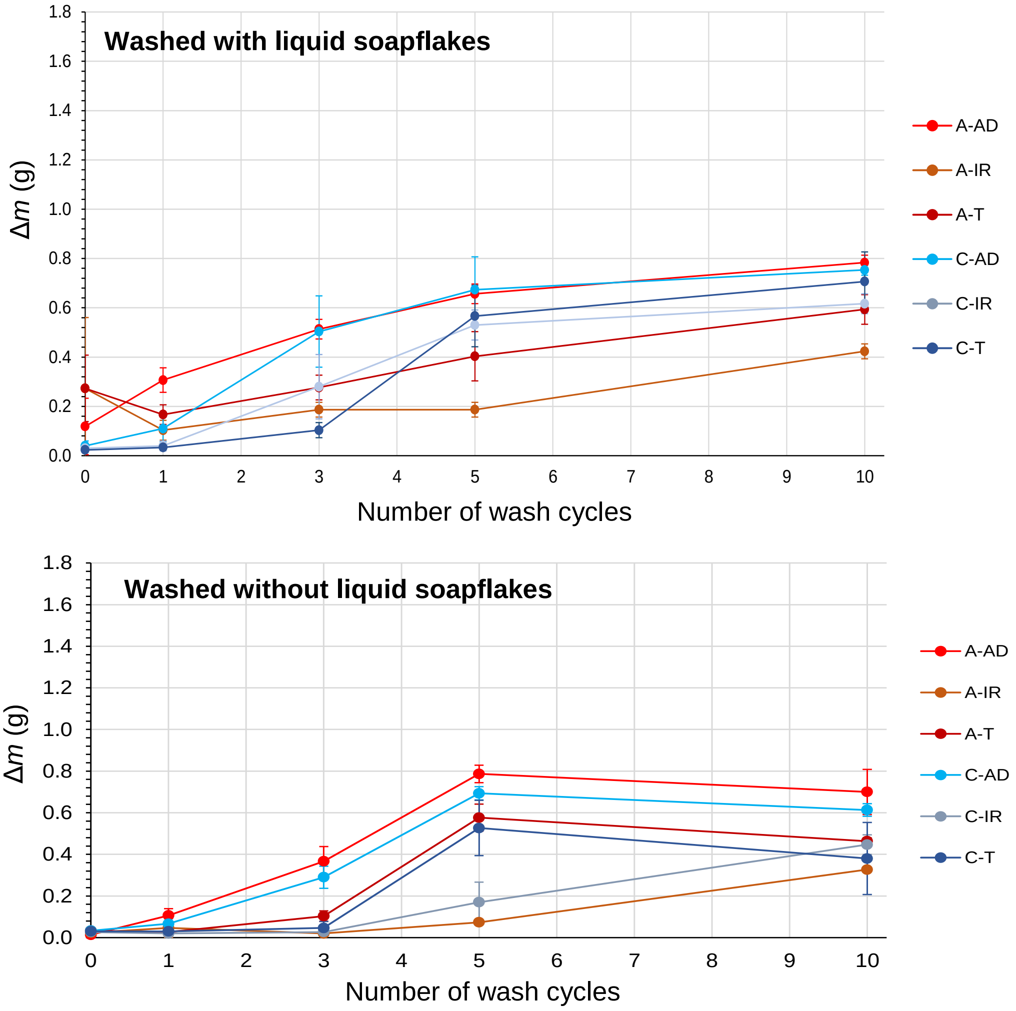
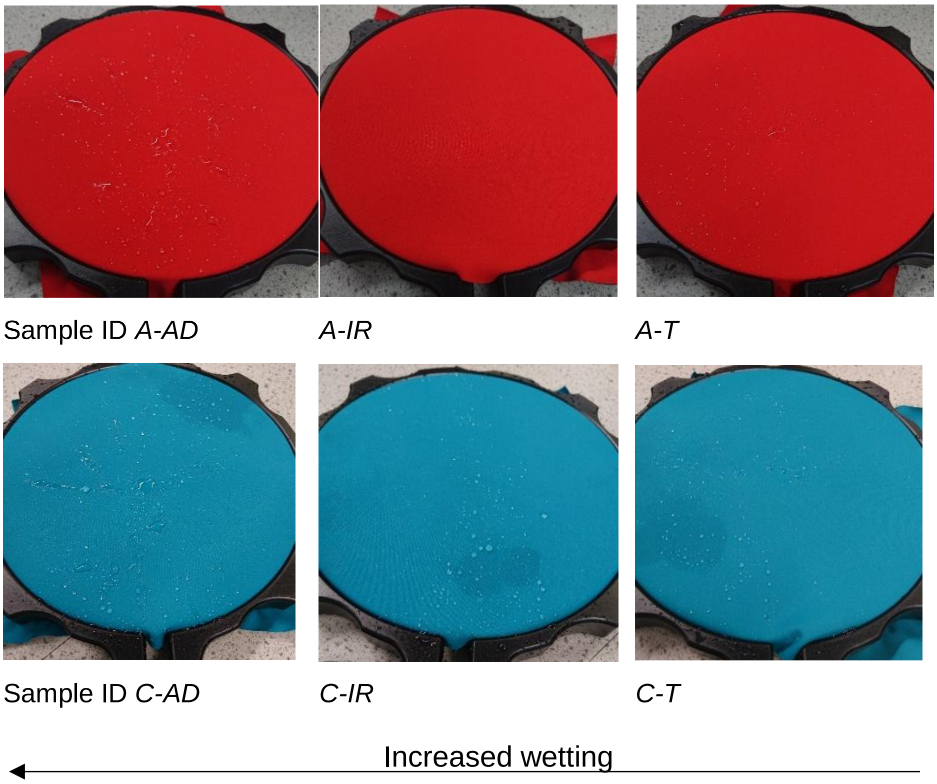


Figure 5.7: Long SFP (C8) DWR samples Δ*m*, following the spray test, washed with and without soapflakes. For sample codes see Table 5.1. Error bars show standard deviation.

The differences in drying/heat application and wettability can be clearly seen specifically by sample *A*, with significantly lower Δ*m*, and therefore greater water repellency after the spray test water shower when ironed (Figure 5.8). Tumble drying sample *A* consistently had a lower wettability than air drying, but greater than ironing;

at five wash cycles with soapflakes *A-AD* Δ*m* 0.66 ± 0.04 g, *A-T* Δ*m* 0.40 ± 0.10 g, *A-IR* Δ*m* 0.19 ± 0.03 g (Figure 5.7). Without soapflakes in the wash, sample *C* follows this similar trend, but tumble drying had a similar impact to ironing until wash cycle 5. With soapflakes in the wash, sample *C-T* demonstrated a lower Δ*m* until wash cycle 5. This change in wettability depending on the drying/heat application was visibly seen after evaluation with the spray test. The difference in wettability of air drying *(AD)* and ironing *(IR)* long SFP (C8) DWR samples *A* and *C* could be clearly seen after three wash cycles (Figure 5.8).


Sample ID *A-AD* *A-IR* *A-T*

Sample ID *C-AD* *C-IR* *C-T*

Figure 5.8: Images taken after evaluation by the spray test at three wash cycles of long SFP (C8) DWR samples A and C. A difference in wetting between the samples can be visually seen with greatest wetting on samples which have been air dried (AD). For sample codes see Table 5.1.

For shorter SFP (C6) DWR samples, air drying increased the wettability of the surface and therefore water repellency was reduced. This is clearly demonstrated by the differences in Δ*m* between sample *J-AD, J-T* and *J-IR* (Figure 5.9). Throughout all ten wash cycles, sample *J-IR* demonstrated a low Δ*m*, significantly different to air drying or tumble drying the sample. When washed without soapflakes, this trend was also clear for sample *M* with a steady Δ*m* increase over the ten wash cycles for *M-AD*; however this differed when washed with soapflakes. There were little differences in the wettability of sample *F* following the three different drying/heat applications (Figure 5.9).

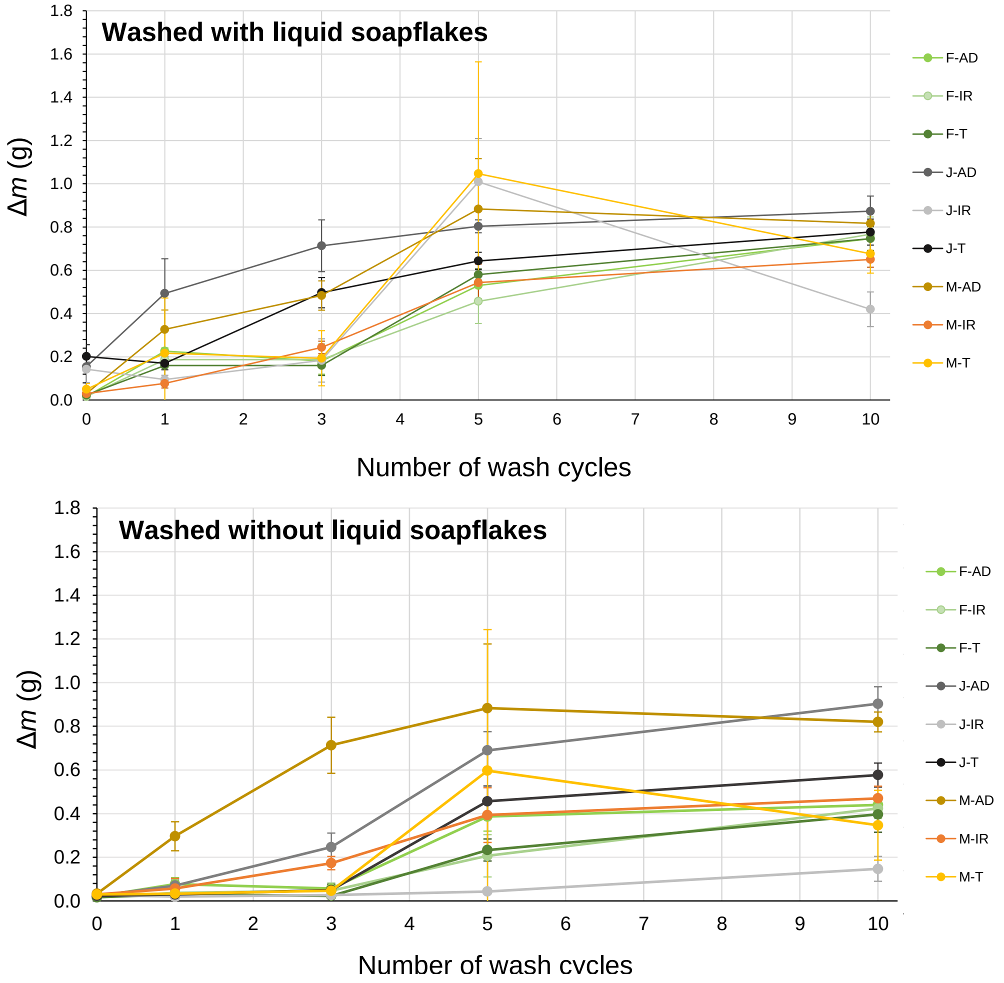


Figure 5.9: Shorter SFP (C6) DWR samples Δ*m*, following the spray test, washed with and without liquid soapflakes. For sample codes see Table 5.1. Error bars show standard deviation.

Over ten wash cycles, differences between the three drying/heat applications on the non-fluorinated DWR fabric samples cannot be seen (Figure 5.10). Overall, after ten wash cycles with soapflakes, the non-fluorinated DWR fabric samples demonstrated a slightly greater Δ*m*, and therefore increased wettability (in the range of 0.65-0.88 g) than the fluorinated fabric samples (long SFP (C8) DWR in the range 0.42-0.78 g; shorter SFP (C6) DWR in the range of 0.42-0.87 g).

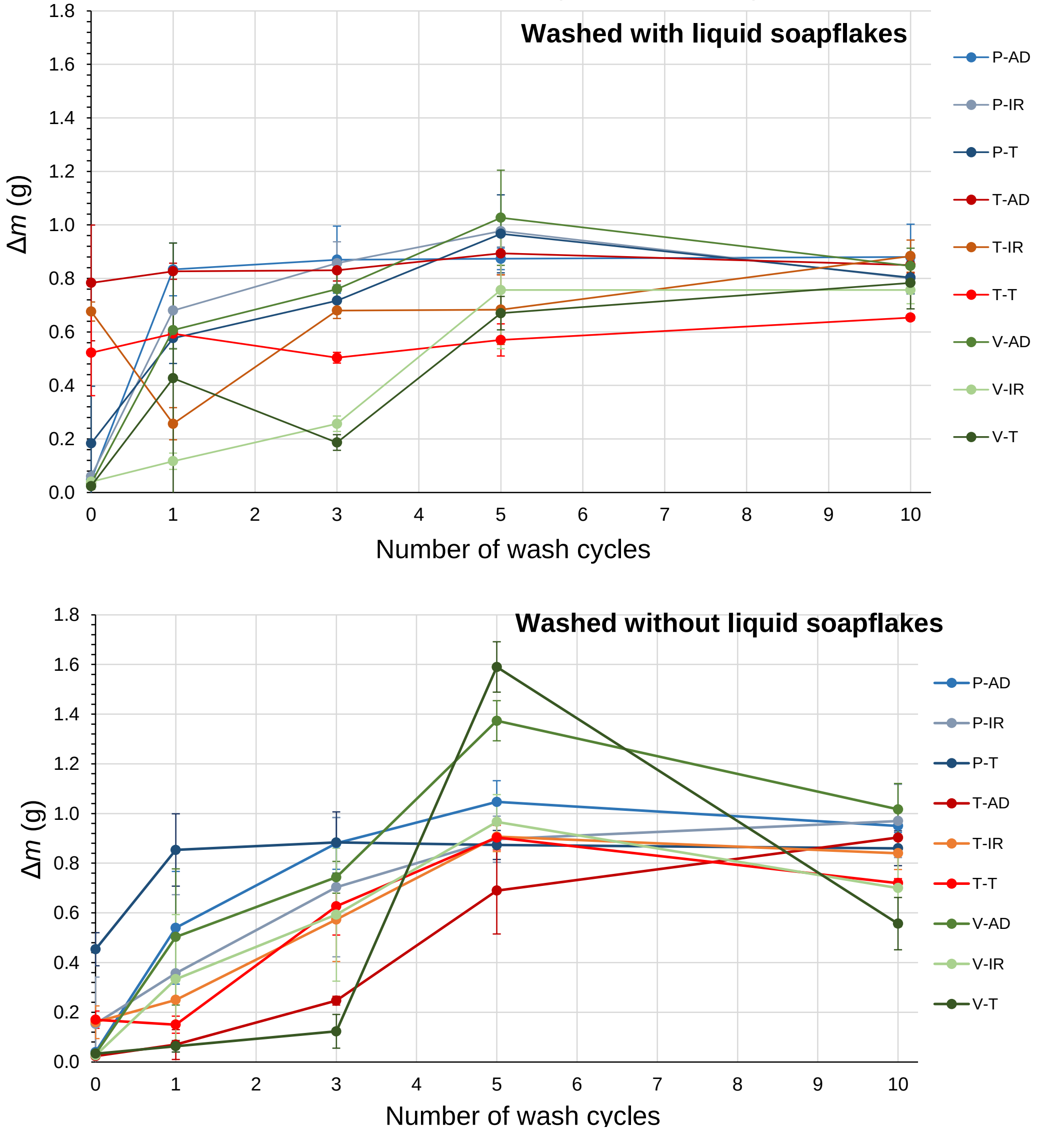


Figure 5.10: Non-fluorinated DWR samples Δ*m*, following the spray test, washed with and without liquid soapflakes. For sample codes see Table 5.1. Error bars show standard deviation.

To further compare the influence of drying/heat application on the fluorinated and non-fluorinated DWR fabric samples, samples *C, M* and *V* were directly compared (same fibre type and fabric construction). Both tumble drying and ironing demonstrated a slower decay in repellency, and therefore increase in wettability, over ten wash cycles (Figure 5.11). Ironing in particular had a smaller impact on wettability for long SFP (C8)

DWR sample *C* and shorter SFP (C6) DWR sample *M* than non-fluorinated sample *V* (Figure 5.11 c). After ten wash cycles, the calculated Δ*m* was less for fluorinated fabric samples that were ironed compared to air drying demonstrating sustained water repellency. Tumble drying followed a similar trend, but after ten wash cycles with soapflakes a greater wettability was observed (Figure 5.11 b). Overall, the standard deviation on repeated evaluation of sample *C* was less than the other fabric samples describing the stable surface of closely packed side-chains in a long-chain fluorinated structure.

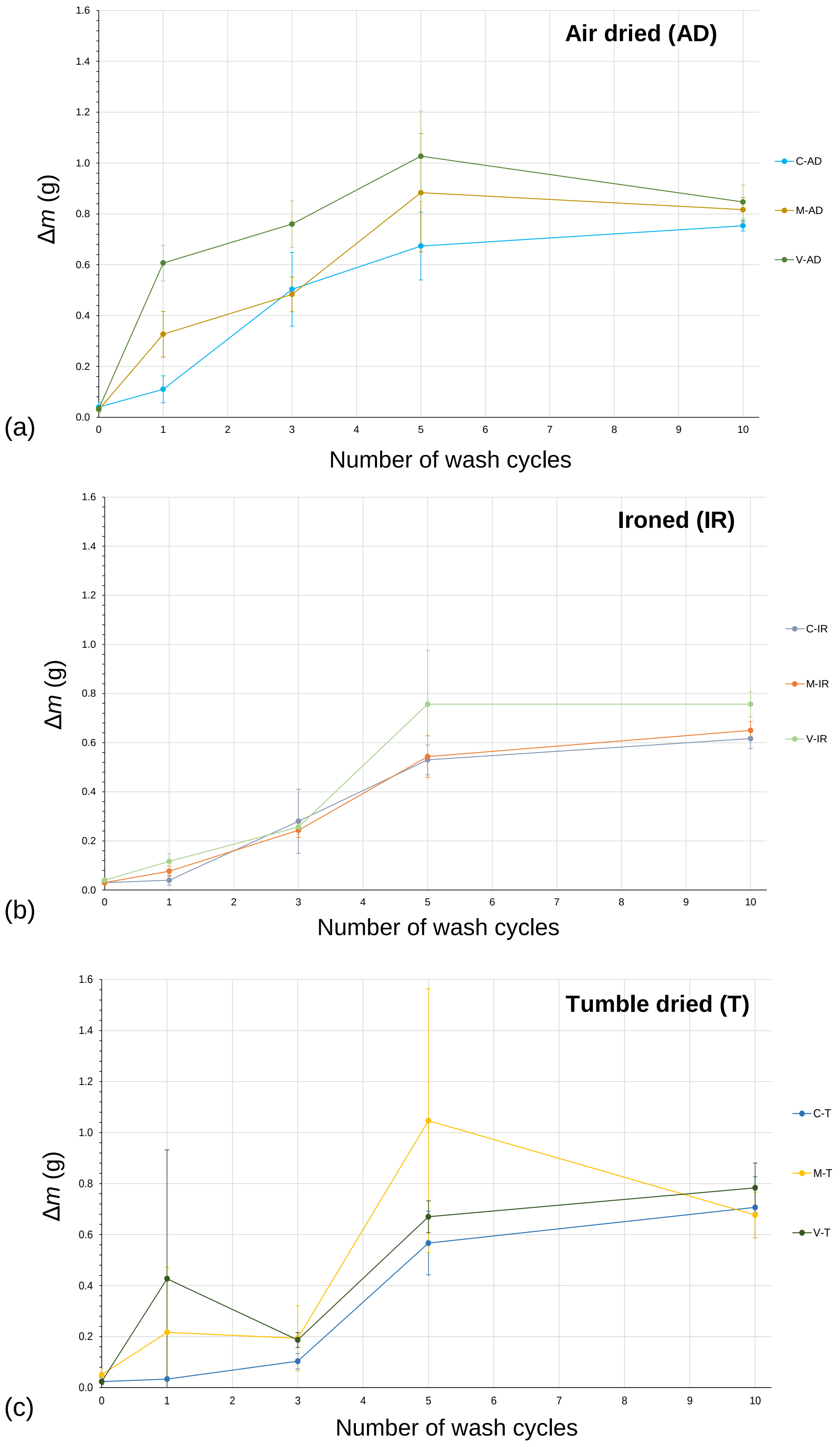


Figure 5.11: Δ*m* calculated after the spray test for samples C, M and V following washing with liquid soapflakes and (a) air drying samples (AD), (b) ironing samples (IR) and (c) tumble drying samples (T). For sample codes see Table 5.1. Error bars show standard deviation.

A two-way between-groups analysis of variance (ANOVA) was conducted to determine if there was a statistical difference between the drying/heat application on sample wettability, indicated by Δ*m*, when washed with soapflakes (A.6.2). This was calculated after one wash cycle, three wash cycles, five wash cycles and ten wash cycles for samples *C*, *M* and *V.*

One wash cycle: After one wash cycle, ANOVA and post-hoc comparisons indicated a statistically significant difference ($p<0.05$) between air drying and ironing ($p=0.022$) (A.6.2). A box and whisker plot shows this statistical difference (Figure 5.12). This is shown by the differing medians and no overlap between the spreads. Air drying has a larger variability than tumble drying and ironing. A statistically significant difference was not seen between air drying and tumble drying ($p=0.393$) due to the close proximity of the spreads nor between tumble drying and ironing ($p=0.264$) with overlapping interquartile ranges.

Three wash cycles: After three wash cycles, ANOVA and post-hoc comparisons indicated a statistically significant difference ($p<0.05$) between air drying and tumble drying and between air drying and ironing. A box and whisker plot shows this statistical difference (Figure 5.13) with no overlapping spreads. A statistically significant difference was not indicated between tumble drying and ironing ($p=0.072$) shown by the overlapping distribution and outliers (A.6.2).

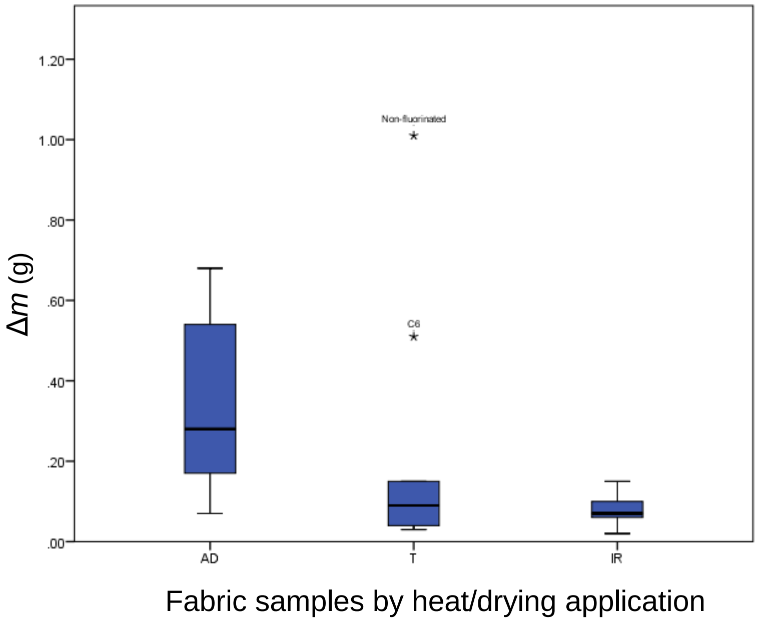


Figure 5.12: Box and whisker plot of Δ*m* according to drying/heat application after one wash cycle with soapflakes; data from samples C, M and V. The length of the box is the interquartile range with the whiskers the lower bound and upper bound with the 95% confidence level. The line across the box represents the median value of the data sets. º = outliers of the dataset.

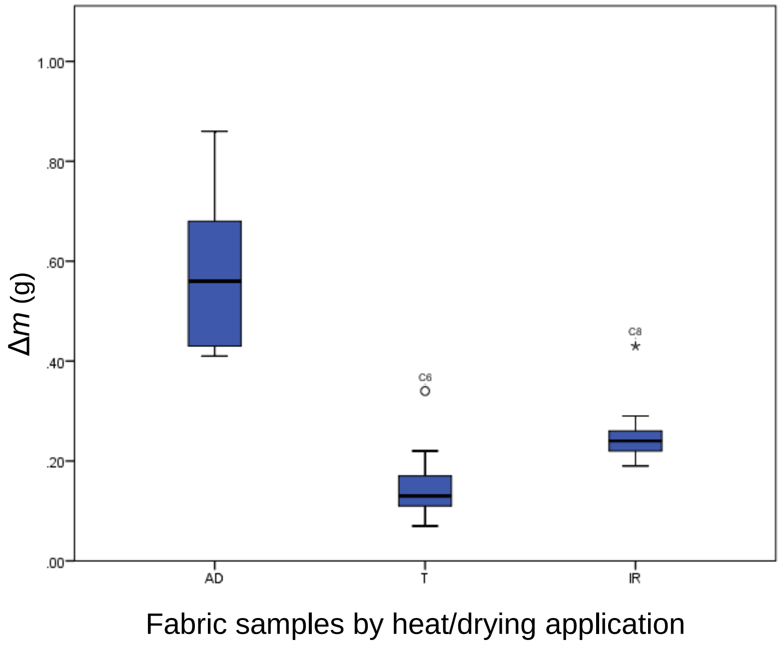


Figure 5.13: Box and whisker plot of Δ*m* according to drying/heat application after three wash cycles with soapflakes; data from samples C, M and V. º = outliers of the dataset.

Five wash cycles: After five wash cycles, ANOVA and post-hoc comparisons indicated that there was not a statistically significant difference between air drying, tumble drying and ironing (A.6.2). A box and whisker plot shows this with overlapping distributions of the ranges (Figure 5.14).

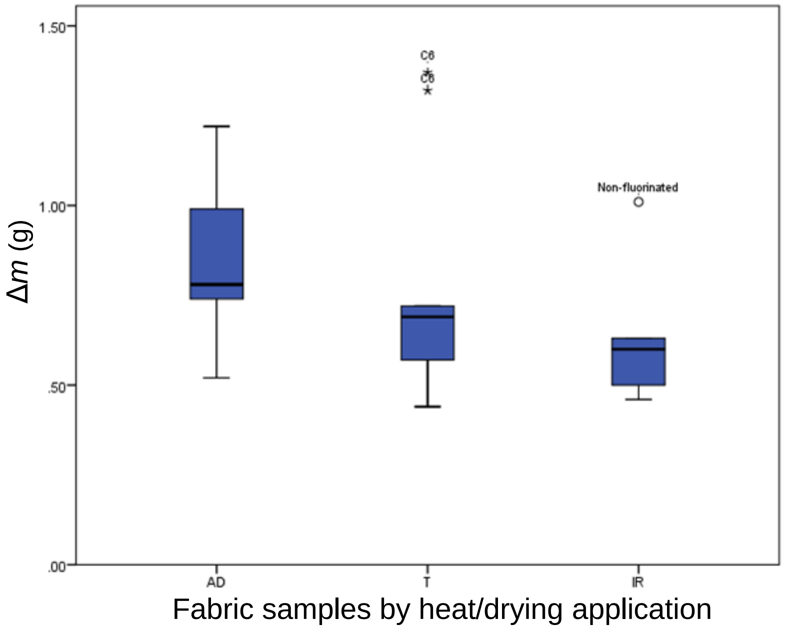


Figure 5.14: Box and whisker plot of Δ*m* according to drying/heat application after five wash cycles with soapflakes; data from samples C, M and V.

Ten wash cycles: After ten wash cycles, ANOVA and post-hoc comparisons indicated that air drying was significantly different to ironing ($p=0.003$) (A.6.2). A box-and whisker plot shows this difference between drying/heat application with no overlap between the interquartile ranges of data from air drying and ironing (Figure 5.15). A statistically significant difference was not indicated between air drying and tumble drying ($p=0.054$), shown by overlapping spreads, nor between tumble drying and ironing ($p=0.342$) with close proximity of the medians.

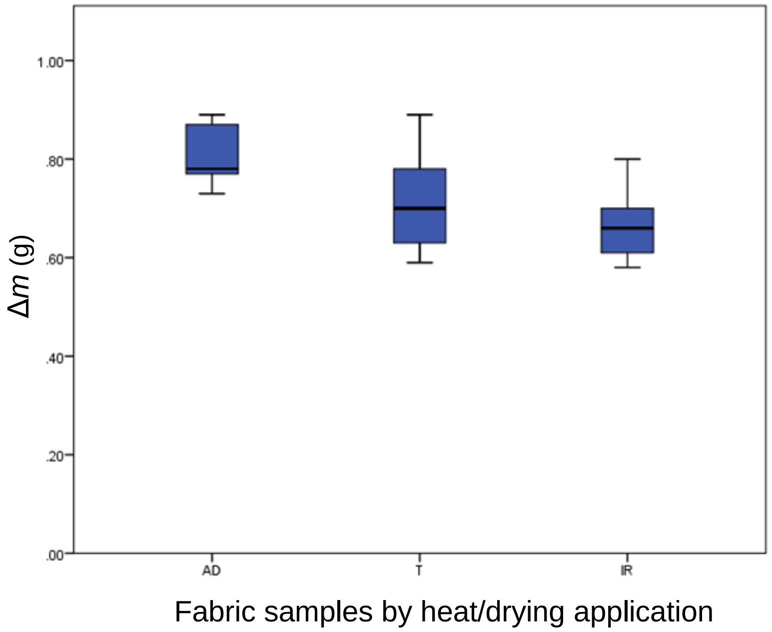


Figure 5.15: Box and whisker plot of Δ*m* according to drying/heat application after ten wash cycles with soapflakes; data from samples C, M and V.

5.3.2 Evaluating aqueous and oil repellency

There was little difference between the aqueous and oil repellency grades of samples washed with soapflakes and washed without soapflakes. Data from washing with soapflakes is presented. Overall, after ten washes a decreased repellency to aqueous-based liquids was demonstrated by long SFP (C8) DWR samples and shorter SFP (C6) DWR samples (Figure 5.16). For sample *C* this was a large decrease in surface energy from 26.5 dyn cm^{-1} to 54.5 dyn cm^{-1} (sample *C*-AD) and to 46 dyn cm^{-1} (sample *C*-*IR*). The aqueous repellency on non-fluorinated sample *T* was similar after ten wash cycles to the initial repellency (grade 3.0-3.5; surface energy ~ 37.5 dyn cm^{-1}). After ten wash cycles all non-fluorinated DWR samples demonstrated sustained repellency to aqueous-based liquids, but the level of repellency was equivalent or less than that demonstrated by long SFP (C8) DWRs.

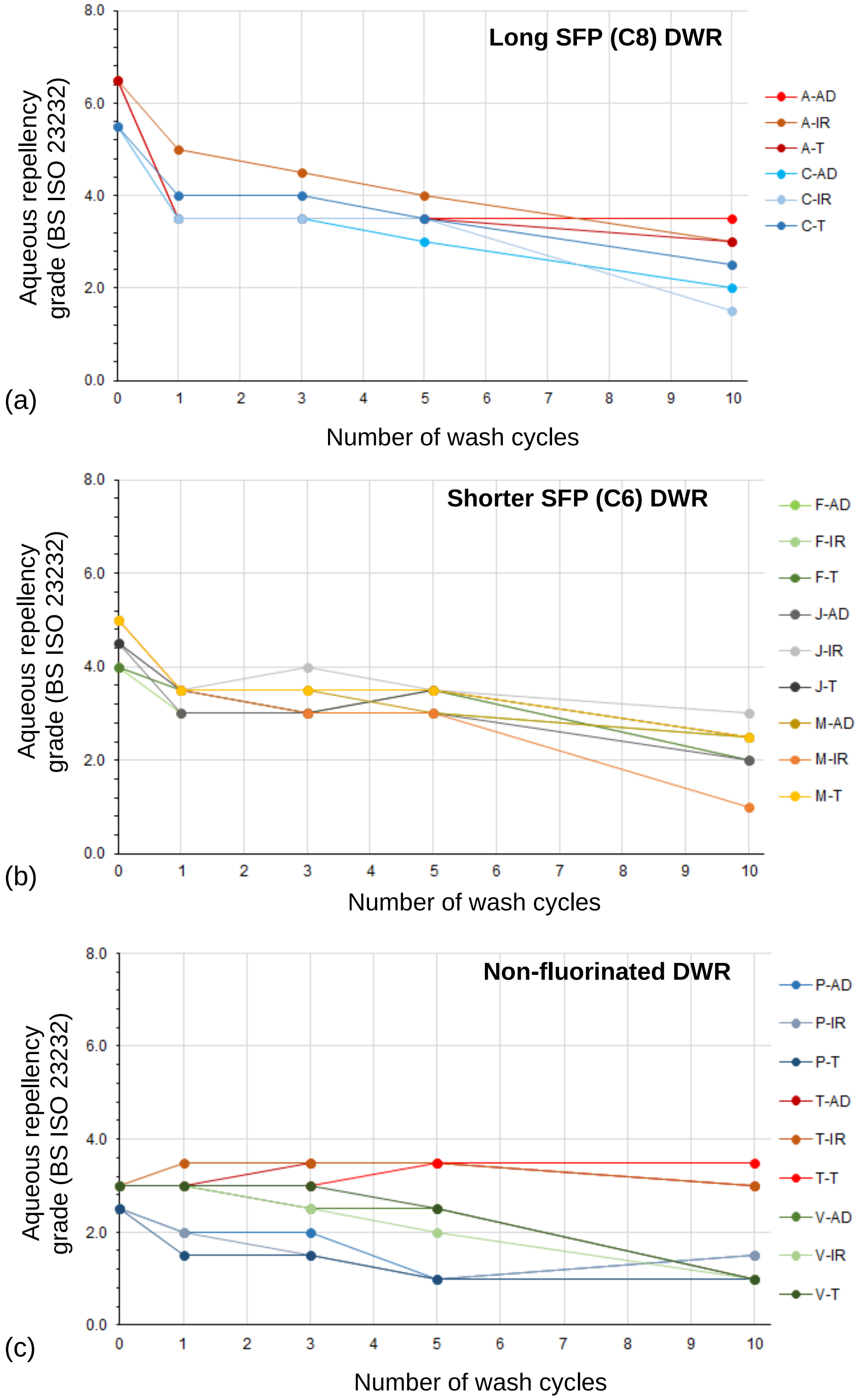


Figure 5.16: Resistance of repellent fabric samples to aqueous-based liquids over ten wash cycles: (a) long SFP (C8) DWR fabric samples; (b) shorter SFP (C6) DWR fabric samples; (c) non-fluorinated DWR fabric samples. For sample codes see Table 5.1.

Non-fluorinated DWR fabric samples demonstrated no oil repellency initially, and laundering did not influence this. Therefore Figure 5.17 shows only the data of (a) long SFP (C8) DWR samples and (b) shorter SFP (C6) DWR samples. Oil repellency of the long SFP (C8) DWR samples decreased greatly after one wash cycle (Figure 5.6). Over the subsequent wash cycles, oil repellency continued to decrease but at a slower rate. This deterioration in oil repellency was quicker for samples that were air dried (samples *A-AD* and *C-AD)* which were assigned grade 0 after three wash cycles (grades as specified in BS EN ISO 14419:2010). The oil repellency of the samples that were ironed deteriorated at a slower rate and were assigned grade 1.0 (surface energy ~ 31.5 dyn cm^{-1}) after five wash cycles. Only sample *A-IR* demonstrated a degree of repellency to oil-based liquids after ten wash cycles (grade 0.5).

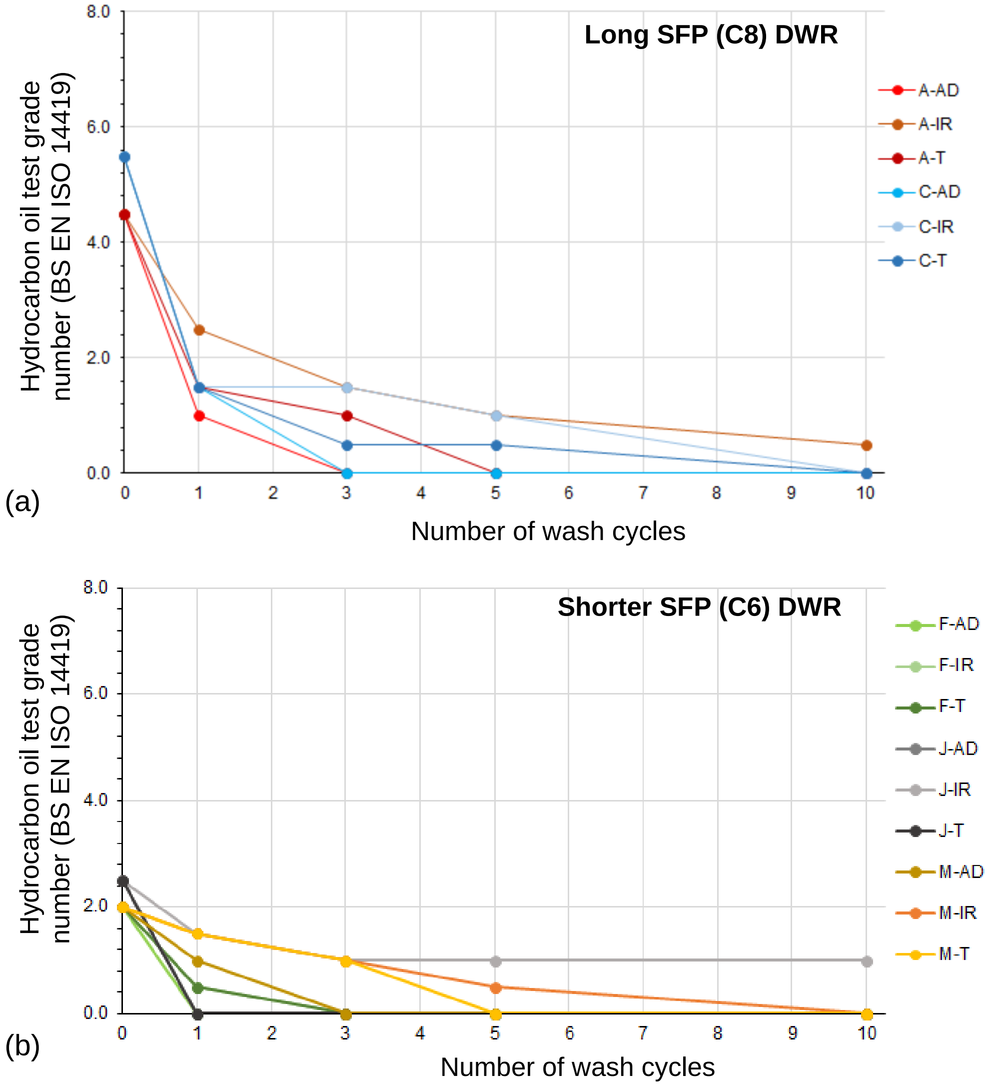


Figure 5.17: Resistance of repellent fabric samples to oil-based liquids over ten wash cycles: (a) long SFP (C8) DWR samples; (b) shorter SFP (C6) DWR samples. For sample codes see Table 5.1.

Oil repellency of shorter SFP (C6) DWR samples deteriorated over ten wash cycles. The oil repellency of sample *F* deteriorated after one wash cycle apart from the samples which were ironed (*F-IR*); however this repellency ceased after three wash cycles (Figure 5.17 b). The oil repellency of samples *M-T* and *M-IR* were similar until after five wash cycles when only the ironed sample demonstrated some oil repellency. Sample J when ironed (*J-IR)* sustained oil repellency over the ten wash cycles whilst the oil repellency decreased when the sample was air dried or tumble dried. Only sample *J-IR* demonstrated a degree of oil repellency after all ten wash cycles (grade 1.0; surface energy ~31.5 dyn cm^{-1}).

5.3.3 Understanding the surface mechanisms due to drying/heat application

Evaluation of wettability, and thus the fabric's surface repellency, has indicated changes following laundering. The effect of heat on restoring the surface repellency has been discussed in section 1.2.4.3. However, whilst it is widely acknowledged, reasoning behind the phenomena is sparse. Whilst heat application on fluorinated DWR surfaces, specifically ironing at average temperature 160°C, has demonstrated that water repellency is sustained over washing, the following section will aim to further explain the mechanisms of re-orientation of the side-chains and aim to collate the literature behind this phenomenon. When washed, the hydrophobicity of the fabric samples deteriorated when they were wetted by washing water. This deterioration of the hydrophobicity is due to the morphological change occurring at the surface interface, explained as the movement of the hydrophobic end groups rotating away from the hydrophilic environment [53,284,288]. Therefore the hydrophobic end-groups are no longer present at the surface allowing wetting to occur.

The crystallinity of long SFP (C8) DWRs has been discussed in section 1.4.3. When dried slowly in the presence of water, i.e. air drying, the fluorinated side-chains arrange randomly, decreasing the number of –CF_3 end groups at the surface-air interface [54,284,288,289]. However, by tumble drying and ironing, energy (heat) is given to the fluorinated structure to orientate back to its crystalline orderly state (Figure 5.18).

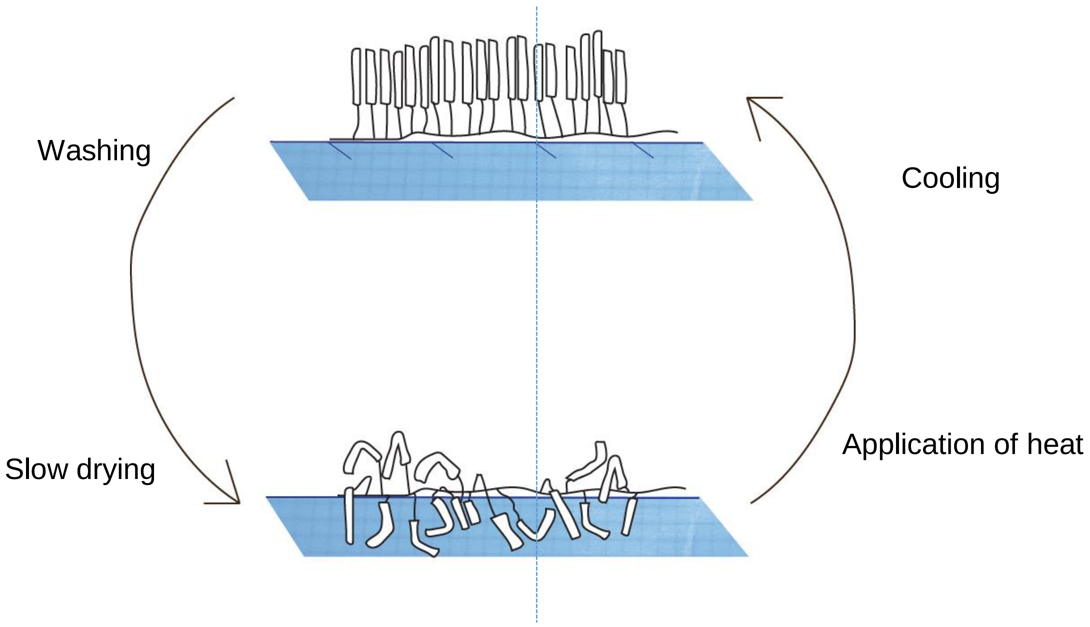


Figure 5.18: The effect of washing on the packing and orientation of fluorinated side-chains and their reorientation following heat application, adapted from [284].

The use of a domestic iron and tumble drier, in this study, simulated consumer laundering more comparably than a laboratory oven or heat press. The temperature of the iron (135-190°C) and temperature of the tumble drier (ranging between 22.6-62.3°C) is different to previous literature [52,112,289]. The temperature of the domestic iron is similar to the temperature reached during the dry and cure stage when applying the DWR aqueous emulsion within factory (section 1.3.1). During this manufacturing stage, the polymer is cross-linked to the textile surface, but crystallisation also occurs from evaporation of solvent. This occurs beyond the glass transition temperature of the repellent surface polymer allowing opportunity to reorder as a crystalline structure [284]. Therefore, after the temperature of the iron, crystallisation is thought to have occurred due to cooling. The difference in temperature between the domestic iron, used within this study, and the domestic tumble drier is thought to have a related effect on the degree of crystallinity occurring.

For long SFP (C8) DWR samples, movement within the polymer chain is restricted due to its high crystallinity and packing [288]. With this, laundering has little impact on the surface configuration due to its rigid structure [288]. This has been demonstrated in the Δm calculations, after the spray test shower, showing lower wetting over the ten wash cycles than the shorter SFP (C6) DWR samples and non-fluorinated fabric samples. The shorter SFP (C6) DWR samples initially exhibited good repellency, but demonstrated a greater deterioration in repellency due to the lower crystallinity of the polymer (section 1.4.7).

The loss of fluorinated hydrophobic end groups at the surface after washing and with air drying has been shown by the reduction of fluorine on the surface [285,289]. On treated cotton fabric, Arunyadej *et al.* [285] found fluorine concentration on the surface was reduced from 37.7 atomic mass % after one wash to 17.9 atomic mass % after ten washes, analysed by X-ray photoelectron spectroscopy (XPS). With heat treatment, the fluorine concentration increased by 3.6 atomic mass % after one wash and 7.2 atomic mass % after ten washes due to the re-orientated hydrophobic end-groups at the surface [285].

For non-fluorinated DWRs, the non-linear structure and therefore lesser degree of crystallinity within the structure (section 1.4.7.2) means a less rigid and ordered structure. Following washing, the polymer reorders randomly and the degree of crystallinity is less. There is greater mobility in the end groups and therefore at the surface-air interface which increases wettability.

Suggested further work for this study would be to carry out elemental analysis at the staged wash cycles to determine if a reduction in chemical composition on the surface can be associated with the deterioration of liquid repellent functionality. Additionally, atomic force microscopy (AFM) would allow the surface morphology to be investigated in relation to this phenomenon.

5.4 Conclusions

This study has investigated the effect of consumer laundering practices on liquid repellent functionality of fluorinated and non-fluorinated DWR samples and its longevity over ten wash cycles. It has specifically investigated textiles simulating consumer washing practises using a domestic washing machine, tumble drier and iron. Along with assigning a spray rating, calculations of Δm following the spray test have given an insight into the wettability of the sample after the wash cycles. Over ten wash cycles, the non-fluorinated DWR samples, overall, demonstrated a greater wettability, and therefore decreased surface energy, than the long SFP (C8) DWR samples.

Washing with soapflakes was seen to negatively affect the repellency of a fluorinated surface. This has been described as the residual hydrocarbon groups of the surfactant remaining on the fluorinated surface affecting the surface energy at the interface. Washing non-fluorinated DWR samples with soapflakes could attribute to prolonged repellency due to the soap residuals being hydrocarbon compounds and therefore not affecting the surface energy.

Ironing fluorinated DWR samples prolonged the liquid repellency over the wash cycles, and the surface mechanism enabling this has been discussed. A statistical difference between air drying and ironing was calculated for samples *C, M* and *V* after one wash cycles, three wash cycles and ten wash cycles with soapflakes. From this, it can be recommended that the optimal laundering practise is to iron fluorinated DWR fabrics; although care should be taken that the temperature of the iron is below the melting point of the polymeric surface. A statistically significant difference was not determined between ironing and tumble drying nor air drying and tumble drying. From this, it can be determined that tumble drying sustains repellency, but it is not as consistently effective as ironing.

One specific drying/heat application cannot be clearly recommended for laundering of non-fluorinated DWR fabrics. A suggested laundering practise will largely depend on the chemical type of the non-fluorinated DWR and initial curing temperature to activate the DWR. However, due to the degree of crystallinity within the structure, liquid repellency will deteriorate with washing and ordered packing, equivalent to that of SFP DWRs, will not be achieved with application of heat.

This chapter has considered consumer laundering of ‘new’ fabrics, whereas during use dirtying of garments would occur by staining and transfer of body oils prompting the consumer to wash the garment. Using dirtied fabrics would have resembled a realistic consumer wash load but added a number of variables including the amount of contamination and variation between samples. This is recommended as further work with verification of a typical consumer wash load. Further work could also be carried out to determine the effect of a number of detergents on wettability and to investigate the interaction of aftercare treatments on sustaining liquid repellency. There is currently not a benchmark, and guidance is unclear on how commercial aftercare products work on textiles with different DWR types. This is particularly important to determine the interaction of commercial aftercare products on non-fluorinated DWR fabrics which, chemically, will interact differently to fluorinated DWR fabrics. This would build upon previous research by Stevens [37] suggesting that the home application binds on to the residue of a factory-applied DWR.

Chapter 6 - Development of test methodology: evaluating water repellency

6.1 Introduction

With the adoption of non-fluorinated DWRs dependent on the textile meeting the criteria and functionality equivalent to fluorinated DWRs, it is important to determine the longevity and durability of the repellency. This helps to determine the lifespan of the garment in end-use and prevent customer returns or complaints. In addition, loss of repellent functionality indicates degradation of the DWR chemistry with loss to the environment during abrasion, weathering or laundering [112].

Test methods to evaluate the water repellency of a textile have been summarised (Table 1.2). The spray test is the most widely used assessment of water repellency on textile fabrics due to its reproducibility and availability. The AATCC rating scale and BS EN ISO rating scale are used interchangeably and correlate comparatively (correlation coefficient r = 0.93) (A.7).

Liquid repellency is analytically determined by evaluation of the static wetting properties by contact angle measurement (section 1.3.3). Imaging of the liquid droplet is analysed to characterise the surface [82]. However, the inherent surface roughness of textile surfaces is not well suited to this traditional determination of wetting properties. The static nature of this analysis does not relate to the end-use of liquid repellent outdoor garments where evaluation under dynamic movement would be greatly applicable due to the properties of rain and movement of clothing when worn.

A subgroup of laboratory textile tests to determine water repellency (section 1.3.3) are those which specifically simulate rain exposure. Each differs in the water volume of the shower, flow rate and distance between the spray and sample (Table 6.1).

Table 6.1: Exisiting laboratory test methods to determine water repellency [18,19,83–87].

Test method	Testing standard	Type of test	Flow rate	Duration of shower	Drop height (mm)
Spray test	BS EN ISO 4920:2012/ AATCC 22-2014	Fabric's resistance to surface wetting – simulating rain shower	500 mL/min	25-30 seconds	150
Bundesmann rain-shower tester	ISO 9865/BS EN 29865	Resistance of textile fabrics to rain shower by absorption and penetration	100 mL/min	10 minutes	1500
Water resistance penetration test	AATCC 42-2007	Fabric's resistance to impact of water	500 mL/ unspecified	unspecified	600
Water resistance rain test	AATCC 35-2006	Fabric's resistance to impact of water	Unspecified	5 minutes	305 (horizontal water spray)
Water resistance to an artificial shower: WIRA shower test	BS 5066	Resistance to absorption and penetration under simulated rain shower	66 mL/min	~7.5 minutes	1000

Whilst literature discusses the use of the spray test in quality control, rather than predicting fabric performance [286], it is the most widely used test method to determine water repellency due to its availability and accessibility. From testing within this work, the predominant limitations of the spray test have been identified as:

1) Subjective assessment of surface wetting;
2) Difficulty to discriminate between similarly performing fabrics;
3) 25-30 second 'rain' shower;
4) Sample under test angled at 45º which does not replicate use;
5) Variation due to tester objectivity.

Throughout this research, a significant adaptation of the subjective assessment has been made using additional ratings to the AATCC standard rating scale (section 4.2.3.2). In addition, calculation of percentage mass change (%) and calculation of mass increase, Δm, (g) have been calculated to evaluate the wetting resistance of the fabric using quantitative data (section 4.2.3.4).

In relation to objective 5 (section 1.7), the aim of this section was to address several of the limitations identified with the spray test and consider other laboratory test methods for water repellency by:

- Analytical evaluation of water repellency;
- Evaluating other textile tests simulating rain exposure with focus on the Bundesmann rain-shower tester to determine water repellency;
- Addressing the length of the spray test.

6.2 Analytical evaluation of water repellency

Analytical evaluation of the static wetting properties of a liquid on a surface traditionally uses contact angle analysis. Contact angle analysis was carried out using a Tensiometer (pendant drop KSV cam 200) with Attension Theta software. Three images were taken of each testing with the software automatically determining the baseline and calculation of contact angle. However, due to the inhomogeneous surface of the samples, the baseline was difficult to define and therefore accurate contact angle calculation was misconstrued (Figure 6.1).

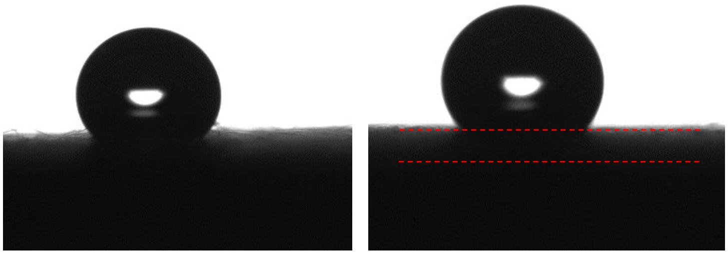


Figure 6.1: Determination of contact angle. The baseline is difficult to determine on the fabric surface.

The difficultly in accurate determination of contact angle on textile fabrics has been highlighted by Zimmermann *et al.* [82]. Within this study, a tilt platform was developed to measure the “water shedding angle” (Figure 6.2). The platform was primarily set at an inclination of 85° and on each fabric sample, five droplets of water were placed onto the surface - if the droplets bounced or rolled off the sample, then the platform’s angle was reduced by 5 ° and the test repeated. The test enabled differences to be seen between coated textiles and suggested further use to detect changes after mechanical, environmental and chemical abrasion [82].

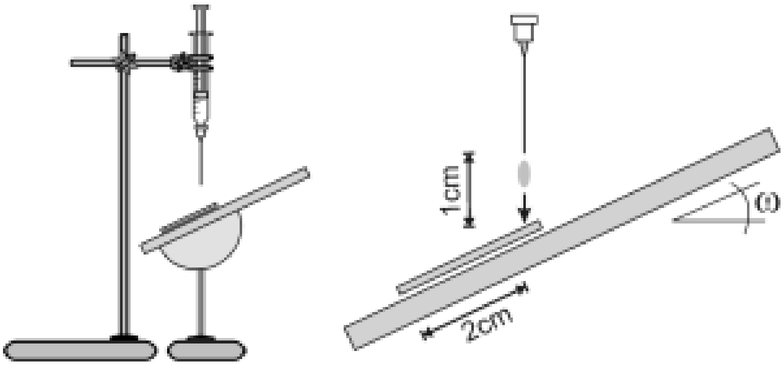


Figure 6.2: Test setup to evaluate water shedding angle (ω) on textile fabrics [82].

This study determined the water shedding angle by inclination of the platform at set intervals. Alternatively, the ‘roll-off angle’ can be calculated as the angle at which the liquid droplet starts to move away from the surface evaluating the adhesive properties of the surface. For this evaluation, a tilting plate is increased continuously, away from the horizontal, and the angle at which the droplet moves is recorded. It was thought that identifying the roll-off angle would have strong reference to the end-use application of outdoor repellent garments.

Unpublished work by Stevens [37] developed a roll-off angle analysis tester. The first iteration used a flat plate, to which the fabric was clipped taut, with a movement wheel causing the plate to turn from the horizontal. Using a protractor, the roll-off angle was recorded and the movement documented with a microscope. Developing upon this, a motor was attached to create a smooth controllable movement. Images were taken of the droplet on the horizontal and analysed using computer software to determine the contact angle; the roll-off angle was calculated using a pentiometer. Initial testing by Stevens [37] showed strong correlation to contact angle measurements and spray test evaluation.

The test apparatus was restored for this study but issues came to light with movement within the flat plate, adding a large experimental error to the readings.

6.2.1 Determination of roll-off angle

Furmidge first described a method to evaluate roll-off angle in explaining surface wetting properties [290]. Relating this to textile surfaces and building upon the work carried out by Stevens [37], a tilting platform was designed and constructed.

This study uses an adaptation of the novel sample holder setup from collaborative work with Schellenberger *et al.* [291].

6.2.1.1 Materials

The samples within this study were those from Chapter 5, washed with soapflakes, analysed at each wash stage (initial, after one wash cycle, after three wash cycles; after five wash cycles and after ten wash cycles). The wash cycles included the drying/application of heat (air drying -*AD*; ironing -IR; tumble drying -*TD*), as discussed in section 5.2.2.2. Samples *A* and *C* were long SFP (C8) DWR, samples *F, J* and *M* were shorter SFP (C6) DWR and samples *P, T* and *V* were non-fluorinated DWR.

For sample codes see Table 5.1.

6.2.1.2 Method

Test set up: A tilt table was assembled from 10 mm metal with dimensions as in Figure 6.3 with additional platforms (highlighted) made from 5 mm foam board. The tilting platform was connected to a stepping motor with increasing inclination at intervals of 0.9º (12°/second at 400 rpm) in an anti-clockwise direction. The tilt of the platform was restricted by the stopper returning to horizontal (0°) and checked prior to each test with a spirit level. The stepping motor was connected to a control unit with a 12V DC power supply. The terminal program ‘PuTTY’ (Windows) was used to log the angle of the tilting platform as it moved.

On the additional platforms, the sample was held by elasticated bands to securely position and keep the fabric taut. These additional platforms were based on collaborative work completed in addition to this study [291].

Prior to each testing, it was ensured that the platform was horizontal using a spirit level. The test sample was securely positioned on the tilting platform with weft direction widthways across the platform. A water droplet (13 µL) was placed centrally on to the test specimen using a syringe with a threaded rotation plunger (Hamilton Model 1001 LT with Kel-F Hub needle attachment) and distilled water. Standing time before start of the test was 10 seconds.

The motor controlling the tilting platform movement was started with a continuous movement (12°/second at 400 rpm) and stopped by pressing a button on the control unit when the droplet moved away from the fabric surface. The angle of inclination was noted. Each specimen was tested separately and an average calculated from five repeat measurements.

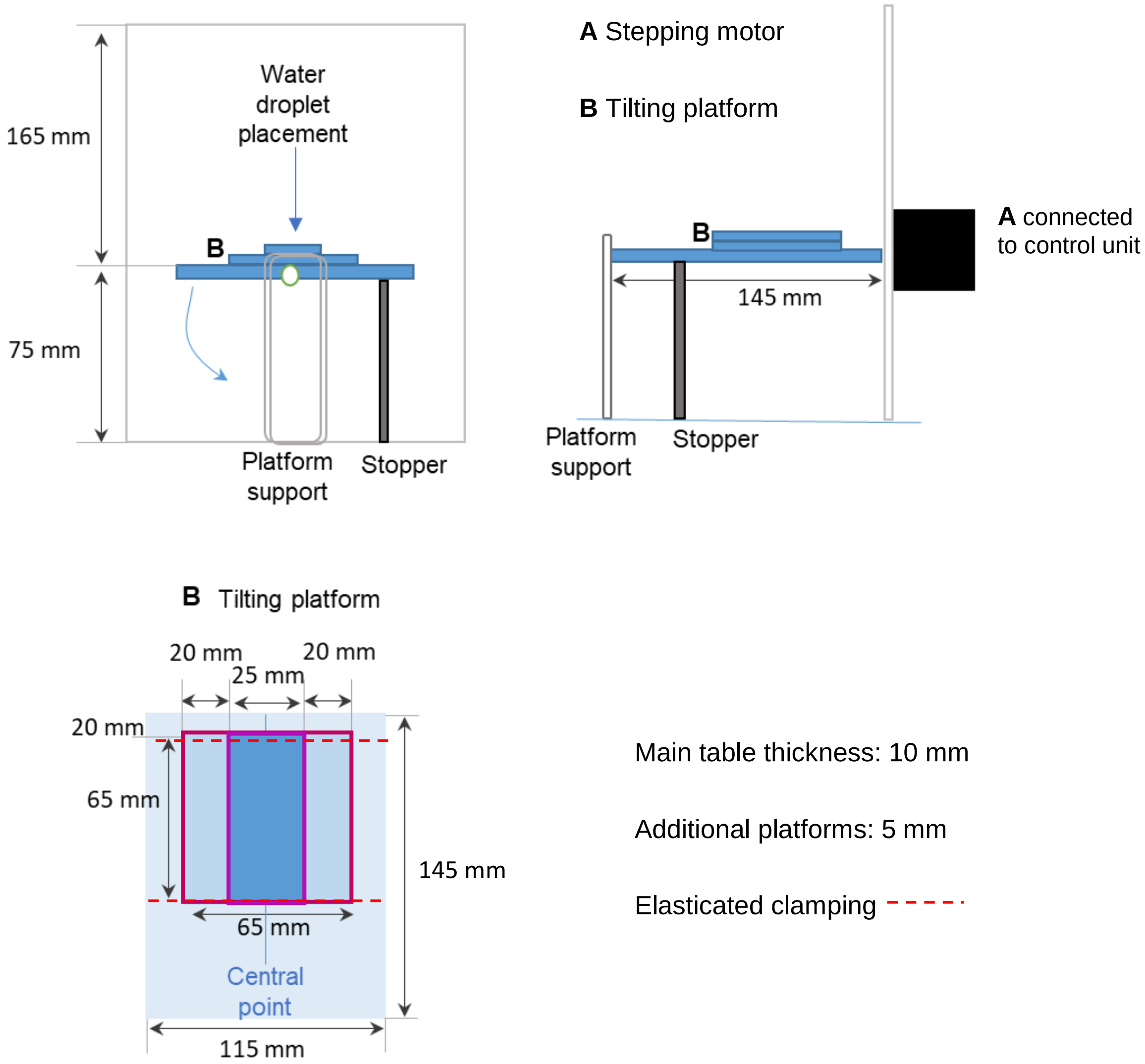
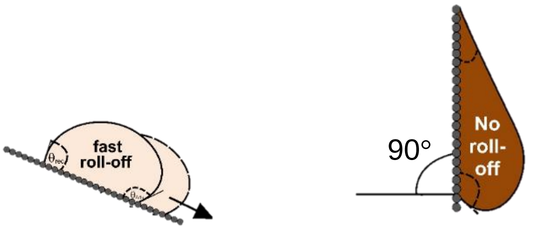


Figure 6.3: Dimensions and set-up of tilt table.

6.2.2 Results and discussion

Roll off angle data has been plotted alongside Δ*m* from section 5.3.1 for evaluation of sample wettability and DWR type simultaneously. During testing, water droplets were seen to either roll along or away from the fabric surface and its initial placement, or seen to stick to the fabric surface, at times wetting the surface (Scenario 1; Figure 6.4).

A water droplet as *Scenario 2* demonstrated no movement when the tilt platform was vertical (90°) and therefore an angle of >90° was noted (Figure 6.4).



Scenario 1 Scenario 2

Figure 6.4: Different scenarios observed between the water droplet and fabric surface during roll off analysis, adapted from [291].

Initial evaluation of the samples indicated a low roll off angle for long SFP (C8) DWR sample *A* (22°) (Figure 6.5). All other samples demonstrated a similar roll off angle (37-46°) apart from sample *P* which demonstrated the highest roll off angle (75°), with greatest standard deviation between repeat measurements. This is in line with the wettability of this sample demonstrated by the Δ*m* (0.33 g), which was the greatest from samples tested (Figure 6.5).

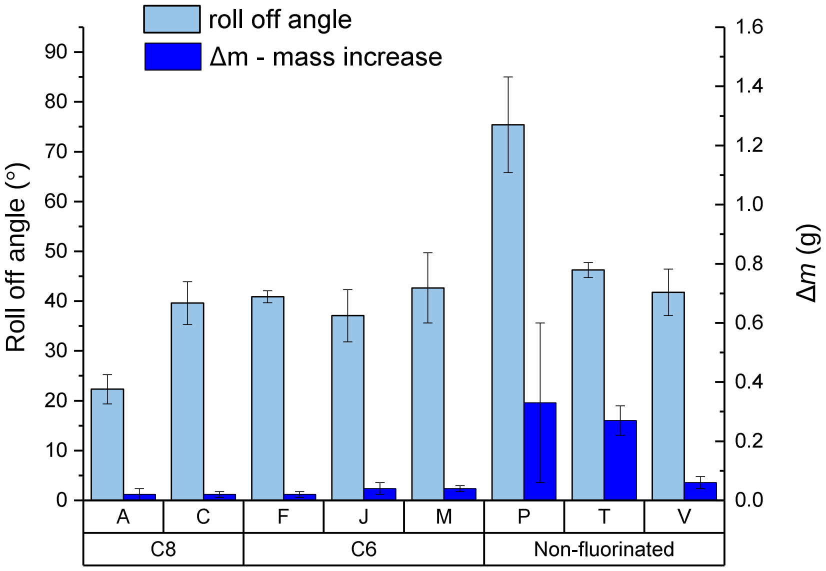


Figure 6.5: Initial Δ*m* and roll-off angle. Samples categorised by sample id and DWR type. Error bars show standard deviation.

6.2.2.1 Effect of washing on roll off angle

After one wash cycle, the roll off angle measured on all samples increased in line with the observed increase of wettability on all samples indicated by Δ*m* (Figure 6.6). Samples *F-IR, P* and *T-AD* demonstrated a roll off angle >90° (Scenario 2; Figure 6.4).

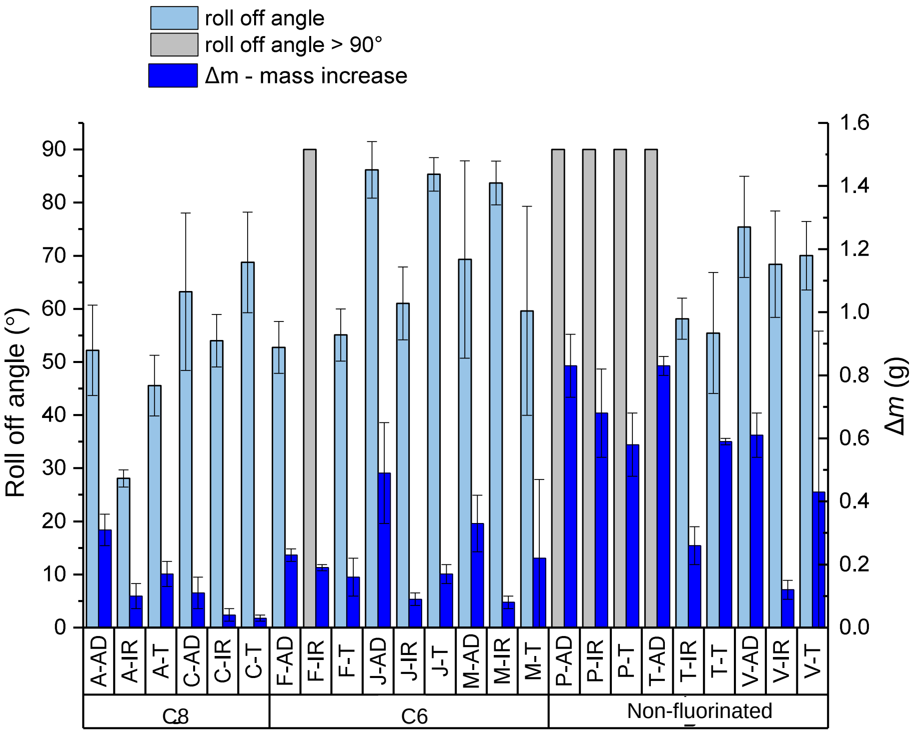


Figure 6.6: One wash cycle: Δ*m* and roll off angle. For sample codes see Table 5.1. Error bars show standard deviation.

After one wash cycle, samples *A-IR* and *C-IR* demonstrated the lowest roll off angle (28° and 54° respectively) compared the air drying or ironing of the same sample (Figure 6.6). This was also demonstrated by the lower Δ*m* for both samples *A-IR* and *C-IR.*

Shorter SFP (C6) DWR samples *F, J* and *M* demonstrated high roll off angles and a trend between air drying (*AD*), tumble drying (*T*) and ironing (*IR*) was not clear (Figure 6.6). The roll off angles of *F-IR*, *J-AD, J-T* and *M-IR* were highest indicating greater wettability. This is in line with the Δ*m* calculation for sample *J-AD* but ironing and tumble drying overall demonstrated low Δ*m* calculations for samples *F, J* and M.

Non-fluorinated sample *P* demonstrated a roll off angle >90° regardless of heat application (scenario 2). The roll off angles determined for samples *T* and *V* were within a range of 55 - >90° range, similar to those determined for shorter SFP (C6) DWR samples, range 53 - >90° (Figure 6.6). Air dried samples *T* and *V* demonstrated the greatest roll off angle compared to other heat applications.

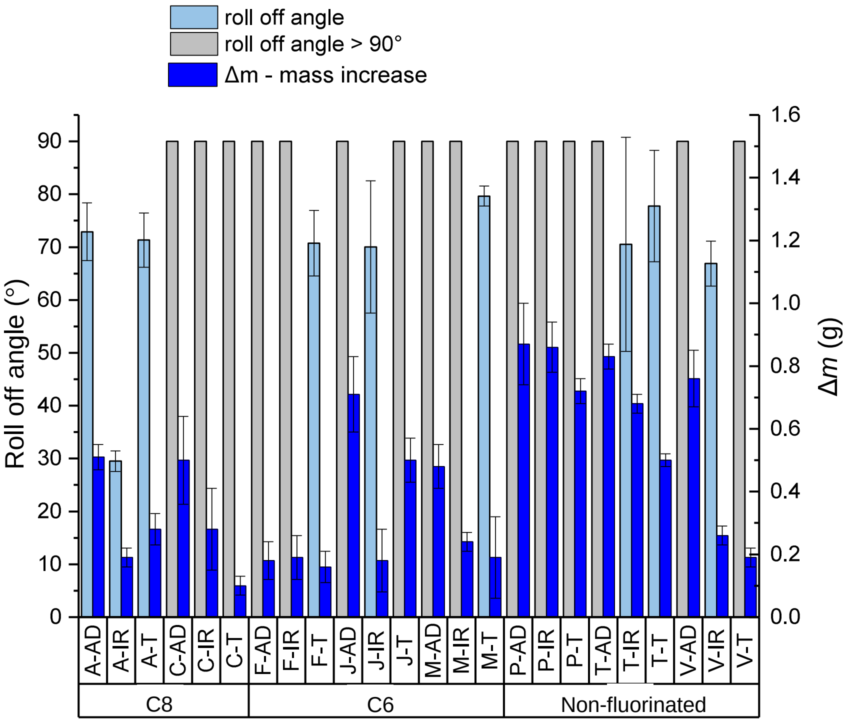


Figure 6.7: Three wash cycles: Δ*m* and roll off angle. For sample codes see Table 5.1. Error bars show standard deviation.

After three wash cycles, sample *C* and *P* demonstrated a roll off angle >90° (Scenario 2) regardless of heat application. Long SFP (C8) DWR sample *A-IR* demonstrated the lowest roll off angle (30°) in line with the low Δ*m* (Figure 6.7). Samples *A-AD* and *A-T* demonstrated similar roll off angles, 73° and 71° respectively, but differed in Δ*m*, 0.51 g and 0.28 g respectively.

All shorter SFP (C6) DWR samples apart from *F-T, J-IR* and *M-T* demonstrated a roll off angle >90° indicating increased wettability following washing (Figure 6.7). Non-fluorinated sample *P* demonstrated a roll off angle >90° (scenario 2), which did not differ to the roll off angle determined after one wash cycle. The lower roll off angles of samples *T-IR* and *V-IR* (71° and 70° respectively) suggests that ironing sustains water repellency. However, this differs to the Δ*m* determined which indicated tumble drying had the lowest wettability.

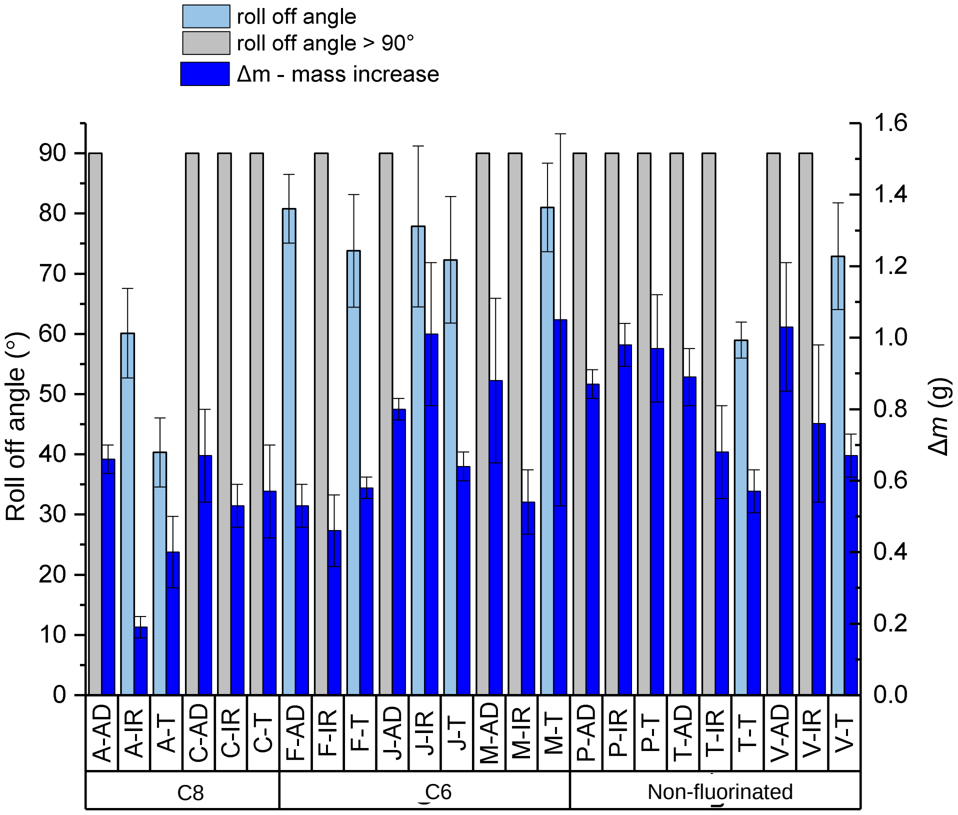


Figure 6.8: Five wash cycles: Δ*m* and roll off angle. For sample codes see Table 5.1. Error bars show standard deviation.

After five wash cycles, most samples demonstrated a roll off angle >90° (Figure 6.8). Long SFP (C8) DWR sample *A* when ironed (*A-IR*) and tumble dried (*A-T*) demonstrated the lowest wettability, indicated by Δ*m*, 0.19 g and 0.40 g respectively, and corresponding low roll off angles, 60° and 40° respectively.

A trend between the roll off angle and Δ*m* calculations for shorter SFP (C6) DWR samples could not be determined. A lower roll off angle was determined when samples *F* and *T* were tumble dried compared to air drying or ironing. However, both *F-T* and *T-T* also demonstrated the greatest Δ*m* than other heat applications.

The roll off angle after five wash cycles was lower for samples *F-AD, J-T* and *V-T* than after three wash cycles when the roll off angle was >90° (Figure 6.7; Figure 6.8). For shorter SFP (C6) DWR sample *F*-AD, this could be attributed to the reordering of the polymer chain differing during air drying (section 5.3.1.2). For non-fluorinated samples *J-T* and *V-T* this can similarly be attributed to the reordering of the polymer structure or due to inhomogeneous distribution of heat during tumble drying.

After ten wash cycles, regardless of heat application long SFP (C8) DWR fabric sample *C* demonstrated a roll off angle >90° (Scenario 2; Figure 6.9). Despite sample *A-IR* demonstrating the lowest Δm, sample *A-T* demonstrated the lowest roll off angle (43°) of all DWR fabrics tested. Air drying this sample (*A-AD*) demonstrated the greatest Δm (0.78 g) and roll off angle (64°). This increased wettability following washing and air drying has previously been discussed within section 5.3.1.2 and this roll off data further supports this understanding.

After ten wash cycles, tumble drying shorter SFP (C6) DWR samples demonstrated the lowest roll off angles from this DWR group, apart from sample *J*. This could be attributed to the application of heat by tumble drying allowing reorientation of the polymer structure.

After ten wash cycles, only non-fluorinated sample *T-T* demonstrated a roll off angle <90° (Figure 6.9). The high roll off angle demonstrated by all non-fluorinated samples shows that the water repellency provided by non-fluorinated DWRs is less durable to washing than fluorinated DWRs.

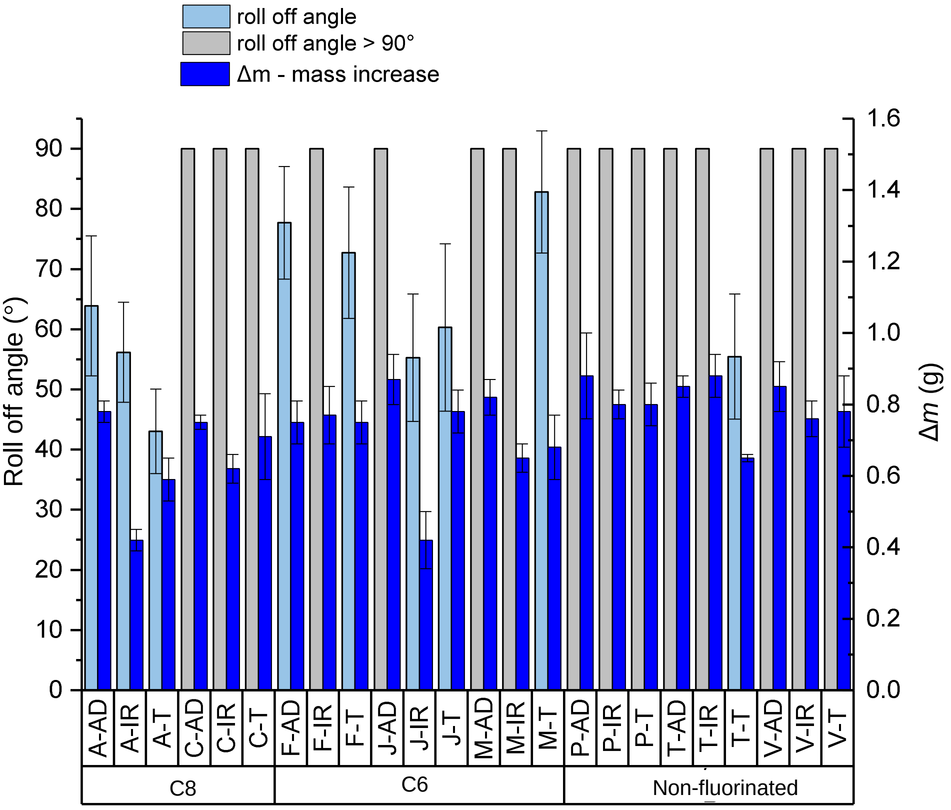


Figure 6.9: Ten wash cycles: Δ*m* and roll off angle. For sample codes see Table 5.1. Error bars show standard deviation.

6.2.2.2 Correlation between roll off angle and Δ*m*

To determine if there is a linear relationship between evaluation of wettability by roll off angle and by the spray test (Δ*m*), correlation was evaluated using Pearson correlation coefficient (*r*) (Table 6.2), which was used to determine whether a linear relationship was obtained. Due to the number of samples demonstrating a roll off angle >90°, these outliers within the data were excluded to omit heavily weighting the data. Therefore the size of each dataset (*n*) evaluated has been given. Weighted and unweighted fits to the experimental data were calculated (A.8).

Table 6.2: Pearson correlation coefficient between evaluation of wettability by roll off angle and by the spray test at each wash stage.

Wash cycle no.	***n***	**Pearson correlation coefficient (*r*)**	
		Unweighted	**Weighted**
Initial	8	0.81	0.90
One	19	0.41	0.73
Three	9	0.25	0.07
Five	9	0.64	0.79
Ten	9	0.51	0.53

There was positive correlation between the roll off angle data and Δ*m*, spray test, at all wash stages. Strongest positive correlation between the two datasets was seen before any washing from testing the samples initially (r = 0.81 unweighted; r = 0.90 weighted). At all other wash stages, the correlation was smaller and therefore a linear relationship between the two datasets could not be determined. From this, it is recommended the two test methods can be used to determine initial wetting properties but comparability following abrasion is not possible. The two test methods should be used independently.

6.2.3 Summary

This section has evaluated roll off angle as a test method to determine the dynamic wetting properties and differences in water repellency between DWR types. Following the development of the test apparatus, roll off angle measurements have been plotted against wettability measurements calculated by Δ*m* using the spray test.

Determination of wettability by roll off angle evaluates the interaction between the water droplet and surface on a micro scale and therefore suits evaluation of samples during development of DWRs. The dynamic nature of determining the angle at which the water droplet moves away from the fabric surface relates to the end use of clothing where rain droplets will make contact with the fabric at various angles. However, determining the wettability over a greater fabric surface area and with a greater number of water droplets, replicating rain, is more closely related to end use of repellent clothing.

The test apparatus and method developed advances upon work completed by Stevens [37] where positive correlation was seen between roll off angle measurements and data from other test methods. Within this work, a strong positive correlation was initially seen but this decreased with an increasing number of washes (Table 6.2). Therefore in determination of the longevity of water repellency, it is recommended that both test methods are interpreted with caution and more than one test method should be used to evaluate water repellency of DWR types and fabrics.

6.3 Textile testing simulating rain showers

6.3.1 Bundesmann rain tester

Increased demand for liquid repellency testing to determine the functionality of non-fluorinated alternative DWRs has led to increased interest in the Bundesmann rain tester as an alternative ISO testing standard. With a rain shower of 10 minutes, there is potential to utilise this test method as an improvement on the short ‘rain’ shower of the spray test, limitation (3).

A comparative study between the Bundesmann rain-shower tester and the spray test was carried out to determine the relationship between the two tests in determining water repellency.

6.3.1.1 Materials

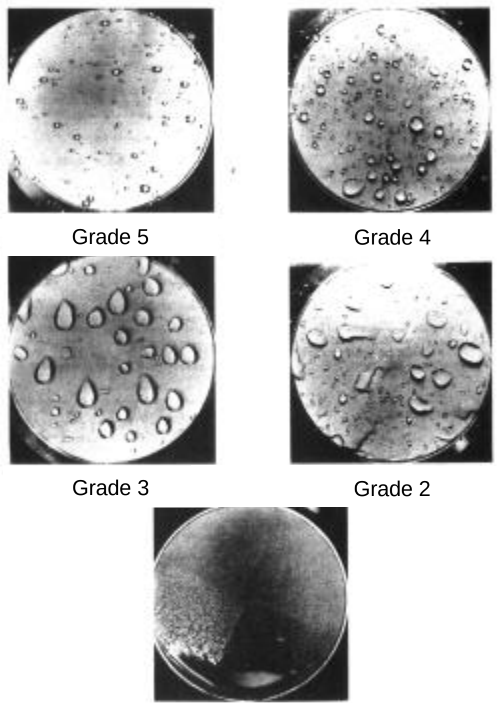
Fabrics selected for this study were long SFP (C8) DWR sample *C*, shorter SFP (C6) DWR samples *J* and *M*, and non-fluorinated DWR samples *T* and *V*. Samples *C, M* and *V* were chosen due to having the same fibre type and fabric construction with only the DWR differing. Samples *J* and *T* were chosen because they had the same fibre type with similarities between their structure and due to their availability to the project. Specimen size for testing was circular with diameter 140 mm.

6.3.1.2 Method

The Bundesmann rain shower tester (BS EN 29865:1993/ISO 9865:1991) is an artificial rain shower subjecting rotating test specimens to a ten minute water shower [84]. The shower head consists of 300 nozzles over a circular area (Figure 6.10) with a drop height of 1500 mm. Conditioned test samples are weighed and mounted on to separate cups with rotating wipers underneath which move against the underside of the fabric during testing (Figure 6.10).

Figure 6.10: The Bundesmann rain shower tester testing equipment with fabric sample holders with wiper attachments.

After the ten minute test, samples are centrifuged for 15 seconds, reweighed and assessed alongside the photographic rating scale (Figure 6.11). The volume of water collected in each sample cup, which had penetrated through the fabric, is weighed to determine the volume (mL).



Grade 5 Grade 4

Grade 3 Grade 2

Grade 1

Grade 5: Fast runoff of small drops

Grade 4: Formation of large drops

Grade 3: Drops adhere to parts of the specimen

Grade 2: Specimen partly wetted

Grade 1: Specimen wet through over complete surface

Figure 6.11: The photographic scale included within BS EN 29865 for the assessment of samples with corresponding rating descriptions.

Bundesmann testing was carried out by Intertek UK. The surface wetting was evaluated against the photographic rating scale, the volume of water penetrating through the sample was measured and the % water absorption calculated, expressed as a percentage mass increase from initial (m_1) to test (m_2) samples according to equation 6.1:

$$\text{Water absorption, } A \ (\%) = \frac{m2-m1}{m1} \text{ x } 100 \qquad (6.1)$$

6.3.2 Results and discussion

Data from the Bundesmann was received from Intertek UK (A.9). Sample error between repeat testing was not included in the test report. Samples *C*, *M* and *V* were rated as grade 4, sample *T* was rated as grade 5 and sample *J* was rated as grade 2. There was no water penetration through the tested samples.

Of the samples tested, shorter SFP (C6) DWR sample *M* demonstrated the greatest *A* (Figure 6.12). The long SFP (C8) DWR samples had the lowest *A*, as expected (sample *C* 25.43%). Non fluorinated DWR samples *T* and *V* demonstrated high *A*, 31.87% and 34.68% respectively.

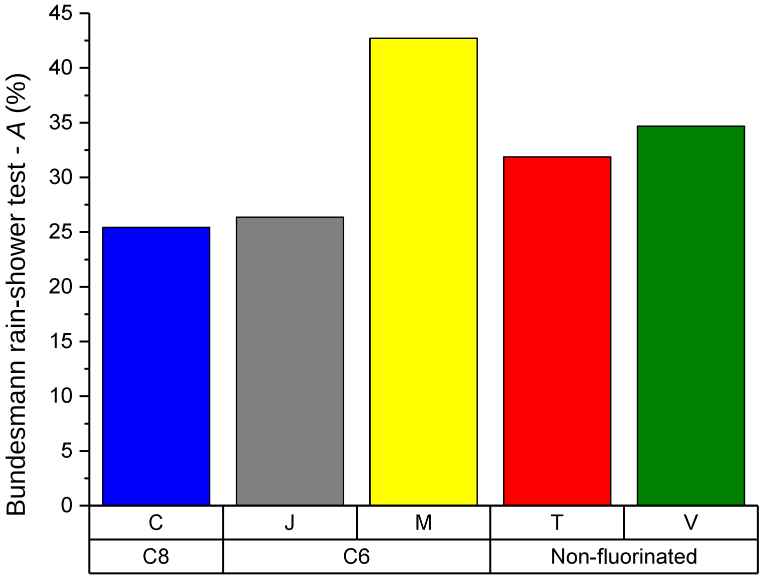


Figure 6.12: Bundesmann rain-shower test average *A*. Samples categorised by sample id and DWR type.

Water absorption, *A*, calculated from Bundesmann testing was plotted against water adherence, m_{A}, from the spray test of the same samples. The *A* during the Bundesmann test was greater than m_A measured during the spray test due to the extended length of the rain shower and larger shower head. Long SFP (C8) DWR sample *C* demonstrated the lowest *A and* m_A on both the spray test and Bundesmann test (Figure 6.13). The non-fluorinated DWR samples *T* and *V* as well as shorter SFP (C6) DWR sample *M* demonstrated similar m_A by the spray test but sample *M* demonstrated a greater *A* on the Bundesmann test. Sample *J* demonstrated a low *A* by the Bundesmann test but the greatest m_A by the spray test. There was no correlation between the two datasets from the two tests. The repellency of the samples differed between the data interpretation of the two test methods.

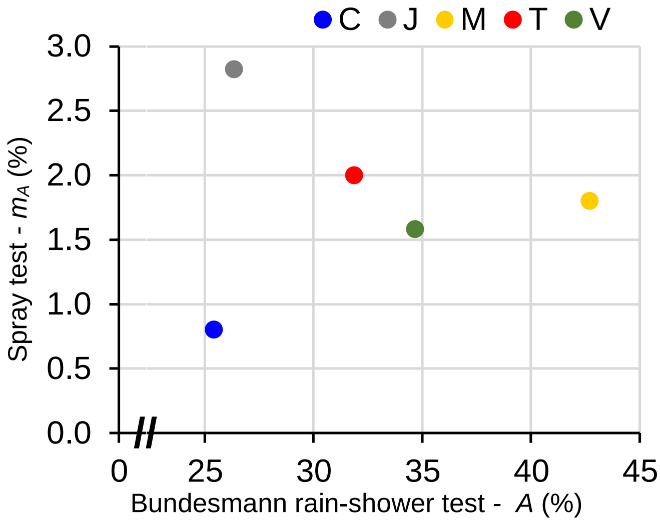


Figure 6.13: Correlation between average m_A calculated on the spray test and average *A* calculated on the Bundesmann test.

6.3.3 Summary

Using the Bundesmann test in addition to the spray test did not clearly distinguish the liquid repellency performance of the samples tested. The liquid repellency of both non-fluorinated DWR samples and fluorinated DWR samples differed between the two datasets from the two test methods. Whilst the Bundesmann rain-shower tester is increasingly being used by outdoor apparel brands to discriminate between non-fluorinated DWRs, the data collected here does not show the tests to be comparable.

6.3.4 Extended spray test

A limitation of the spray test is the ‘rain’ shower of 25-30 seconds which is exceptionally short compared to rainfall within the end-use environment and other laboratory test methods for water repellency (Table 6.1). Testing liquid repellency over a longer time period replicates conditions experienced during end-use where shelter cannot be immediately sought. The Bundesmann rain-shower tester (6.3.1) simulates a rain shower of ten minutes and therefore an alteration to the existing spray test was carried out to prolong the rain shower and to establish if repellent functionality differed under these longer test time periods.

6.3.4.1 Materials

Fabrics selected for this study were long SFP (C8) DWR sample *C*, shorter SFP (C6) DWR samples *J* and *M*, and non-fluorinated DWR samples *T* and *V*. Samples *C, M* and *V* were the same fibre type and fabric construction with only the DWR differing.

Specimen size was 165 x 165 mm (27225 mm^2 in area).

6.3.4.2 Method

Test set-up: To extend the standard testing period of the spray test (25-30 seconds), a continuous system was devised in which the water flows consistently through the funnel and nozzle on to the fabric. The rain shower was devised to be at the same flow rate (500mL/min) of the testing standard (Table 6.1).

In addition to the existing spray test equipment, a water pump (Blagdon 550 model with max flow rate 550 litres/hour) was used to circulate the water in a closed loop system (Figure 6.14). To establish the correct flow rate, a holding container (2L volume, 140 mm h x 142 mm w x 138 mm d) held water above the testing funnel (Figure 6.14; A) supported on a 3mm Perspex support platform. An overflow pipe and drum tap (with opening diameter 15 mm) were inserted into the holding container to adjust flow to the funnel. Hosepipe (with diameter 10 mm) was used to connect the water pump to the holding container using a hosepipe connector. As within the testing standard, water flowed from the funnel through the nozzle on to the fabric (Figure 6.14; B). Run-off water was collected in a reservoir (Figure 6.14; C) and was circulated back through the system.

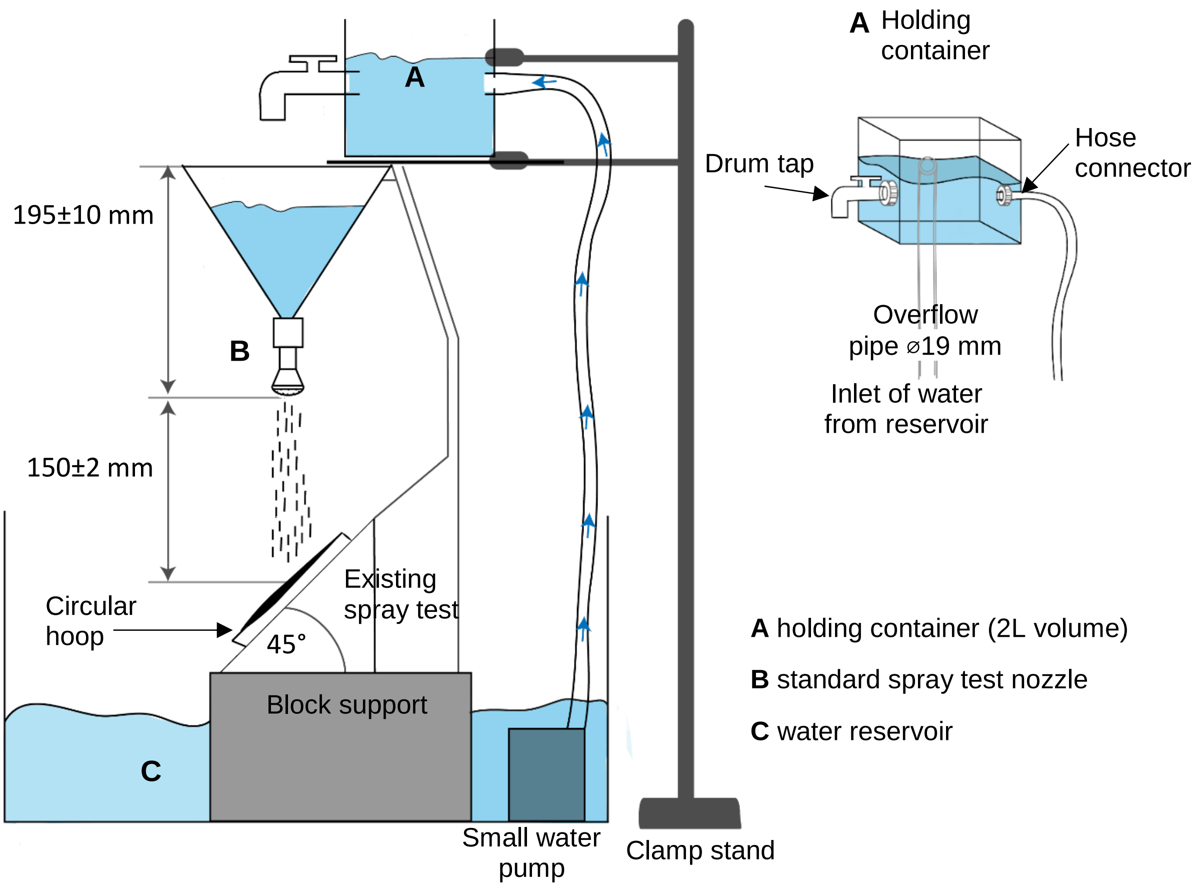


Figure 6.14: Setup of extended spray test with further details of the holding container.

A separate specimen was used for each test; three specimens were tested from each fabric sample. Distilled water was used in all experiments. Prior to each test, the flow rate was checked as an average of ten water volume measurements. For each test, the conditioned test sample was mounted on to the circular hoop and placed on to the support. Separate tests were run for each specimen at four time durations: standard test, 10 minutes (in line with the duration of the Bundesmann test), 60 minutes and 120 minutes.

At the end of the testing period, the sample was tapped twice as stated in the testing standard and subjectively assessed in line with the rating scale used throughout this work (section 4.2.3.2). The mode of the spray rating was assigned. In addition, the mass increase, Δm, was calculated in line with testing throughout this work (section 4.2.3.4).

6.3.5 Results and discussion

The spray rating assigned to the fabric samples decreased with test time**.** Long SFP (C8) DWR sample *C* showed a good level of water resistance after all extended tests and was rated at 85 after the 120 minute shower (Figure 6.15). Both shorter SFP (C6) DWR samples *J* and *M* demonstrated a decrease in water repellency after an extended ten minute test. However both samples were assigned a spray rating of 80 after the 60 minute extended shower and the 120 minute extended shower. Non-fluorinated DWR sample *V* demonstrated prolonged water repellency over the extended tests (assigned a spray rating of 80 after 120 minutes) compared to the other non-fluorinated DWR sample *T* (assigned a spray rating of 75 after 120 minutes) (Figure 6.15).

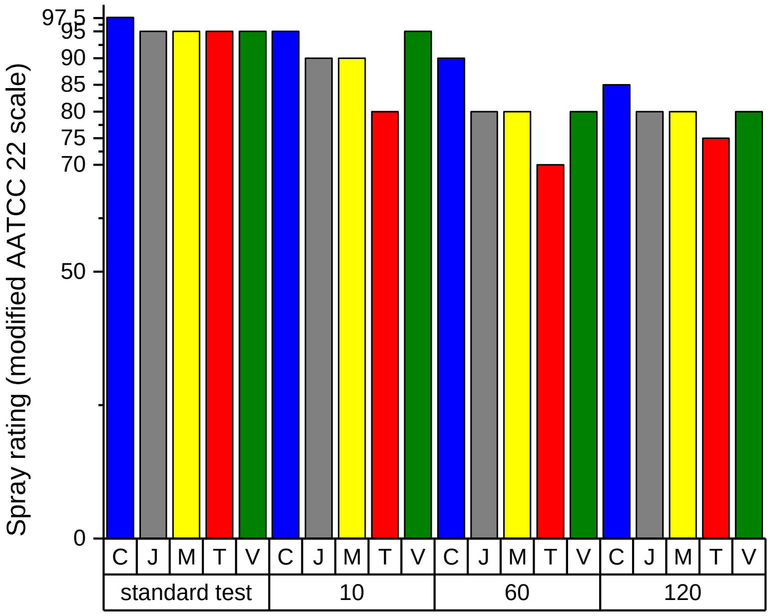


Figure 6.15: Spray test rating of samples at each extended spray test. Fabric samples categorised by sample ID and extended spray test duration (minutes).

The Δ*m*, and therefore water uptake, increased over the extended spray test durations (Figure 6.16**).** Sample *T* exhibited the greatest Δ*m* after the extended ten minute spray test (0.65 g). This demonstrates a decrease in water repellency and this continued over subsequent extended spray testing.

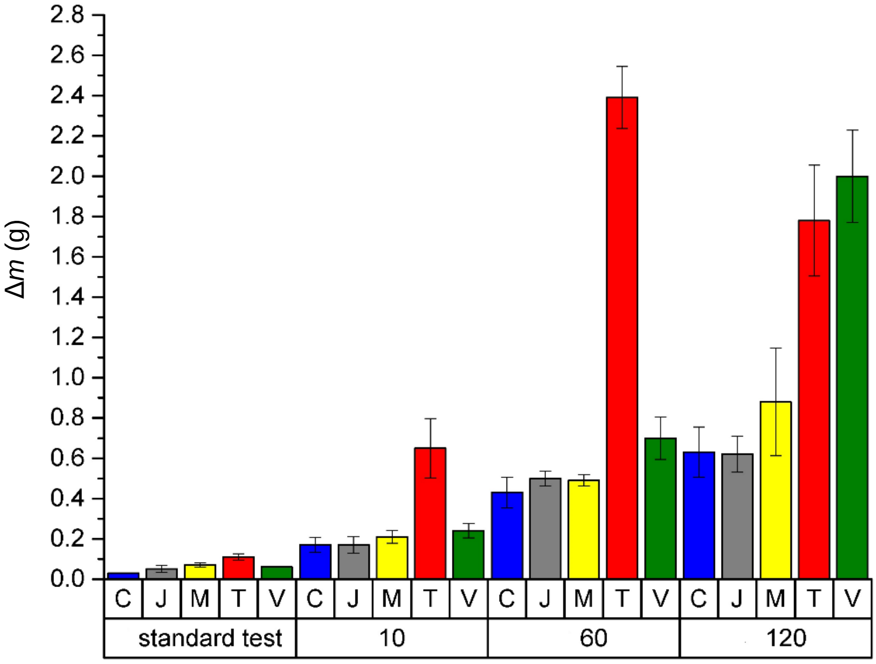


Figure 6.16: Δ*m* over the extended spray tests. Fabric samples categorised by sample ID and extended spray test duration (minutes). Error bars show standard deviation.

The Δ*m* over the extended spray test durations were as expected for samples *C*, *M* and *V* with sample *C* (long SFP (C8) DWR) demonstrating a consistent lower Δ*m*, and therefore greater level of water repellency, compared to the shorter SFP (C6) DWR sample *M* and the non-fluorinated DWR sample *V.*

After an extended spray shower of 60 minutes, long SFP (C8) DWR sample *C* demonstrated the greatest water repellency with lowest Δ*m* (0.43 g). However, after 120 minutes the Δ*m* of sample *C* and shorter SFP (C6) DWR sample *J* were similar (0.63 g and 0.62 g respectively).

After 120 minutes, both non-fluorinated DWR samples tested demonstrated a high Δm and therefore water uptake (sample *T* 1.71 g; sample *V* 2.00 g). This decrease in water repellency is in line with the lower spray rating grades assigned to both samples after 120 minutes. Both samples also demonstrated a greater variation, shown by the error bars of standard deviation, between repeat testing, after the 120 minute shower compared to fluorinated DWR samples.

Data from the standard spray test (spray duration 25-30 seconds) shows a similarly low Δm and therefore good water repellency between the non-fluorinated DWR samples and fluorinated DWR samples. However, the extended spray durations allow a greater discrimination between these initially similarly performing samples. After a spray shower of 120 minutes, there are clear differences between fluorinated and non-fluorinated samples. Fluorinated DWR samples (*C*, *J* and *M*) demonstrated a $\Delta m <$ 0.88 g whilst the Δm for non-fluorinated samples (*T* and *V*) was between 1.7-2.0 g.

Testing at the extended ten minute test period allowed a direct comparison with the Bundesmann rain-shower test of ten minute duration. Water adherence as a percentage mass increase, m_A, (section 4.2.3.3) was calculated in line with the water absorption, *A,* from Bundesmann test data (supplied by Intertek). There was a greater m_A during the extended ten minute spray test (Figure 6.17). The correlation between the ten minute spray test and the Bundesmann test was similar to that using the initial spray test data (Figure 6.13).

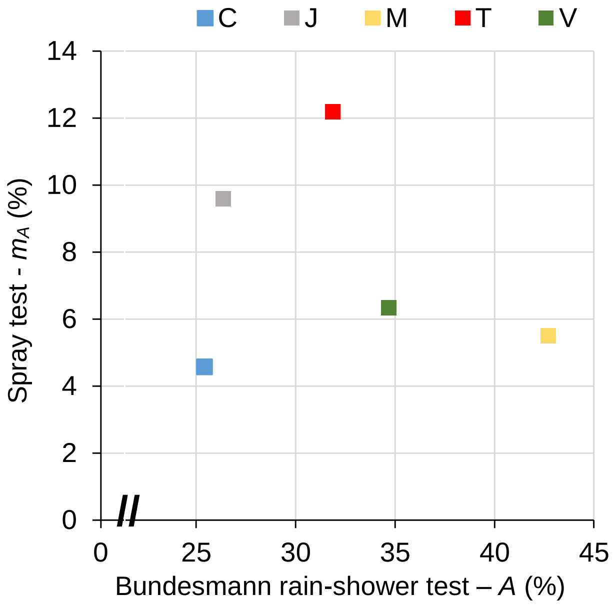


Figure 6.17: Correlation between average m_A calculated on the extended ten minute shower spray test and average *A* calculated on the Bundesmann test.

The water repellency differed between the two datasets of the two test methods and no correlation was determined. Non-fluorinated DWR sample *V* demonstrated a high *A* (34.7%) by the Bundesmann test but a lower m_A by the extended spray test (6.3%) than samples *T* (12.2%) and *J* (9.6%). Similarly sample *M* demonstrated a high *A* by the Bundesmann test (42.7%) but the second lowest m_A by the extended spray test (5.5%).

A one-way analysis of variance (ANOVA) was conducted to determine if there was a statistical difference between the different DWR types at each extended spray test duration and therefore used to recommend the most suitable spray shower duration to discriminate between the DWR types (A.10). The wettability, indicated by Δm, of samples *C*, *M* and *V* were directly compared (sample fabric type and construction).

After the standard spray test, a statistically significant difference was indicated by post-hoc tests (Tukey HSD) between the long SFP (C8) DWR (sample *C*) and the shorter SFP (C6) DWR (sample *M*) ($p<0.05$) but not between these two DWR types and the non-fluorinated DWR (sample *V*) where p=0.165 (A.10). No statistically significant difference was indicated between the DWR types after the extended spray test of ten minutes (A.10). Therefore this shower duration is not recommended for discrimination between the DWR types.

In both the extended spray shower tests of 60 minutes and 120 minutes a statistically significant difference was indicated between both the long SFP (C8) DWR (sample *C*) and the shorter SFP (C6) DWR (sample *M*) with the non-fluorinated DWR (sample *V*) ($p<0.05$) (A.10). After both extended shower durations, a statistically significant difference was not indicated between the two fluorinated DWR types (sample *C* and sample *M*).

6.4 Conclusions

Differences between similarly performing samples, evaluated by the standard spray test, can be seen after the extended spray test allowing discrimination between DWR types which initially demonstrated comparable wettability. After an extended spray test of 60 minutes and after 120 minutes, differences in wettability were clearly seen between the samples tested and the fluorinated and non-fluorinated DWR types. Following statistical testing, it is recommended that the spray test shower duration is extended to both 60 minutes and 120 minutes to allow differentiation between fluorinated and non-fluorinated DWRs.

Developing upon the comparison between the Bundesmann rain-shower tester and the standard spray test in section 6.3.2, within this section the extended spray test of a 10 minute shower duration was compared to the Bundesmann rain-shower tester. Therefore, in both tests, the samples were subjected to a ten minute shower. However, as seen in the comparison between the standard tests and durations (section 6.3.2), the datasets did not correlate and showed different interpretations of the sample wettability.

6.4.1 Recommendations

This chapter has considered approaches to overcome the limitations highlighted throughout this research with the determination of water repellency by the spray test. Determination of the roll off angle evaluated dynamic wetting properties, overcoming the issue with static contact angle evaluation on textile fabrics. Whilst it is recommended for use during fabric development, it is not a replacement to textile tests which simulate rain showers. Correlation was positive but not significant.

There has been an increased interest in using the Bundesmann rain-shower tester to determine water repellency, in light of non-fluorinated DWR use. However, a correlation was not determined between the spray test data and Bundesmann data.

Adaptations have been made to the spray test which is widely available and used. It is recommended that the spray test is adapted with the adaptations described in this chapter, which are easily accessible and cost-effective. An extended spray duration of 60 and 120 minutes allows a greater level of differentiation between similarly performing water repellent fabrics and therefore would aid the determination of non-fluorinated DWR functionality compared to fluorinated DWRs.

Chapter 7 - Development of test methodology: simulated abrasion

7.1 Introduction

Durability to abrasion is evaluated on textile materials to determine resilience and stability prior to commercial use. The Martindale test method (BS EN ISO 12947-1998) is commonly used and evaluates the durability of a fabric when rubbed against an abrasive medium in a Lissajous motion [292]. Subjective evaluation of the breakdown of fibres on the specimen surface is carried out at predetermined rub intervals [293]. Within the testing standard the specified abradant is worsted wool [293] however this does not simulate the end-use of outdoor apparel which will be in contact with rucksacks, harnesses and abrasive rock environments. Maintaining liquid repellency during abrasion and use implies that the DWR remains on the surface and that the surface chemistry is not lost to the environment. This potential exposure pathway has been highlighted and could directly affect the consumer [119,162].

One study has considered durability of DWRs to weathering, abrasion and laundering[‡‡‡] [112]. The study by Schellenberger *et al.* found that water repellency degraded on shorter side-chain fluorinated DWR fabrics and on non-fluorinated DWR polyester fabrics following abrasion testing [112]. However, wearers of outdoor repellent apparel are likely to encounter abrasive surfaces such as rock at climbing crags or during scrambling, vegetation such as bracken and grasslands and adjacent abrasion to other textiles such as worn apparel. Data collected from the consumer survey (Chapter 2) has shown that most respondents would wear either a rucksack or

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[‡‡‡] This study has previously been discussed in Chapter 5 in relation to the application of heat during laundering.

a harness and rucksack. This existing study used the standard wool abradant during abrasion testing, up to 3000 rub cycles only, which does not simulate environments encountered during end-use of an outdoor repellent garment [112].

As non-fluorinated repellent chemistries are considered and used in outdoor apparel, it is important to fully establish their functionality and have appropriate test methodology. Within this chapter the durability of fluorinated and non-fluorinated DWRs and the liquid repellent functionality to abrasion was studied, using an adapted Martindale method, addressing objective 6 (section 1.7).

7.2 Experimental

7.2.1 Materials

Fabrics selected to be used were samples *A* and *C,* long SFP (C8) DWRs, samples *F*, *J* and *M*, shorter SFP (C6) DWRs, and samples *P*, *T* and *V*, non-fluorinated DWR samples. Samples *C*, *M* and *V* were the same fibre type and fabric construction with only the DWR differing. Specimen size was 165 x 165 mm (27225 mm^2) and samples were conditioned at 20 ± 2°C, 65 ± 5% relative humidity (RH) for 24 hours prior to testing.

Abradant materials: Three abradants simulating end-use contact with liquid repellent outdoor apparel were chosen (Figure 7.1). Fine sandpaper (grade 400) was used to simulate end-use abrasion to rocky terrain. A knit spacer fabric (with hexagonal polyamide mesh outer layer structure and warp knitted backer) and webbing fabric (plain woven polyamide 9x18/cm), both supplied by Equip Outdoor Technologies, were used to replicate rucksack/harness straps in adjacent contact to clothing.

Figure 7.1: Three abradant materials were chosen: Grade 400 sandpaper; a rucksack spacer fabric and a rucksack webbing material.

7.2.2 Modified method

A James Heal 1305 Midi-Martindale with five stations was used in a controlled testing environment of 20 ± 2°C, 65 ± 5% relative humidity (RH). Testing standard BS EN ISO 12947-1:1998 and BS EN ISO 12947-2:2016 [292,293] were followed with an abrasion load of 795 ± 7 g (nominal pressure of 12kPa).

The following modifications to the testing standard were made:

- The test specimen was mounted on to the bottom specimen holder (Figure 7.2).
- The abradant material (38 mm in diameter) was mounted within the specimen holders (Figure 7.2). This was either sandpaper, spacer fabric or webbing material with foam backing.
- Each specimen was tested against each abradant separately. Three repeat specimens were evaluated for each fabric type and abradant.
- The number of rub cycles and intervals for testing were defined by preliminary work with different sandpaper grades, the spacer fabric and webbing material determining when abrasion was visible on the surface. The testing intervals are discussed in section 7.2.3.
- At the predetermined intervals, liquid repellency was evaluated, with reference to BS EN ISO 12947-3:1998 [294]. The specimens were removed, evaluated and remounted on to the test apparatus.

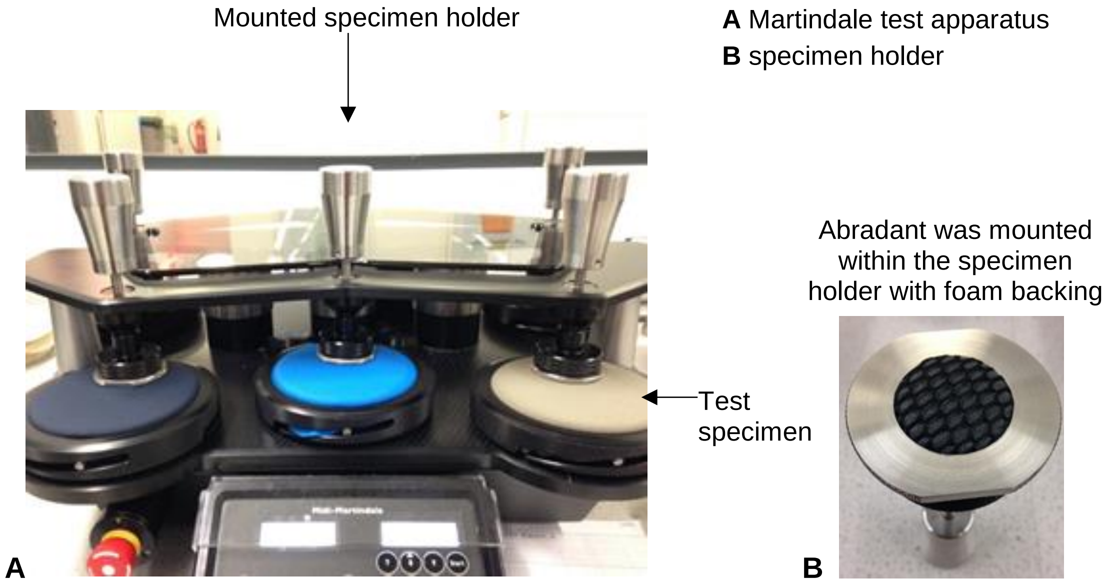


Figure 7.2: Setup of the Martindale test apparatus and specimen holder.

7.2.3 Evaluating repellency

At each test interval, or number of rubs, the water repellency was evaluated, differing from BS EN ISO 12947-2:2016 where each specimen is inspected for breakdown of two separate threads.

With the sandpaper as the abradant, the water repellency of specimens were evaluated at the following rub cycles:

50, 100, 250, 500, 1000, 2000.

Aqueous and oil repellency were evaluated after 100, 500 and 2000 rub cycles.

With the spacer and webbing materials as abradants, specimens were evaluated at the following rub cycles:

1000, 3000, 5000, 7500, 10000, 15000, 20000.

Aqueous and oil repellency were evaluated after 5000, 10000 and 20000 rub cycles.

7.2.3.1 Water repellency

AATCC 22-2014 [18] was followed to determine the resistance of the abraded fabric specimen to surface wetting. A mode spray rating was assigned using the modified rating scale used throughout this work (section 4.2.3.2) and the mass increase, Δm, calculated (section 4.2.3.4).

7.2.3.2 Aqueous and oil repellency

Aqueous liquid repellency was evaluated using BS ISO 23232:2009 [282]. The procedures and grade assignment detailed in section 4.2.3.5 were followed.

Resistance to oil-based liquids were evaluated using BS EN ISO 14419:2010 following the procedure and grade assignment as previously discussed in section 4.2.3.5 [283].

7.2.3.3 Microscope imagery

Images were taken of fabric samples using a Lynx Stereo Dynascope connected to a GXCAM and GXCapture software (magnification x10; set at auto-exposure).

7.3 Results and discussion

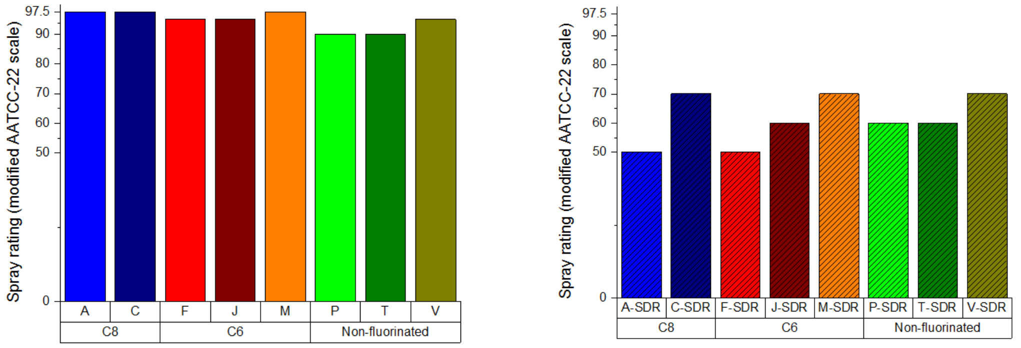
Table 7.1 shows the samples tested against the abradant type. Samples were subjected to 2000 rubs by the sandpaper abradant; 20000 rubs by the spacer fabric as abradant and 20000 rubs by the webbing material as abradant.

Table 7.1: DWR type and sample ID with abradant type. The three abradant materials used were sandpaper (SDR); spacer fabric (SP) and webbing material (WB).

DWR type	**Sample ID**	**Abradant type**
Long SFP (C8) DWR	*A*	*SDR*
		SP
		WB
	C	*SDR*
		SP
		WB
Shorter SFP (C6) DWR	*F*	*SDR*
		SP
		WB
	J	*SDR*
		SP
		WB
	M	*SDR*
		SP
		WB
Non-fluorinated DWR	P	*SDR*
		SP
		WB
	T	*SDR*
		SP
		WB
	V	*SDR*
		SP
		WB

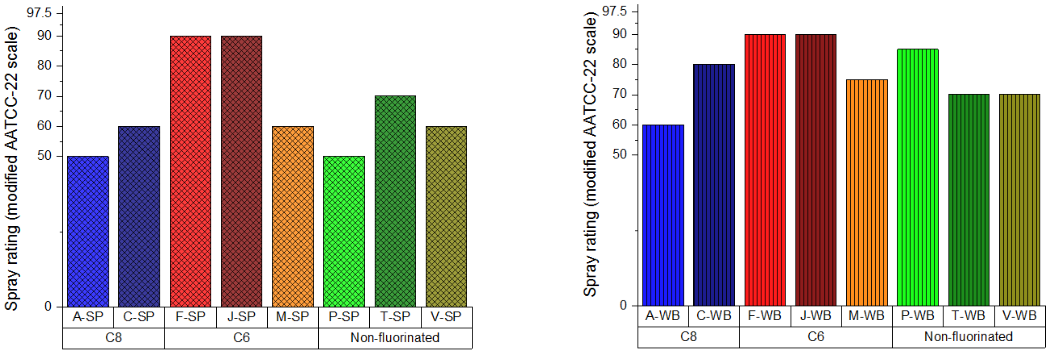
7.3.1.1 Evaluating water repellency

The spray ratings assigned to all fabrics after the maximum number of rubs with sandpaper, spacer fabric and webbing material were lower than the initial rating (Figure 7.3). The spray ratings differed by abradant type. The water repellency of samples abraded by sandpaper decreased substantially after 2000 rubs (Figure 7.3 b) due to the coarse nature of the abradant. Samples F and J were both assigned a spray rating of 90 after 20000 rubs by the spacer fabric and webbing material (Figure 7.3 c; d). This is ascertained to the greater yarn density of these two fabrics and therefore the tighter fabric construction resisting abrasion (A.3). Whilst liquid repellency demonstrated after rubs by the three abradant types cannot be directly compared it can be used to indicate the durability of DWRs during end use.



Initial spray ratings

2000 rubs with sandpaper abradant



20000 rubs with spacer abradant

20000 rubs with webbing abradant

Figure 7.3: Spray ratings of samples initially, after 2000 rubs with sandpaper (SDR), after 20000 rubs with spacer fabric (SP) and after 20000 rubs with webbing material (WB). For sample codes see Table 7.1**.**

Δ*m* was calculated to determine the surface wetting relative to the sample surface area. The wetting properties are indicative of the surface chemistry functionality and change in surface structure influencing liquid repellency.

Abradant: Sandpaper

The wettability of all samples, and the standard deviation between repeat specimen measurements, increased with the number of rubs (Figure 7.4). Changes in wettability were clearly visible after 500 rubs by sandpaper as the abradant. The Δ*m* ranged between 0.02-0.33 g initially to 0.75-1.27 g after 500 rubs.

Comparing samples *C*, *M* and *V* (same fibre type and fabric construction), long SFP (C8) DWR sample *C-SDR* and non-fluorinated DWR sample *V-SDR* demonstrated a similar increase in wettability after 50 rubs (Δ*m* 0.58 g and 0.59 g respectively). After 2000 rubs, all three samples demonstrated a similar increased wettability (sample *C-SDR* Δ*m* 1.75 g; sample *M-SDR* Δ*m* 1.61 g; sample *V-SDR* Δ*m* 1.40 g).

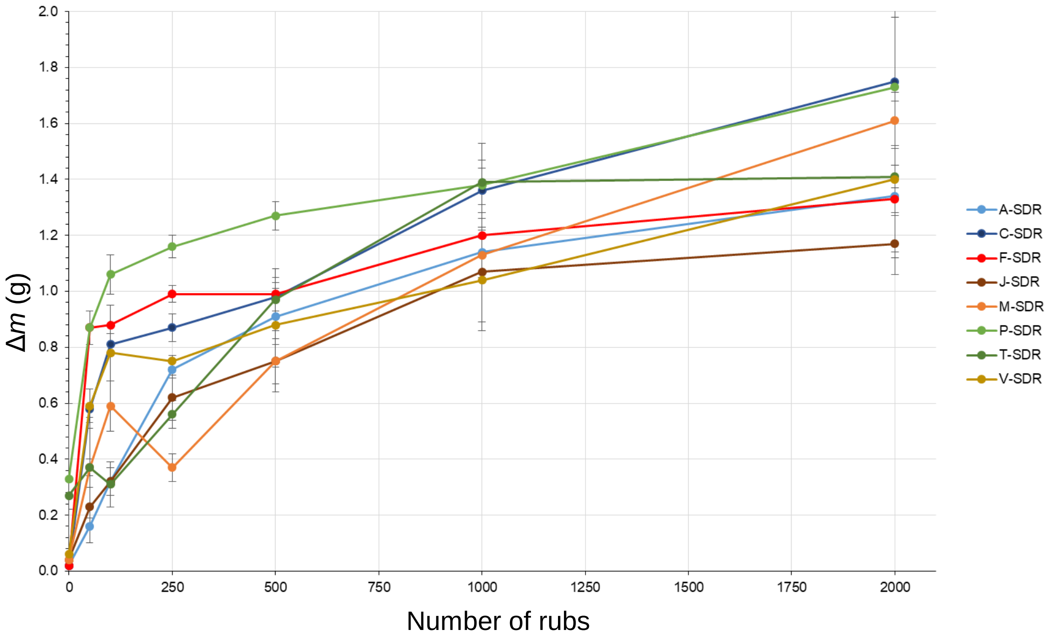


Figure 7.4: Sandpaper abradant: Δ*m* after the spray test at rub number intervals. For sample codes see Table 7.1. Error bars show standard deviation.

Abradant: Spacer fabric

With spacer fabric as the abradant, all samples demonstrated a lower Δ*m* than with sandpaper as the abradant. Samples *F-SP* and *P-SP* demonstrated the greatest increase in wettability throughout abrasion by spacer fabric. This was clearly seen after 1000 rubs: *F-SP* Δ*m* 0.65 g and sample *P-SP* Δ*m* 0.91 g (Figure 7.5)**.** Sample *J-SP* demonstrated the least change in wettability with minimal Δ*m* of 0.04- g at 1000, 3000 and 5000 rubs.

Comparing samples C, M and V (same fibre type and fabric construction), long SFP (C8) DWR sample *C-SP* demonstrated the greatest increase in wettability between 0-10000 rubs with the wettability of samples *M-SP* and *V-SP* increasingly similarly with number of rubs (Figure 7.5). At 10000 rubs, all three samples demonstrated similar wettability (sample *C-SP* Δ*m* 0.59 g; sample *M-SP* Δ*m* 0.56 g; sample *V-SP* Δ*m* 0.56 g). After 20000 rubs, shorter SFP (C6) DWR sample *M-SP* demonstrated a slightly greater wettability (0.99 g) than long SFP (C8) DWR sample *C-SP* (0.82 g) and non-fluorinated DWR sample *V-SP* (0.88 g).

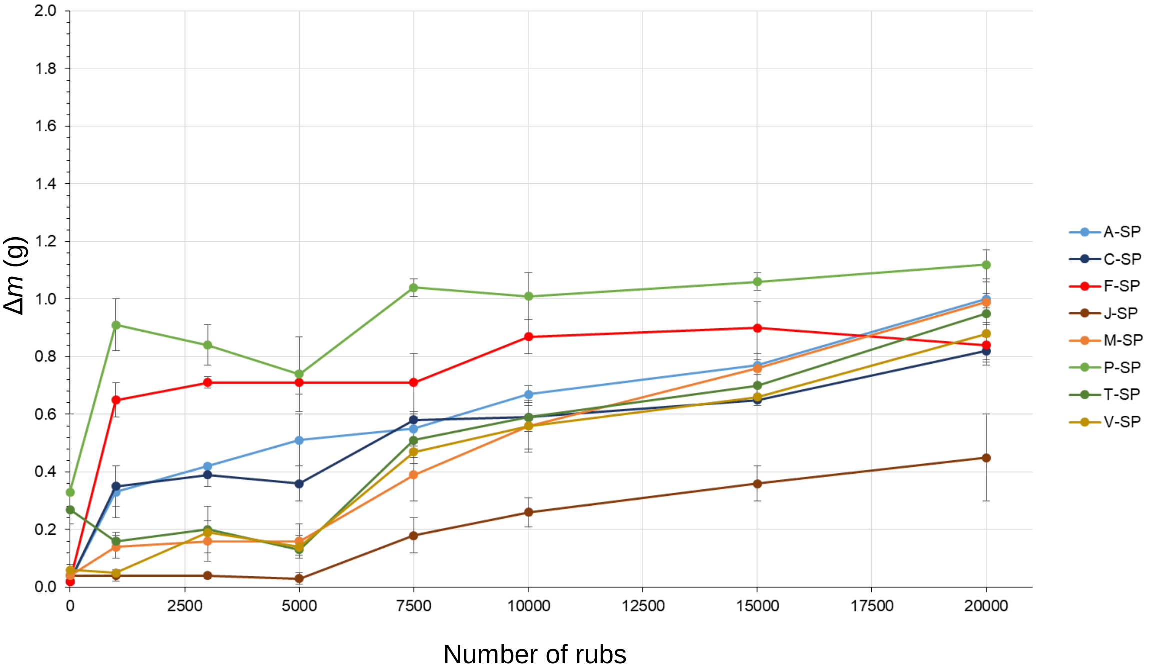


Figure 7.5: Spacer fabric abradant: Δ*m* after the spray test at rub number intervals. For sample codes see Table 7.1. Error bars show standard deviation.

Abradant: Webbing material

Abrasion by webbing material demonstrated the lowest Δ*m* and therefore change in wettability, than by the two other abradants. Δ*m* after 20000 rubs was between 0.33-1.06 g (Figure 7.6). Samples *F-WB* and *P-WB* demonstrated the greatest increase in wettability; after 1000 rubs sample *F-WB* had a Δ*m* of 0.77 g and sample *P-WB* had a Δ*m* of 0.78 g. Throughout, sample *J-WB* demonstrated the least change in wettability.

Comparing samples C, M and V (same fibre type and fabric construction), long SFP (C8) DWR sample *C-WB* demonstrated the greatest Δ*m* between 0-7500 rubs whilst non-fluorinated sample *V-WB* demonstrated the least change in wettability (Figure 7.6). After 10000 rubs, a similar wettability was observed for all three samples (sample *C-WB* Δ*m* 0.27 g; sample *M-WB* Δ*m* 0.21 g; sample *V-WB* Δ*m* 0.25 g). After 20000 rubs, non-fluorinated sample *V-WB* demonstrated an increased wettability (0.67 g) compared to the SFP DWR samples *C-WB* and *M-WB* (Δ*m* 0.53 g and 0.54 g respectively).

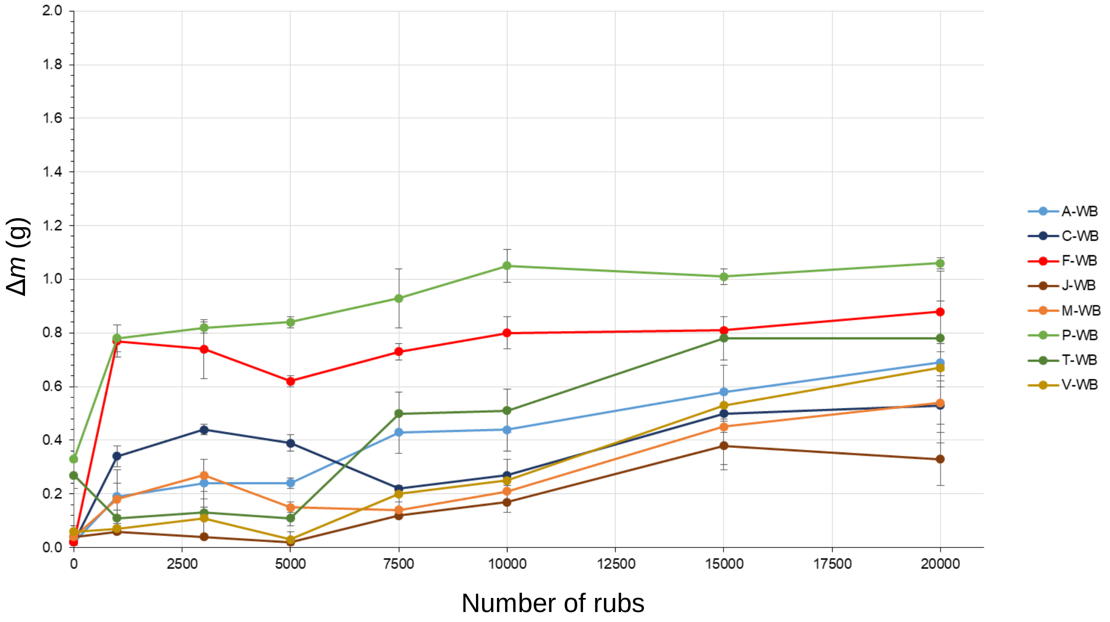


Figure 7.6: Webbing material abradant: Δ*m* after the spray test at rub number intervals. For sample codes see Table 7.1. Error bars show standard deviation.

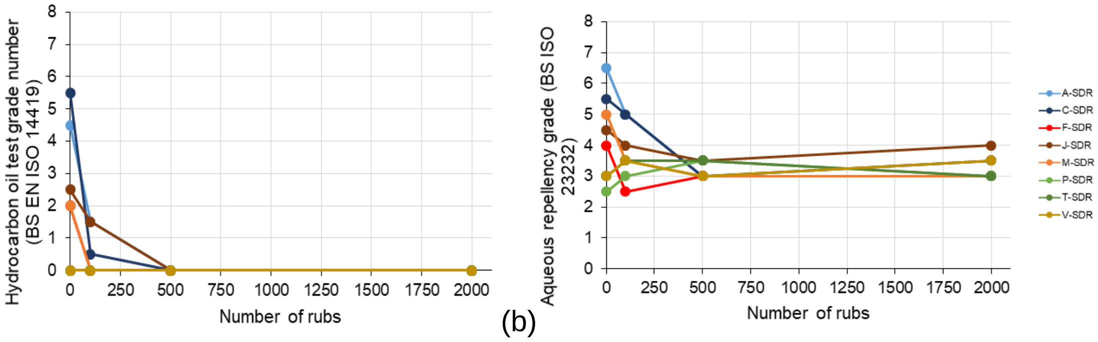
7.3.1.2 Evaluating oil and aqueous repellency

Abradant: Sandpaper

The oil repellency demonstrated initially by fluorinated DWR samples decreased after 50 rubs with sandpaper as the abradant (Figure 7.7). After 500 rubs, oil repellency was no longer demonstrated by these samples. Non-fluorinated DWR samples demonstrated no oil repellency initially and this was not changed with abrasion (Figure 7.7 a).

A decreased repellency to aqueous-based liquids was demonstrated by all fluorinated samples after 100 rubs with sandpaper as the abradant. The aqueous repellency of non-fluorinated samples increased after 100 rubs (Figure 7.7 b) with a surface energy increase of ~4 dyn cm^{-1} for all samples.

After 500 rubs, the greater aqueous repellency initially demonstrated by long SFP (C8) DWR sample *C-SDR* (at 100 rubs grade 5; surface energy ~27.5 dyn cm^{-1}) decreased and was comparable to that of shorter SFP (C6) DWR sample *M-SDR* and non-fluorinated DWR sample *V-SDR* (grade 3; surface energy ~42.0 dyn cm^{-1}).



(a) (b)

Figure 7.7: Sandpaper abradant: (a) resistance to oil-based liquids according to BS EN ISO 14419 over rub number intervals; (b) resistance to aqueous-based liquids according to BS ISO 23232 over rub number intervals. For sample codes see Table 7.1.

Abradant: Spacer fabric

Oil repellency decreased for all fluorinated DWR samples and after 10000 rubs no oil repellency was demonstrated (Figure 7.8 a). Non-fluorinated DWR fabric samples demonstrated no oil repellency initially and abrasion did not change this.

Aqueous repellency demonstrated by fluorinated DWR samples overall decreased with the number of rubs with spacer fabric as the abradant (Figure 7.8 b). The aqueous repellency demonstrated by sample *P-SP* increased after 5000 rubs (grade 3 to 3.5; surface energy decrease ~4 dyn cm^{-1}). The greater aqueous repellency demonstrated by long SFP (C8) DWR sample *C-SP* initially (grade 5.5) decreased to the same aqueous repellency demonstrated by shorter SFP (C6) DWR sample *M-SP* and non-fluorinated DWR sample *V-SP* (grade 3 after 5000 rubs, surface energy ~42 dyn cm^{-1}; grade 2.5 after 20000 rubs, surface energy ~46 dyn cm^{-1}).

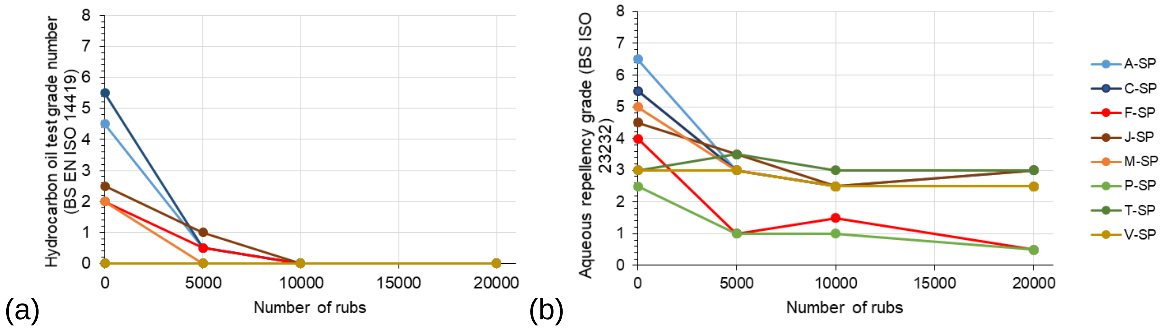


Figure 7.8: Spacer fabric abradant: (a) resistance to oil-based liquids according to BS EN ISO 14419 over rub number intervals; (b) resistance to aqueous-based liquids according to BS ISO 23232 over rub number intervals. For sample codes see Table 7.1.

Abradant: Webbing material

Oil repellency of fluorinated DWR samples decreased with the number of rubs by webbing material as the abradant (Figure 7.9 a). After 10000 rubs all samples demonstrated no oil repellency. Non-fluorinated DWR samples demonstrated no oil repellency initially and abrasion did not influence this.

All samples demonstrated a decrease in aqueous repellency with the number of rubs apart from sample *V-WB* where the aqueous repellency increased after 5000 rubs (grade 3 to grade 3.5; surface energy decrease ~4 dyn cm^{-1}) (Figure 7.9 b). The initial aqueous repellency demonstrated by long SFP (C8) DWR sample *C-WB* decreased after 5000 rubs to the same aqueous repellency demonstrated by shorter SFP (C6) DWR sample *M-WB* and non-fluorinated DWR sample *V-WB* (grade 3.5 after 5000 rubs, surface energy ~37.5 dyn cm^{-1}; grade 2.5 after 20000 rubs, surface energy ~46 dyn cm^{-1}).

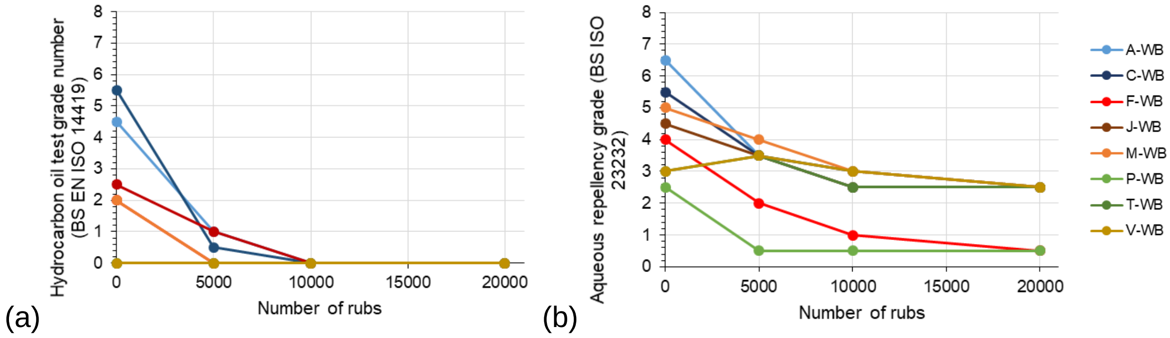


Figure 7.9: Webbing material abradant: Resistance to oil-based liquids according to BS EN ISO 14419 over rub number intervals; resistance to aqueous-based liquids according to BS ISO 23232 over rub number intervals. For sample codes see Table 7.1.

7.3.1.3 Understanding the effect of surface abrasion on liquid repellency

Evaluation of the fabric samples liquid repellency, and wettability, has indicated the surface changes from abrasion. For all samples, liquid repellency decreased with increased rubs by the abradant indicating increased wettability and loss of DWR. Abrasion created surface roughness on a macro scale; this was most clearly seen on the samples abraded by sandpaper (Figure 7.10).

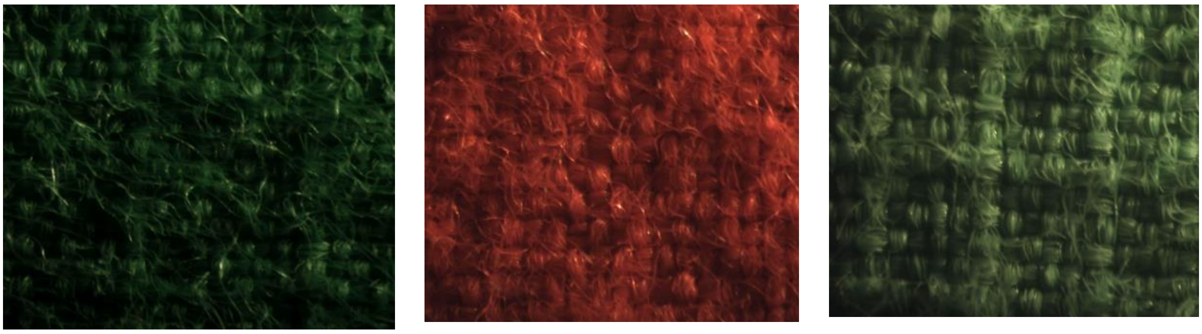


Figure 7.10: Selected images of fabric samples (magnification x10) after abrasion by sandpaper.

The effect of micro roughness and thermodynamic theories has been discussed in section 1.3.2.2. However, the roughness created by abrasion using sandpaper, webbing material and spacer material has changed the surface on a macro scale, lifting and breaking the fibre construction on the fabric face.

The roughness created the abradants used within this study has increased the fabric surface area and therefore number of contact points with the water. The uniform yarn and fabric construction has been broken creating a multitude of points to which the liquid can make contact (Figure 7.11).

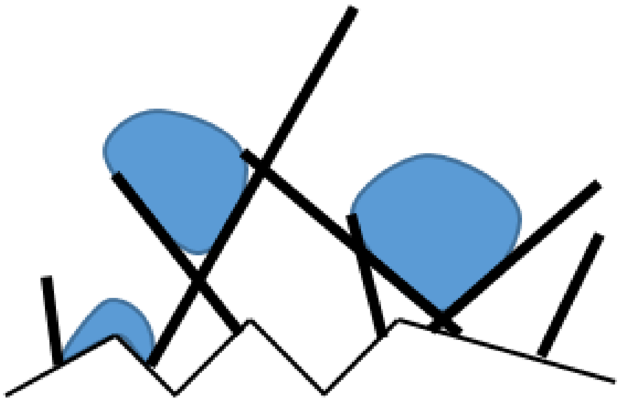


Figure 7.11: Schematic diagram of water droplets on an abraded surface where the yarn structure and fabric construction has been disrupted.

The roughness created by the abradants within this work has destructed the surface and is not linked to micro roughness as defined by Wenzel (section 1.3.2.2). Further investigation on the effect of abrasion at lower rub cycles should be considered and may show an enquiry of greater interest. The sharp increase of Δ*m* between 0 - 250 rub cycles using sandpaper suggests a further area to be considered. Similarly, 0 – 2500 rub cycles for spacer fabric and webbing material show a sudden increase in Δ*m* which has been overlooked within this study.

7.4 Conclusions

Within this study the Martindale test method, used widely to determine durability to abrasion, has been adapted to simulate abrasion to rocky terrain and adjacent apparel abrasion, with reference to the consumer data collected in Chapter 2. The use of the different abradants has shown accelerated abrasion to the fabric samples. Water repellency degraded with abrasion by all abradants. The spray ratings and calculations of Δ*m* at the end of the rub cycles did not differentiate between fluorinated and non-fluorinated DWRs. Differences in the wettability between samples *C*, *M* and *V* (same fibre type and fabric construction) were minimal.

Oil repellency quickly degraded after the first rub cycles with all samples demonstrating no oil repellency at the end of testing. Aqueous repellency demonstrated by both fluorinated and non-fluorinated DWR samples was similar at the end of testing. A similar rate of water repellency degradation between long SFP (C8) DWR samples and shorter SFP (C6) DWR samples has been shown. This contrasts to the conclusions presented by Schellenberger *et al.* [112] where the deterioration of water repellency, due to abrasion, was greater with decreasing fluorinated chain length. It is thought that the number of rub cycles used within this study was excessive and further investigation should be carried out to consider the effect of micro roughness at limited rub cycles (sandpaper< 250 rubs, webbing and spacer fabric < 2500 rubs).

Further work would be to assess the degradation of the surface chemistry by abrasion analytically by calculating transfer to the abradant or loss of surface chemistry over the rub cycle intervals. Whilst the loss of liquid repellency has suggested this occurs, further quantification is important to define this exposure pathway.

Adverse weather conditions should also be considered repeating the work with wet abrasion and within cold environments where freezing of the fabric may occur. Ultimately, field trials should take place and data from this study correlated to ensure the modified Martindale method is truly replicating the end use environment.

Chapter 8 - The role of a DWR on moisture vapour transfer

8.1 Introduction

During exercise, moisture vapour transfer through clothing is essential to maintain wearer thermophysiological comfort and heat balance (section 1.2.3). Clothing that prevents transfer of excess heat and moisture vapour to the external environment leads to build-up of moisture vapour within the microclimate of the clothing system and insufficient thermal regulation, potentially leading to heat exhaustion or hypothermia. A build-up of moisture vapour can result in condensation forming leading to wearer discomfort due to wet, clammy clothing. At the same time, wetting of clothing promotes conductive transfer due to the conductive properties of water (section 1.2.3.1).

Water vapour transfer through fabrics and clothing assemblies has been evaluated in simulated and “realistic” environments [37,295,296]. Wearer trials are carried out in controlled environments or within the field. Wearer trials allow the relationship between the human body, clothing and environment to be evaluated altogether. They enable the clothing system, as a whole, to be assessed and its dynamic interaction with the wearer. Wearer trials allow assessment of the clothing in environmental conditions; however this can add uncontrollable variables such as wind, rain and terrain. Controlled wearer trials take place in a simulated environment or environment chamber. These allow environmental conditions to be controlled to a greater degree minimising variables to consider during data analysis and interpretation.

8.1.1 Wearer thermal comfort in rain conditions

It has previously been suggested that the water repellency of a fabric strongly influences the moisture vapour transfer when in rain conditions [295,297]. The relationship between wearer thermal comfort and activity in rain conditions is affected by three main factors:

1) Transfer of moisture vapour through the clothing is fundamental to maintain thermal balance and wearer comfort [298]. However, during activity heat production is increased leading to a higher level of perspiration. Accumulation of moisture vapour pressure can condense within the clothing layers if above the saturation vapour pressure at the local temperature (Figure 8.1) [299]. This leads to a build-up of heat within the inner clothing layers leading to overheating and onset of hyperthermia.

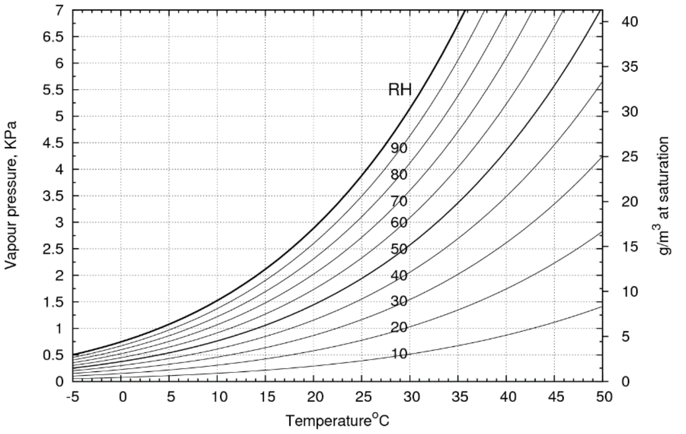


Figure 8.1: Vapour pressure is a function of moisture vapour content at a specific temperature. Relative humidity is the ratio of the water vapour pressure to the saturation vapour pressure [3,34].

2) Accumulation and penetration of rain wetting the fabric face results in increased thermal heat loss. The temperature of the shell layer is closer to the ambient temperature than skin temperature [34] and further lowered in rain conditions where the water cools the fabric. The face fabric, therefore, can act as a 'cold wall' causing condensation of moisture vapour [295,297]. When clothing is wetted, evaporative heat transfer decreases and heat transfer is reliant on convection, conduction and radiation [38]. The major route of heat exchange is via conduction with water within the fabric and water in contact with the skin; therefore at a greater rate [45].This is, however, dependent on the temperature of the rain, its effect on lowering clothing temperature

and the surface area of clothing that is wet or in contact with water. A sufficient DWR prevents wetting of the fabric face and subsequently the temperature of the fabric would remain higher preventing condensation.

3) Water vapour permeability is determined by the pressure difference across the fabric [3] and transfer rate (*WVT*) can be derived from equation 8.1:

$$WVT = \frac{k(p1-p2)}{d} \tag{8.1}$$

where the $p1 - p2$ is the pressure difference across the fabric; d is the fabric thickness and k is a constant.

For transfer of moisture vapour through the clothing, the moisture vapour pressure within the clothing system, or microclimate, needs to be greater to allow movement to the atmosphere of a lower moisture vapour pressure. When the vapour pressure gradient governing transfer through the clothing is negative, the driving force across the clothing inhibits moisture vapour movement to the environment [3,39].

Rainfall brings an elevated vapour pressure. Climates such as the UK have an average relative humidity in rain of 70-95% [34]. In addition, the vapour pressure within the shell layer is close to the saturated vapour pressure, due to low temperature of the face fabric and moisture vapour content. This results in a low pressure difference across the shell layer and therefore dynamic equilibrium where moisture vapour transfer is equal in both directions [34,299]. The ability of moisture vapour to transfer from within the clothing system to a rainy environment (~100%) is reliant on the absolute moisture content within the air and dependent on the temperature gradient between the clothing microclimate and environment. Activity during rainy conditions is a complex physiological situation and understanding of moisture vapour transfer in rainy environments remains an area of further research.

The reconsideration of chemistry used for DWRs adds an additional variable. The lesser water repellency demonstrated by non-fluorinated DWRs could lead to garments quickly wetting out in prolonged rainy environments and consequently this would affect wearer comfort.

A study by Gore [300] evaluated a number of split jackets in wearer trials evaluating non-fluorinated and fluorinated DWR chemistries. The repellency was evaluated after every 10 hours of use, up to 50 hours of use, using the spray rating and showed that repellency of a non-fluorinated DWR diminished at 40 hours. This study is the only published wearer trial comparing the functionality of DWR chemistry types. However, wearer comfort and the effect of the DWR on moisture vapour transfer was not considered.

To address this, wearer trials were planned and executed to address objective 7 (section 1.7). The main focus of this study was to understand the role that a DWR plays in allowing moisture vapour transfer and heat transfer, and to determine if wetted fabric inhibits moisture vapour transfer in rainy conditions.

8.1.2 Split jacket design

Wearer trials were devised using split jackets specifically made for this research study. Two garments were manufactured from long SFP (C8) DWR sample *C* and untreated sample *Y* (Figure 8.2). These two fabrics had identical fabric structures and composition with one DWR treated and one untreated; full fabric details given in A.3*.* The jackets were manufactured in a split jacket construction with tapped seams, pull cords at the waist and cuff tabs on the sleeves without pit zips. On both garments, the hood was made from fabric sample *C.* The jackets were identical in style and manufactured in one size 10 female and one size medium male.

Figure 8.2: Split jacket design made from long SFP (C8) DWR sample *C* and untreated sample *Y.*

The split design of these garments allows the two fabrics to be assessed at the same time and therefore the conditions are the same. The design allows a comparative study between the two sides of the jacket, and therefore between the long SFP (C8) DWR fabric and untreated fabric.

8.1.3 Clothing system

Test subjects wore a synthetic base layer and the test jacket. The jackets were fully zipped, with the hoods up and ventilation minimised by adjustment of the toggles and cuff tabs. They were worn with synthetic trousers and over-trousers.

Wearer trials are predominantly assessed subjectively by asking the subject their opinions using rating scales. Within this study, it was decided that rating scales were not suitable to assess the impact of a DWR on moisture vapour transfer and thermal comfort as these mechanisms are extremely difficult to define as a wearer. Data was solely collected by data logging sensors and thermal imagery to collect quantitative data.

8.1.4 Data logging sensors

Data logging sensors (DS1923 iButton hygrochron) were used logging both temperature and humidity simultaneously. The stainless steel sensors were housed in open mesh pockets, specifically made to carry the sensors, measuring 35 mm by 30 mm and fixed to the clothing using safety pins.

The data logging sensors were capable of recording 8192 recordings at 8-bit resolution (0.4ºC) with a delayed start function. The operating range of these sensors was -20°C to +85°C; 0 to 100% RH. Prior to testing, the sensors were programmed using OneWireViewer [301] to record at 10 second intervals.

Preliminary trials (15 minute route) were undertaken to determine positioning of the sensors and the number of sensors required for each subject during the trials. From this initial data collection, positioning of the sensors and number of sensors to be used was determined (Figure 8.3). For subsequent testing, sensors were placed in identical positions on both sides of the body.

The sensors were fixed within the clothing system between the base layer and the test jacket on both test subjects. Ambient conditions were recorded using DS1923 iButton hygrochron logger sensors.

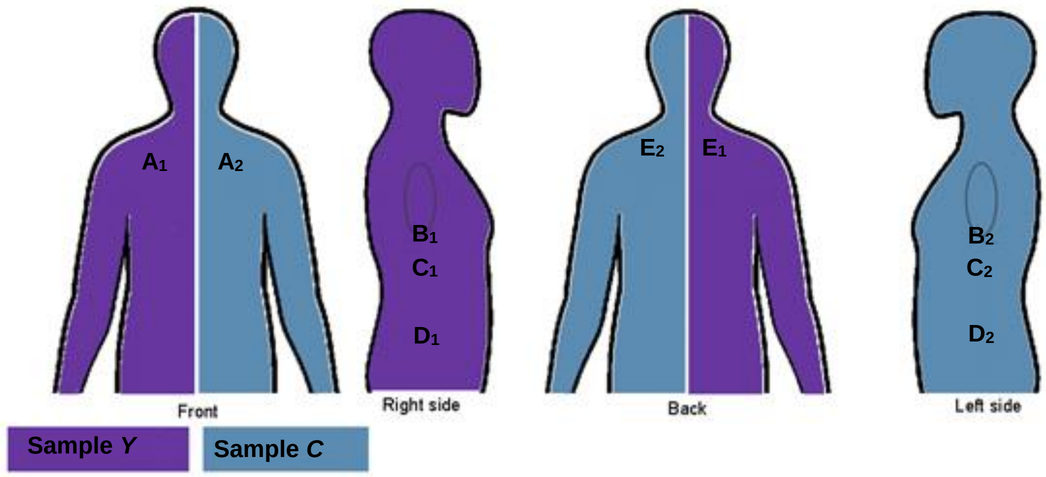


Figure 8.3: Positioning of data logging sensors on test subjects between the two sides of the split jacket – untreated sample *Y* and long SFP (C8) DWR sample *C*.

Test subjects were recruited for the study following ethical approval LTDESN-064. A risk assessment and an information sheet were compiled and available to participants. Participation was voluntary and could be withdrawn at any time during the study.

8.2 Initial field trials

Initial field trials were undertaken with two test subjects (one male, one female) on a low level route (Figure 8.4), with a section of elevation. The route (27 minutes) was undertaken twice by the same subjects; total testing time of 54 minutes. There was a 10 minute rest between the two routes (route #1 and route #2) in a dry shelter. The ambient temperature and relative humidity were recorded at the same time of testing.

Figure 8.4: Route taken during the initial field trials and elevation of the route.

8.2.1 Discussion

8.2.1.1 Ambient conditions

These field trials were undertaken in rainy and windy conditions with ambient temperature ~10ºC and relative humidity reaching 100 RH% (saturated environment) (Figure 8.5).

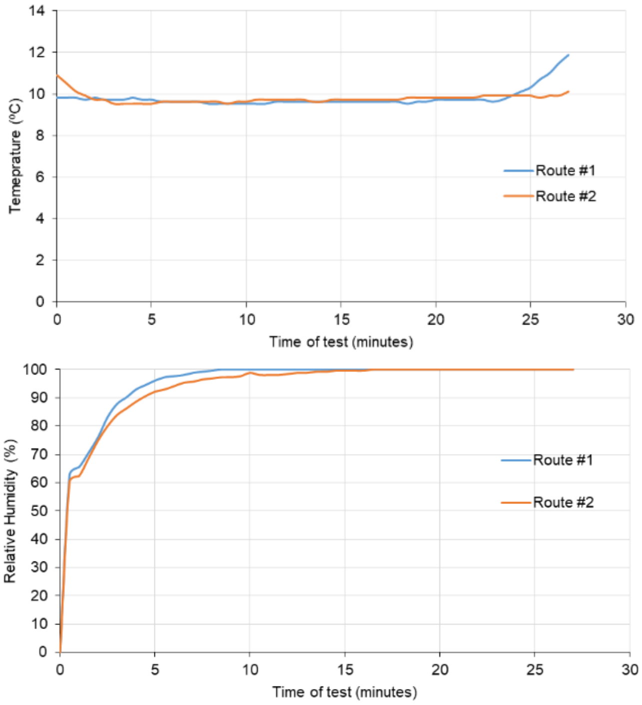


Figure 8.5: Ambient temperature and relative humidity (RH) during initial field trials.

Over the duration of the field trial, the difference in repellency between the two sides of the jacket could be visually seen (Figure 8.6). The fabric on the untreated side wet out whilst rain beaded and initially ran off the long SFP (C8) DWR treated side of the jacket.

Figure 8.6: The difference in repellency between the treated and untreated sides of the jacket could be visually seen. The treated side remained repellent with rain beading away from the fabric surface.

8.2.1.2 Difference between the sides of the split jacket

To understand the effect of the treated and untreated fabrics on temperature and relative humidity during testing, the difference between the untreated side of jacket and the treated long SFP (C8) DWR side of the jacket was determined.

Calculation of temperature difference: The difference between the temperature data collected within the clothing system between the treated long SFP (C8) DWR side of the garment and the untreated side of the garment was calculated as equation 8.2:

$$\Delta T_A = T_{A2} - T_{A1} \tag{8.2}$$

where ΔT_A is the difference in temperature data between the data from the long SFP (C8) DWR side of the jacket (sensors A2-E2), $T_{A2\text{-}E2}$, and the temperature data from the untreated side of the garment (sensors A1-E1), $T_{A1\text{-}E1}$.

Calculation of relative humidity difference: The difference between the relative humidity data collected within the clothing system of the treated long SFP (C8) DWR side of the garment and untreated side of the garment was calculated as equation 8.3:

$$\Delta RH_A = RH_{A2} - RH_{A1} \tag{8.3}$$

where ΔRH_A is the difference in relative humidity between the relative humidity data from the long SFP (C8) DWR side of the garment (sensors A2-E2), $RH_{A2\text{-}E2}$, and the relative humidity data from the untreated side of the garment (sensors A1-E1), $RH_{A1\text{-}E1.}$

8.2.1.3 Subject one

On both routes, a 0-3ºC difference was calculated between the treated and untreated sides of the garment (Figure 8.7). The temperature was lower on the untreated side of the jacket, apart from at sensor positioning A1/A2 on route #1. During route #2, the temperature was lower on the untreated side of the jacket throughout the route. This lower temperature is due to the cold wall created by the rain wetting the outer fabric face.

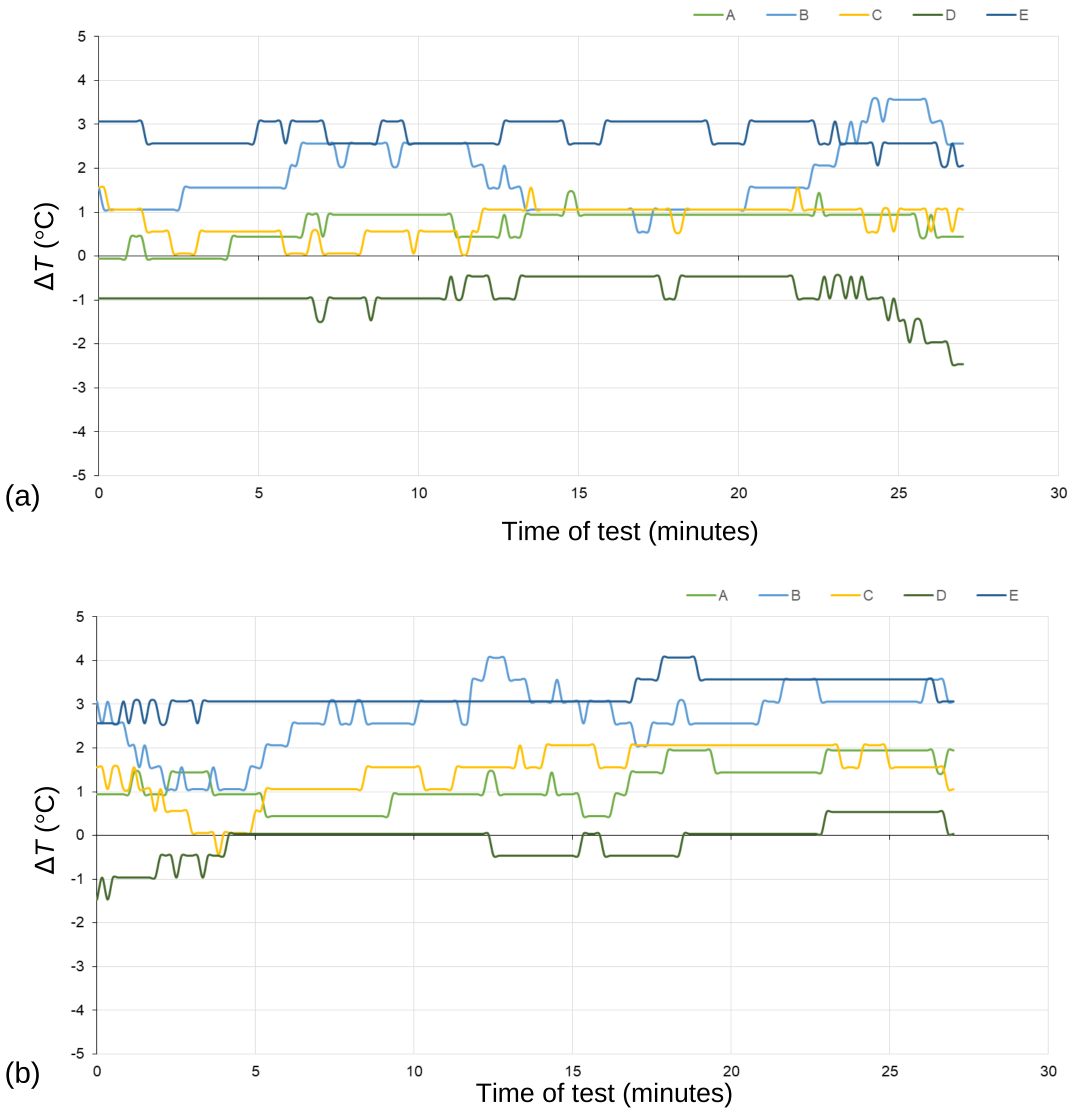
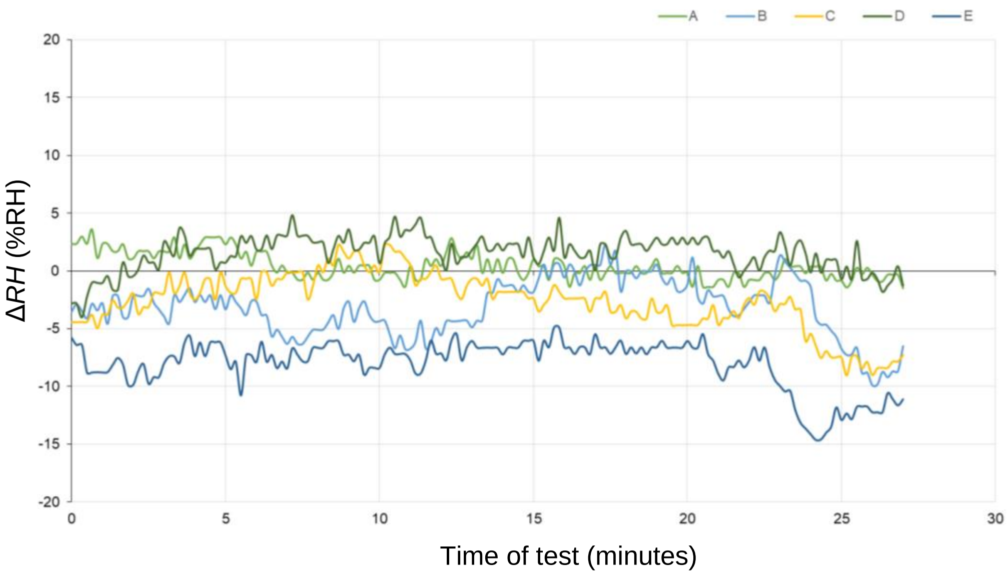


Figure 8.7: Temperature difference (Δ*T*) between the two sides of the split jacket – subject 1, (a) route #1 and (b) route #2.

Relative humidity was greater on the untreated side of the jacket (Figure 8.8). The lower temperature on this side results in a lower saturated vapour pressure and could explain the increase in RH. At sensor positioning E1/E2, the RH was consistently greater on the untreated side than on the treated side of the jacket.



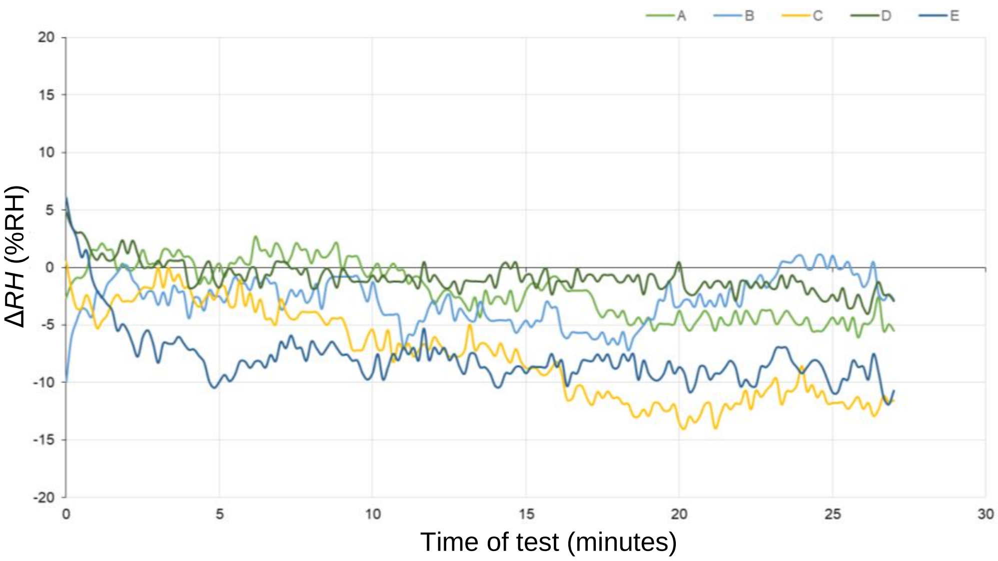


Figure 8.8: Relative humidity difference (Δ*RH*) between the two sides of the split jacket –subject 1, (a) route #1 and (b) route #2.

8.2.1.4 Subject two

A 0-3 ºC temperature difference was calculated between the two sides of the garment throughout route #1 and route #2 (Figure 8.9). Unlike subject 1, from the beginning of testing on route #1, the temperature on the untreated side of the jacket was lower than the treated side of the jacket. On route #2, temperature was lower on the untreated side at sensor positioning A1 and D1 throughout.

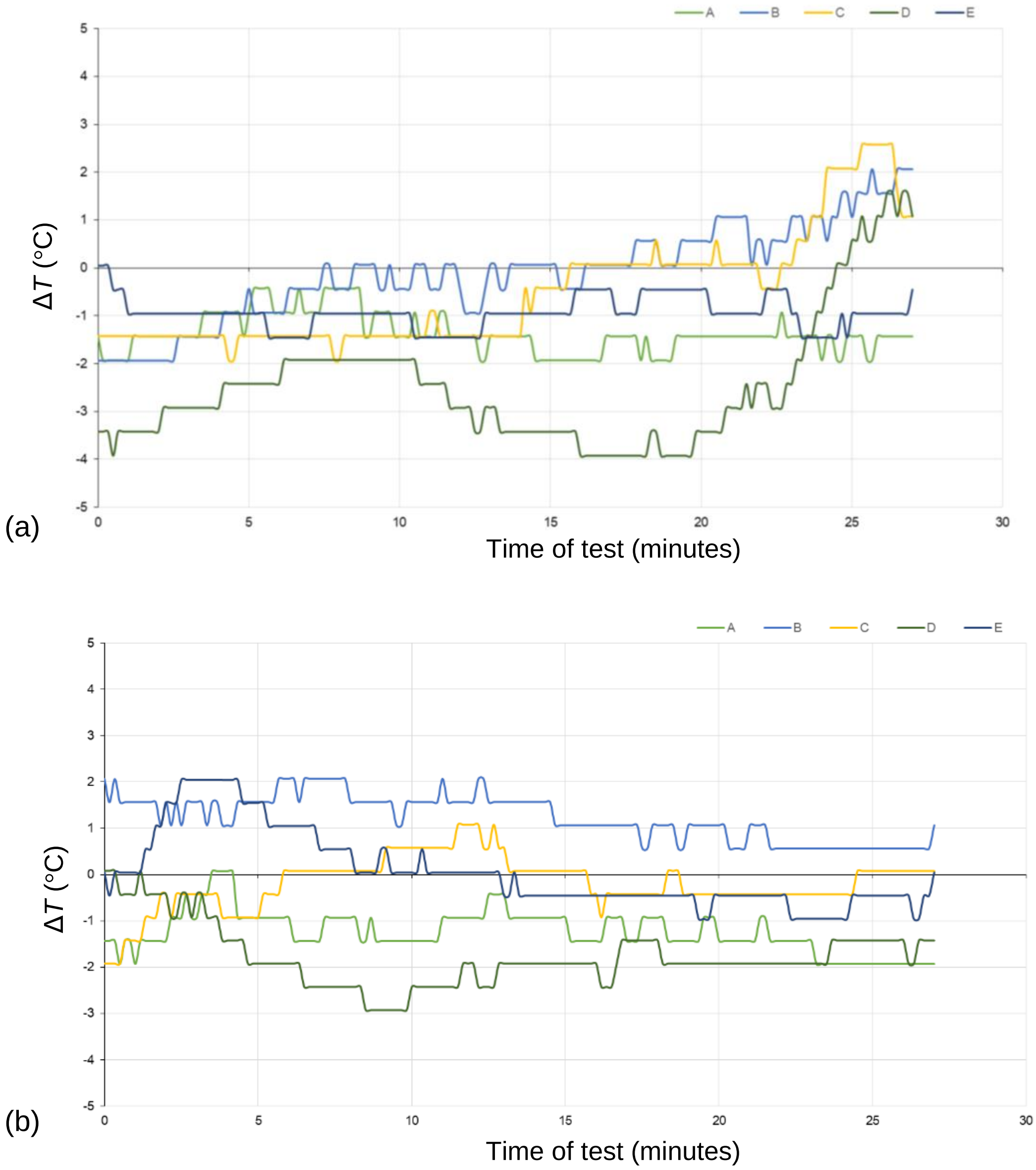


Figure 8.9: Temperature difference (Δ*T*) between the two sides of the split jacket - subject 2, (a) route #1 and (b) route #2.

On route #1, the RH within the clothing system of subject two was greater on the treated side than the untreated side (Figure 8.10). At 20 minutes, the RH under the arms of the subject (sensor positioning B/B2) was greater on the untreated side of the garment.

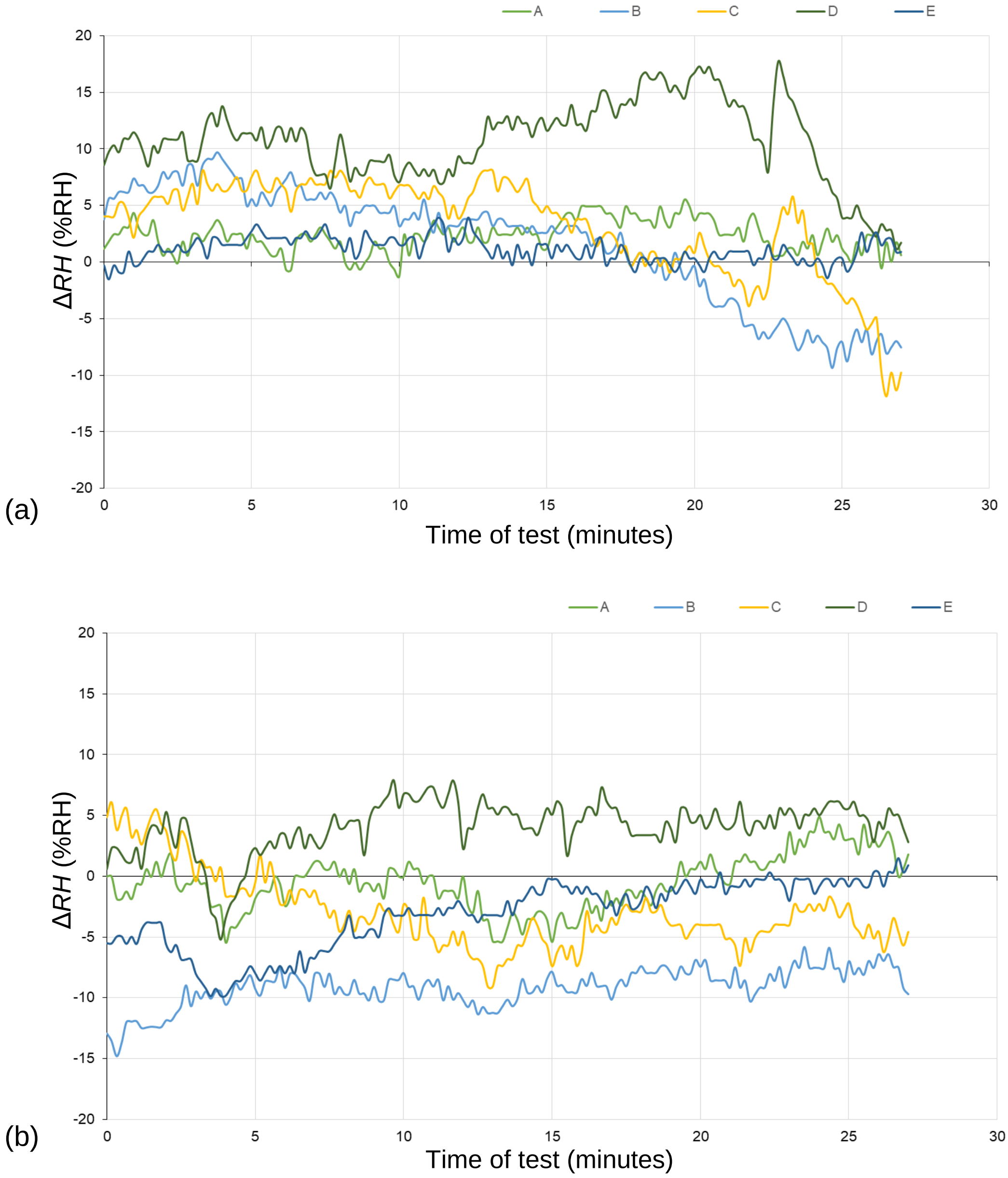


Figure 8.10: Relative humidity difference (Δ*RH*) between the two sides of the split jacket – subject 2, (a) route #1 and (b) route #2.

This differed on route #2, where the relative humidity was greater on the untreated side of the jacket for the majority of the test duration (sensor positions B1, C1, E1).

8.2.2 Summary

These initial wearer trials were carried out in the field and showed a temperature difference between the treated and untreated sides of the garment. However, weather conditions were an additional variable and there was a strong effect of wind during testing. This added bellows ventilation due to movement during activity.

These initial field trials were limited due to the number of test subjects and the severity of the weather conditions. As a result of this, it was decided to conduct additional wearer trials in a controlled environment.

8.3 Wearer trials under simulated rain

Further wearer trials were carried out under a simulated rain shower in the rain chamber, University of Leeds. They enabled a greater number of test subjects to participate in the trials and removed any effect by wind or variation in rain, in terms of duration and intensity.

8.3.1 Simulated rain shower

The rain chamber consisted of a rain shower with flow meter. The rain shower simulated rain at an intensity of 15 mm per hour with drop diameter 0.5 to 3.5 mm. Compared to previous data on the intensity and drop size of different rain types, this simulated rain shower compared to heavy rain in intensity (Table 8.1).

Table 8.1: Intensity and drop diameter of rain droplets [73].

Type of rain	**Rain intensity (mm/hr)**	**Drop diameter (mm)**
Drizzle	0.25	0.20
Light rain	1.00	0.45
Moderate rain	4.00	1.00
Heavy rain	15.00	1.50
Simulated rain shower	15.00	0.50-3.50
Excessive rain	40.00	2.10

Ambient conditions (temperature and relative humidity) were recorded using two DS1923 iButton hygrochron logger sensors which were positioned in two different locations within the rain chamber.

The trial involved cycles of rest and work in dry conditions, followed by periods of rest and work under the simulated rain shower (Table 8.2).The work period involved bench stepping to a metronome set at 90 beats per minute. The duration of the rest/work cycles were based on previous research conducted by Gretton [295] and Stevens [37]. The duration of the work period included stepping allowing the subjects to become warm and perspire due to the physical activity. Data logging temperature and humidity sensors, as discussed in section 8.1.4, were used with identical positioning as Figure 8.3**.**

Table 8.2: Time periods of rest and stepping in dry conditions (0-30 minutes) and under the simulated rain shower (30-65 minutes).

Time (minutes)	0-5	5-15	15-20	20-30	30-35	35-45	45-50	50-60	60-65
Activity	Rest	Step	Rest	Step	Rest	Step	Rest	Step	Rest
Conditions	Dry				Under simulated rain shower				

8.3.2 Test subjects

Four test subjects, two female (subject 1 and subject 2) and two male (subject 3 and subject 4) took part in these wearer trials. Two subjects participated at the same time.

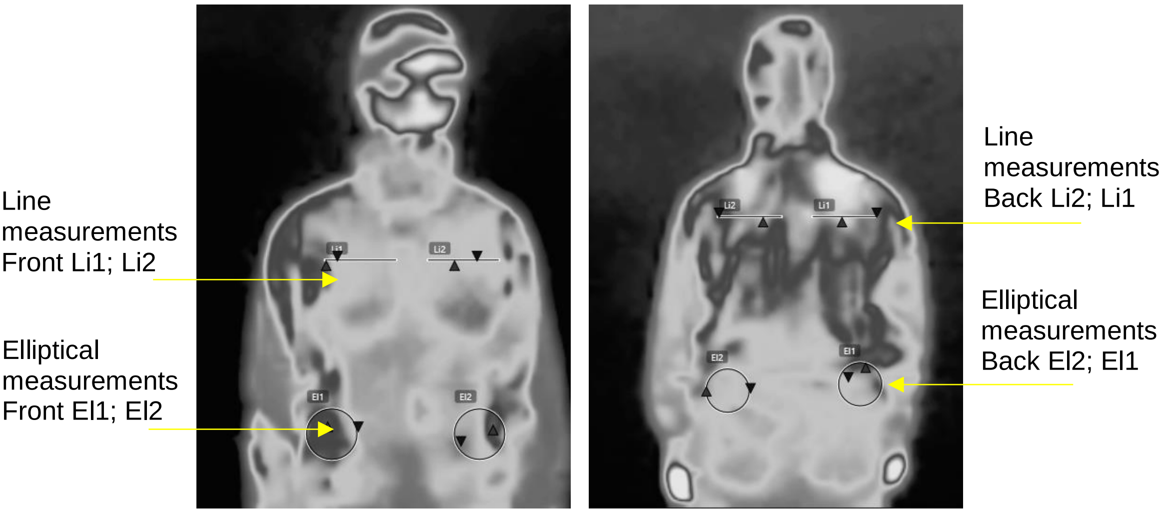
8.3.2.1 Clothing system

The same split jackets were worn, as discussed in section 8.1.2. Additional clothing worn was as described in section 8.1.3.

8.3.3 Thermal imaging

A FLIR C2 thermal imaging camera was used during the rain room trials, with touchscreen 3" display and digital camera (640 x 480 pixels) with spotmeter; temperature range -10°C - +150°C ± 2%, 7.5-14 µm spectral range, 80 x 60 (4800 measurement pixels) IR sensors, 9 Hz image frequency and 41° x 31° field of view. Photographs in both thermal mode and digital mode were taken. Thermal imaging was taken after stepping during dry conditions and after stepping under simulated rain. Photographs of the subject were taken from the front and from the back each time.

Thermography software FLIR Tools [302] was used to analyse the thermograms. Calculations of thermal temperature where made as a line measurement on the chest (Li1: untreated fabric; Li2: treated long SFP (C8) DWR fabric) and an elliptical measurement at the side of the torso (El1: untreated fabric; El2: treated long SFP (C8) DWR fabric) (Figure 8.11).


Line measurements Front Li1; Li2

Elliptical measurements Front El1; El2

Line measurements Back Li2; Li1

Elliptical measurements Back El2; El1

Figure 8.11: Line and elliptical measurements calculated on the front torso and back of each subject.

The average, minimum and maximum value of each measurement was calculated using the infrared (IR) software. Temperature difference between the two sides of the upper body were calculated as equation 8.4 and equation 8.5:

$$\Delta tA = Li_2 - Li_1 \tag{8.4}$$

where ΔtA is the difference in temperature between the line measurements of the treated long SFP (C8) DWR side of the jacket (Li_2) and untreated side of the jacket (Li_1).

$$\Delta tB = El_2 - EL_1 \tag{8.5}$$

where ΔtB is the difference in temperature between the elliptical measurements of the treated long SFP (C8) DWR side of the jacket (El_2) and the untreated side of the jacket (El_1).

Thermal imaging allowed data on the temperature of the outer fabric face to be determined during testing.

8.3.4 Discussion

8.3.4.1 Ambient conditions

The ambient conditions within the rain room differed during the two tests (Figure 8.12). During test #1, the temperature was consistent at ~19ºC. However, the temperature fluctuated during test #2 with a decrease in temperature at 25 minutes when the rain shower was turned on. Relative humidity during the two tests was similar with an increase when the simulated rain shower started.

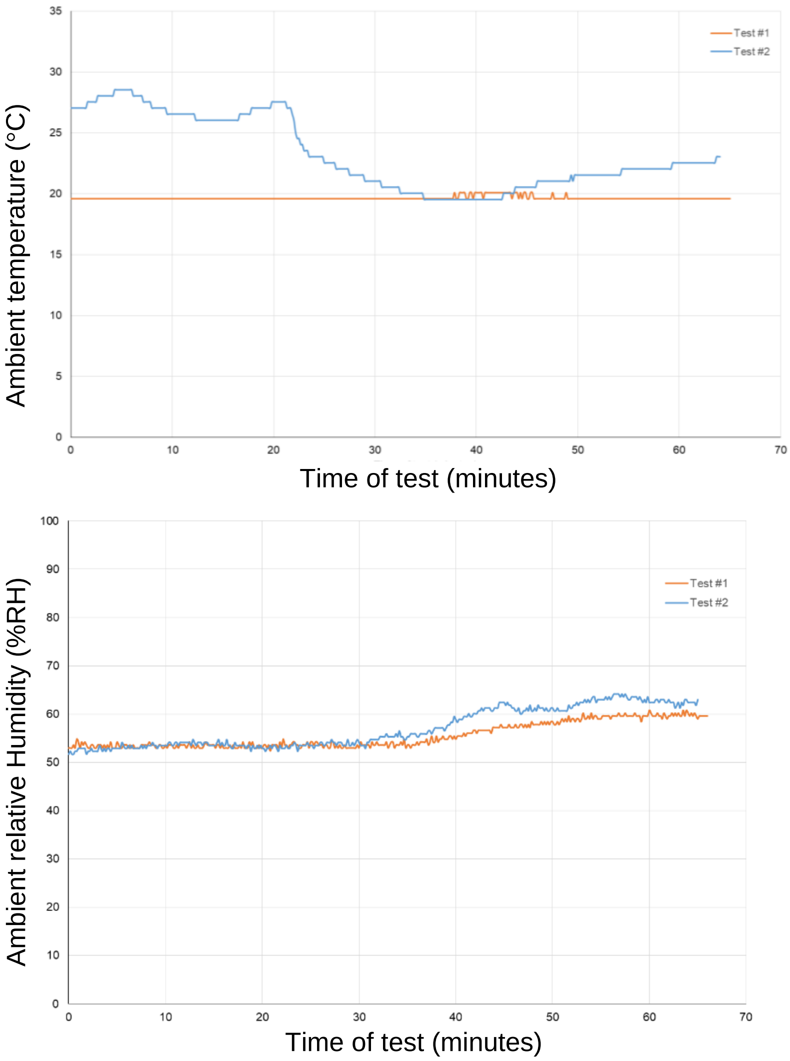


Figure 8.12: Ambient temperature and RH during simulated rain wearer trials.

8.3.4.2 Calculation of driving force across the outer layer

The driving force across the outer shell was calculated to determine the effect of rain. From this, similarities between the test subjects could be observed.

The saturation vapour pressure (p) at each sensor position was calculated as [303]:

$$p = p_s.e(13.3815t - 1.9760t^2 - 0.6445t^3 – 0.1299t^4) \quad (8.6)$$

where p_s is standard atmospheric pressure (101.325 N m^{-2}) and t is calculated as [303]:

$$t = (1 - \frac{T_S}{T_K}) \quad (8.7)$$

in which T_K is absolute temperature calculated by converting temperature data, $T_{A1\text{-}E1;\,A2\text{-}E2}$, to Kelvin and Ts is steam point (375.15K).

From this, vapour pressure (VP) is calculated by equation 8.8 at each sensor position, $VP_{A1\text{-}E1;A2\text{-}E2}$, and for the ambient environment, $VP_{AMB.}$

$$VP_A = p_A RH_A \tag{8.8}$$

where RH is the relative humidity sensor data from all sensor positions (A1-E1; A2-E2).

The driving force (mbar) at each sensor position was therefore calculated by equation 8.9 at all sensor positions A1-E1; A2-E2:

$$\text{Driving force}_A = VP_A - VP_{AMB} \tag{8.9}$$

8.3.4.3 Subject one

The temperature difference between the sides of the split jacket was calculated (Figure 8.13). Temperature fluctuated with stepping periods reflecting the increase of heat due to physical exertion and this being dissipated by the body. At sensor positioning D1/D2, temperature within the clothing system was greater on the untreated side of the jacket than the treated side. Yet at sensor C1/C2 positioning, the inverse was observed.

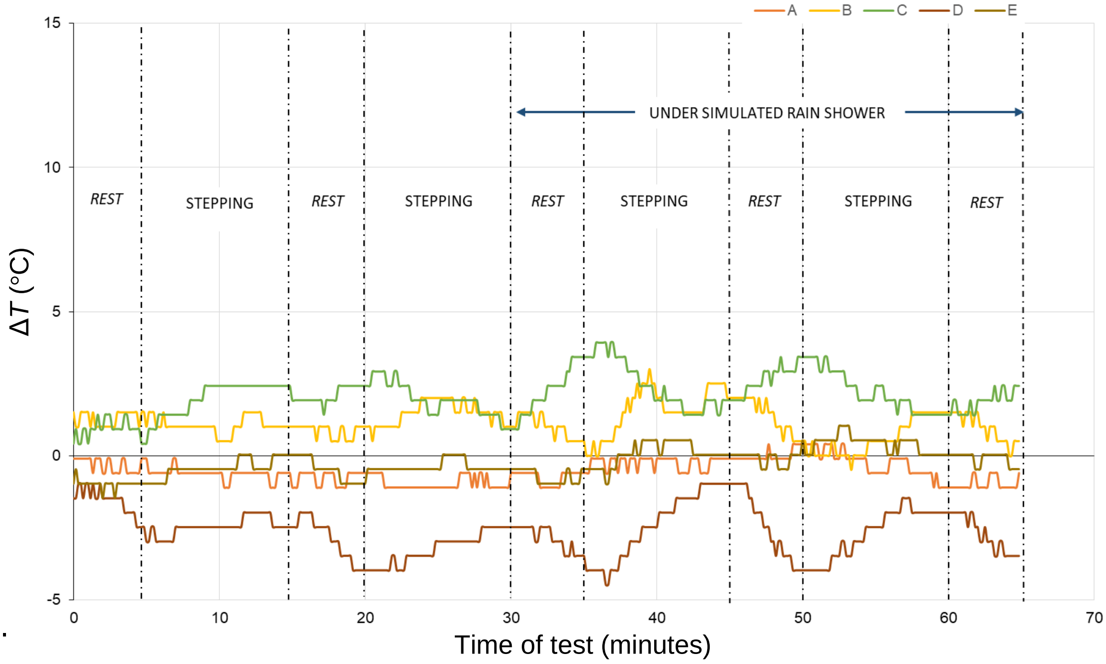


Figure 8.13: Subject one - Temperature difference (Δ*T*) between the two sides of the split jacket.

Under the simulated rain, the temperature within the outer layer was 1ºC to 4.5 ºC lower than in dry conditions (Table 8.3). A lower temperature during the simulated rain was observed at all sensor positioning after the first stepping period (Table 8.3).

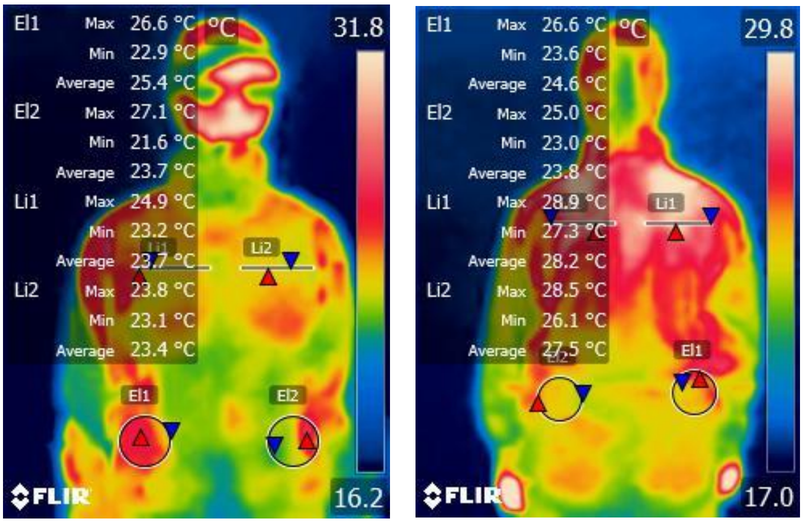
Table 8.3: Subject one - Temperature under the outer layer in dry conditions and simulated rain.

Sensor positioning	**Temperature (ºC) at end of first stepping period**	
	Dry	**Simulated rain**
A1	30	27
B1	32	30
C1	27	26
D1	29	24
E1	29	26
A2	29	27
B2	33	28
C2	29	24
D2	27	25
E2	29	26

Thermal imaging showed little difference between the two sides of the jacket both after stepping in dry conditions and after stepping in wet conditions; Δ*T*<2ºC (Figure 8.14).

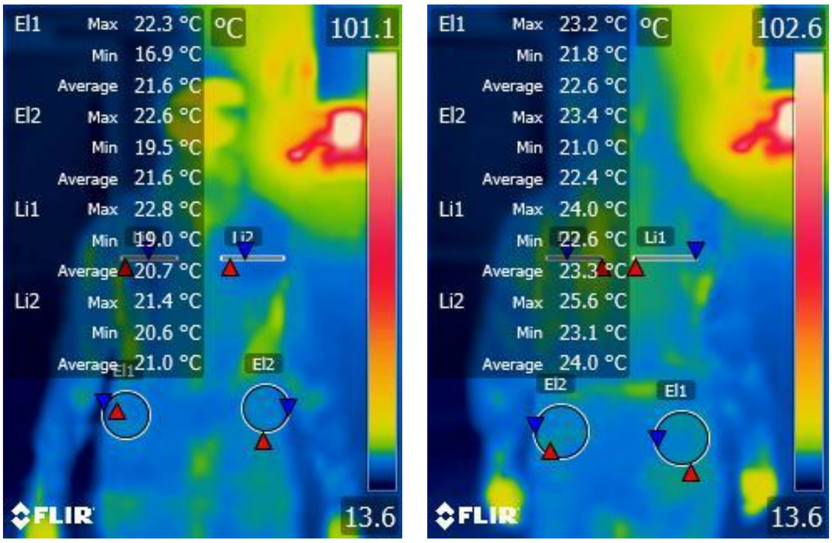
However, thermal imaging showed a decrease in temperature at the fabric outer face under the simulated rain shower (Figure 8.14). This calculated temperature difference was 1.4ºC to 4.9 ºC lower in rain conditions than in dry conditions (Figure 8.14). This decrease in observed temperature was due to the cooling of the outer fabric face by the rain.

(a)



ΔtA= -0.3 ºC; **Δ**tB = -1.7 ºC **Δ**tA= -0.7 ºC; **Δ**tB = -0.8 ºC

(b)



ΔtA= +0.3 ºC; **Δ**tB = 0 ºC **Δ**tA= -0.2 ºC; **Δ**tB = +0.7 ºC

Figure 8.14: Thermograms of subject one after (a) first stepping period in dry conditions and (b) after first stepping period under simulated rain.

In the simulated rain, higher relative humidity underneath the outer layer was observed than in dry conditions (Table 8.4). The decreased temperature means a decrease in saturated vapour pressure level and therefore the same moisture vapour content could be present but saturating at the lower temperature under simulated rain.

Table 8.4: Subject one - Relative humidity (RH %) under the outer layer in dry conditions and simulated rain.

Sensor positioning	RH (%) at end of first stepping period	
	Dry	Simulated rain
A1	62	93
B1	50	91
C1	68	96
D1	59	93
E1	90	100
A2	64	95
B2	47	95
C2	58	92
D2	70	98
E2	66	97

The driving force across the outer layer did not differ greatly between the two sides of the jacket (Figure 8.15). A build-up of moisture vapour due to activity can be clearly seen between 0-15 minutes of the testing period beginning. Driving force fluctuated with stepping and rest periods under simulated rain. The lower driving force at the end of the stepping periods, under simulated rain, were due to the increased water vapour concentration within the clothing system and in the inhibited transfer to the ambient air with high water vapour concentration. At sensor positioning B1/B2 the driving force differed greatly between stepping and rest periods under simulated rain. This was thought to be due to bellows ventilation by arm movement.

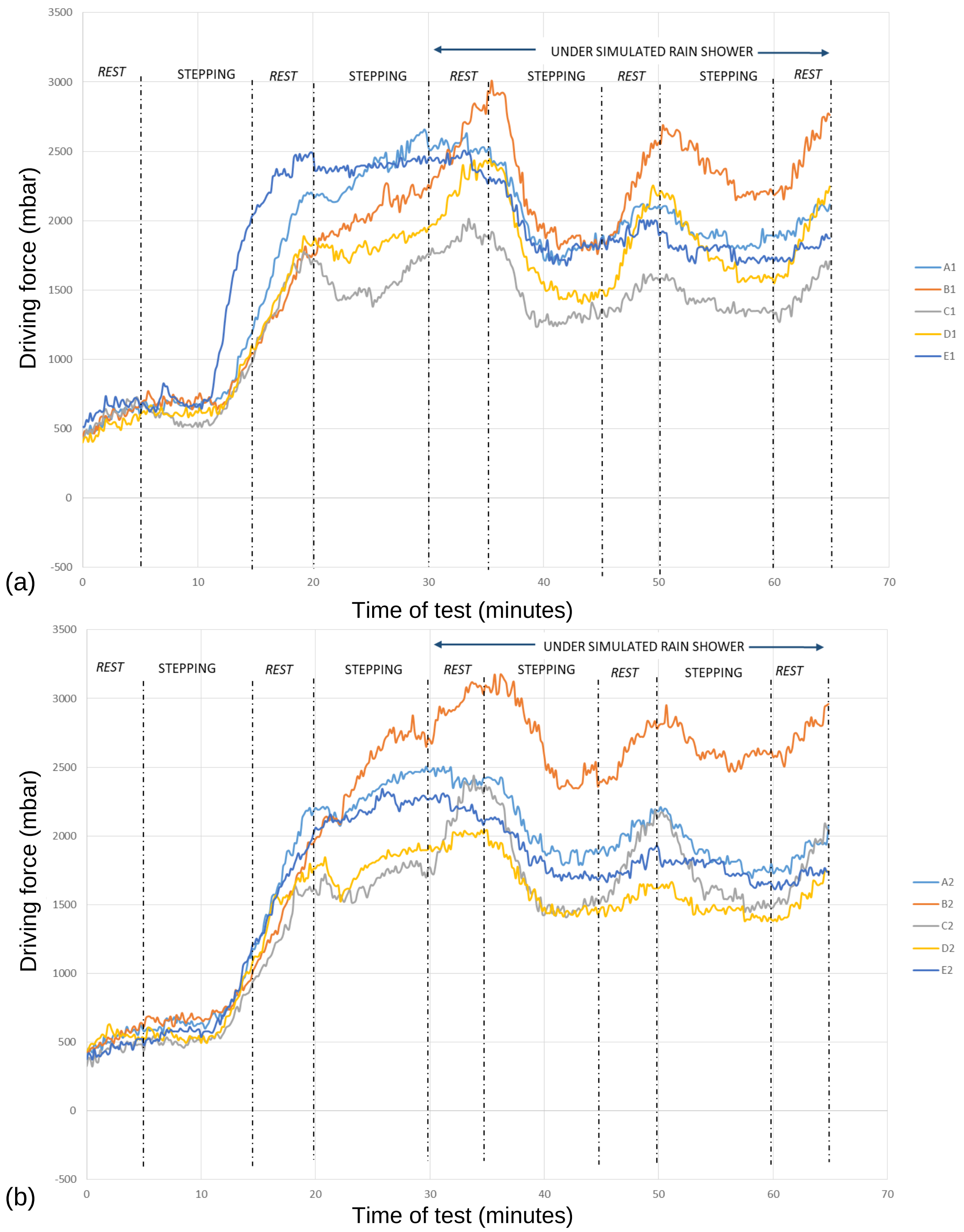


Figure 8.15: Subject one - Driving force across the outer layer: a) Untreated side of the jacket; b) Long SFP (C8) DWR side of the jacket.

8.3.4.4 Subject two

Temperature fluctuated during periods of stepping and rest (Figure 8.16). Under the simulated rain, the temperature was lower on the untreated side of the jacket by ~2 ºC. However, this was not consistent across all sensor positions.

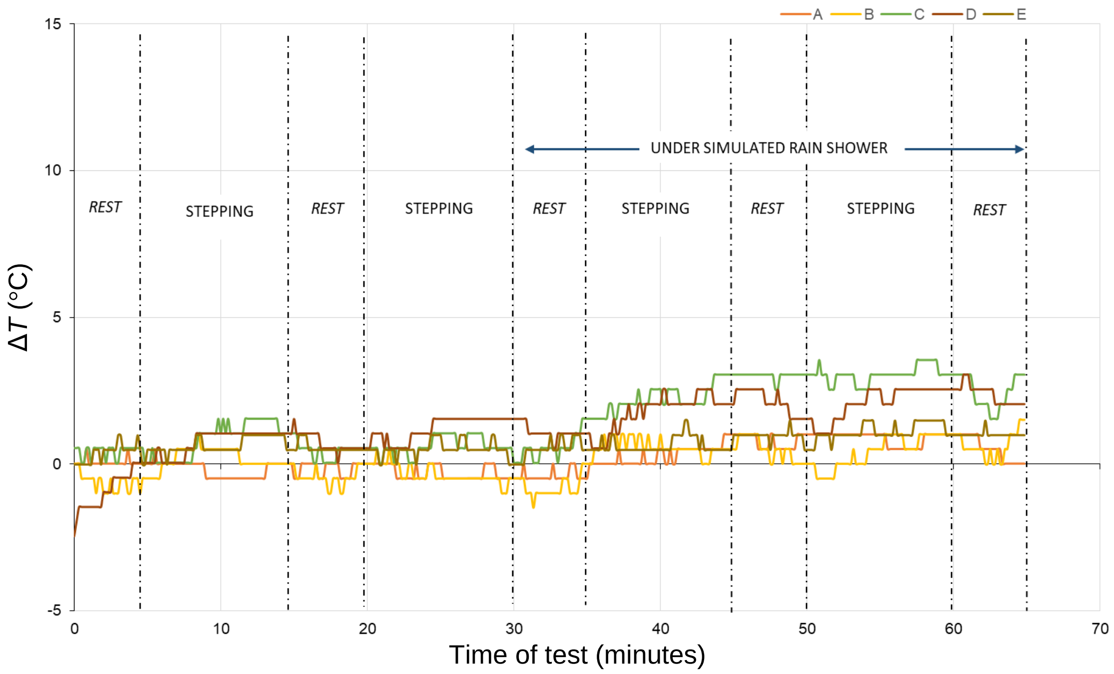


Figure 8.16: Subject two - Temperature difference (Δ*T*) between the two sides of the split jacket.

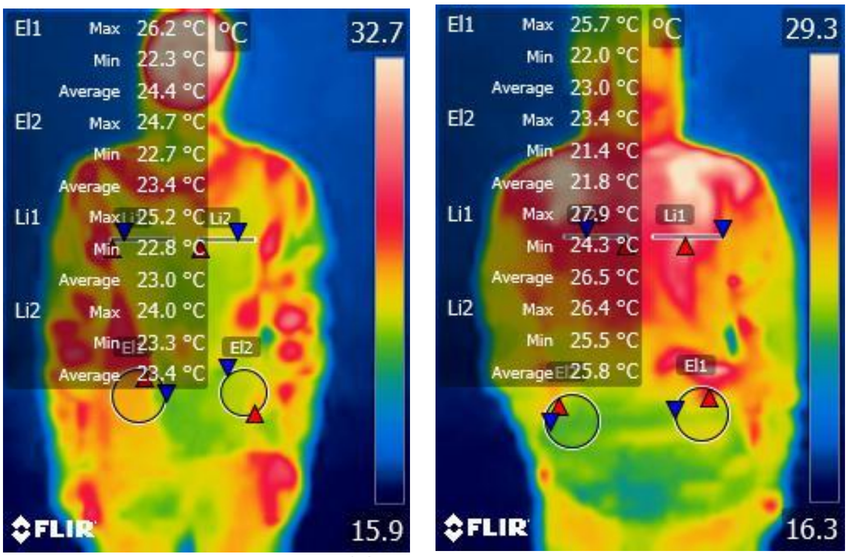
After the first stepping period under the simulated rain shower, the temperature beneath the outer layer was lower than in dry conditions (Table 8.5).

Table 8.5: Subject two - Temperature under the outer layer in dry conditions and simulated rain.

Sensor positioning	**Temperature (ºC) at end of first stepping period**	
	Dry	**Simulated rain**
A1	29	24
B1	28	23
C1	28	24
D1	26	22
E1	31	27
A2	29	25
B2	28	24
C2	29	27
D2	28	24
E2	32	28

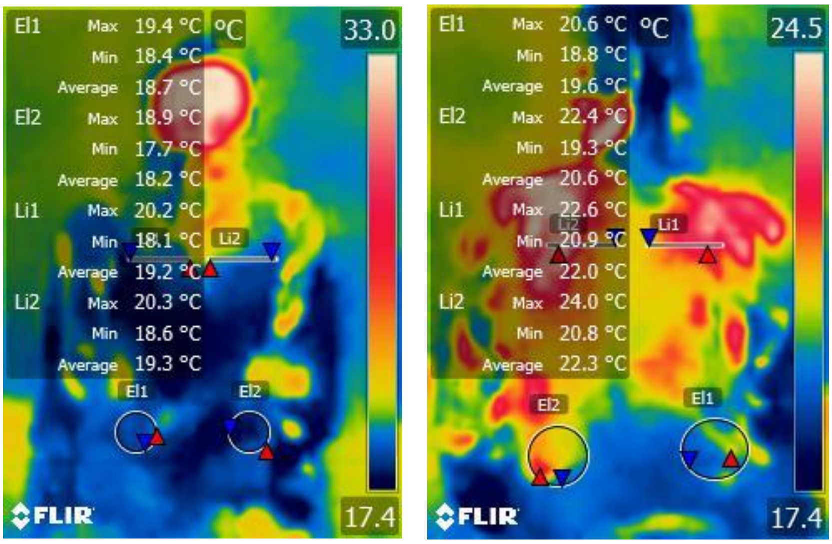
In addition, thermal imaging showed this temperature difference on the outer fabric face. The variance between the temperature in wet and dry conditions differed by 2.5ºC to 5.7ºC (Figure 8.17). Under the simulated rain shower, thermal imaging showed a temperature difference between the two sides of the jacket on the outer fabric face largely at the lower torso (ΔT = 1-1.2 ºC).

(a)



ΔtA= +0.4 ºC; **Δ**tB = -1.0 ºC **Δ**tA= -0.7 ºC; **Δ**tB = -1.2 ºC

(b)



ΔtA= +0.1 ºC; **Δ**tB = -0.5 ºC **Δ**tA= +0.3 ºC; **Δ**tB = +1.0 ºC

Figure 8.17: Thermograms of subject two after (a) first stepping period in dry conditions and (b) after first stepping period under simulated rain.

As subject one, a higher relative humidity within the clothing system was observed during simulated rain compared to dry conditions, apart from at sensor positioning C2 (Table 8.6). On the untreated side of the jacket, the RH was greater under simulated rain than the treated side of the jacket. This was ascertained to be due to the inhibited transfer of moisture vapour with the saturated ambient air and saturated air within the fabric interstices, and the lower water vapour pressure content within the microclimate air due to the lower temperature.

Table 8.6: Subject two - Relative humidity under the outer layer in dry conditions and simulated rain.

Sensor positioning	**RH (%) at end of first stepping period**	
	Dry	**Simulated rain**
A1	73	87
B1	80	85
C1	77	79
D1	68	84
E1	96	100
A2	71	81
B2	60	78
C2	77	68
D2	64	76
E2	63	68

The driving force during dry conditions on the untreated side of the jacket was greater than on the treated side of the jacket (Figure 8.18). This could be due to limited transfer of moisture vapour from within the jacket to the environment through the untreated fabric. Throughout, the driving force at sensor positioning E1 was greater.

The driving force across the outer layer decreased during the simulated rain due to the high ambient air water vapour concentration. This encouraged accumulation of moisture vapour within both sides of the jacket resulting in higher RH (Table 8.6).

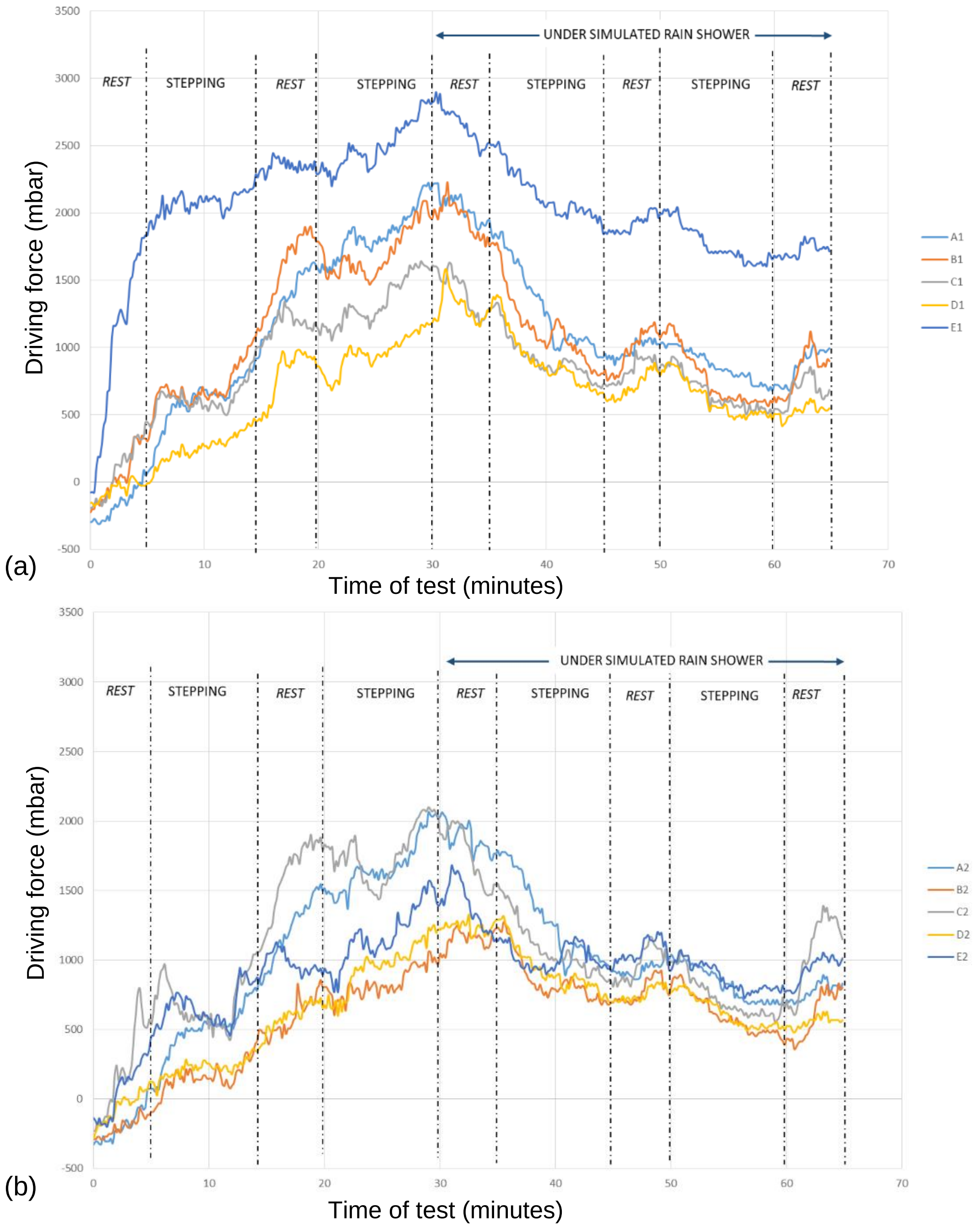


Figure 8.18: Subject two - Driving force across the outer layer: a) Untreated side of the jacket; b) Long SFP (C8) DWR side of the jacket.

8.3.4.5 Subject three

Temperature within the clothing system fluctuated with stepping and rest periods (Figure 8.19). There was less temperature difference between the two sides than observed for other test subjects. However, the temperature within the outer layer was lower under simulated rain at all sensor positions (Table 8.5) after the first stepping period.

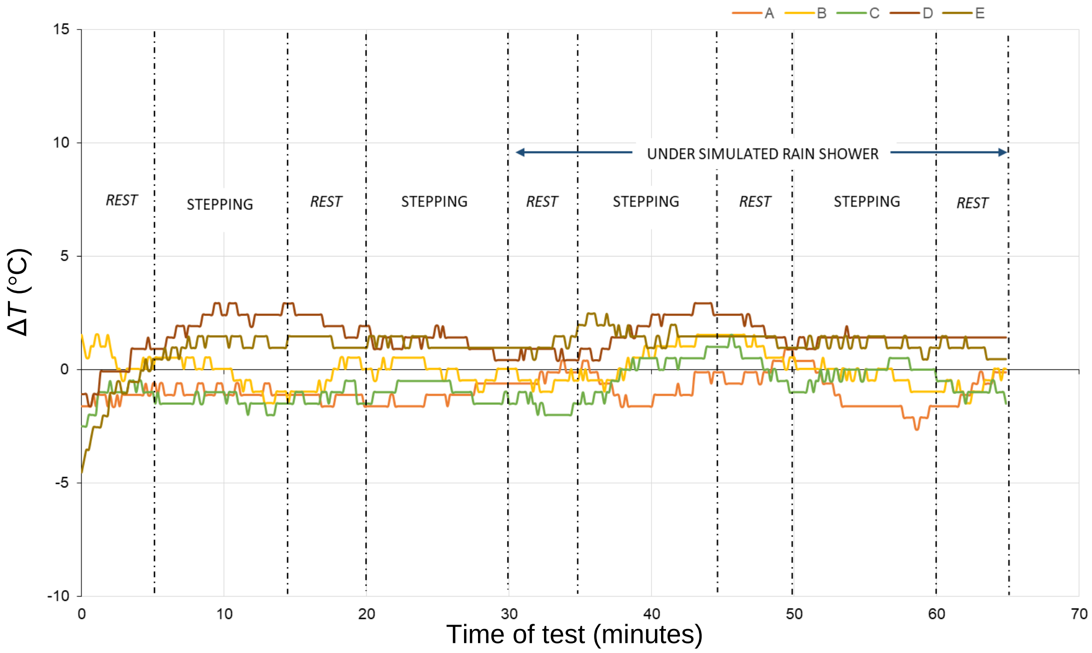
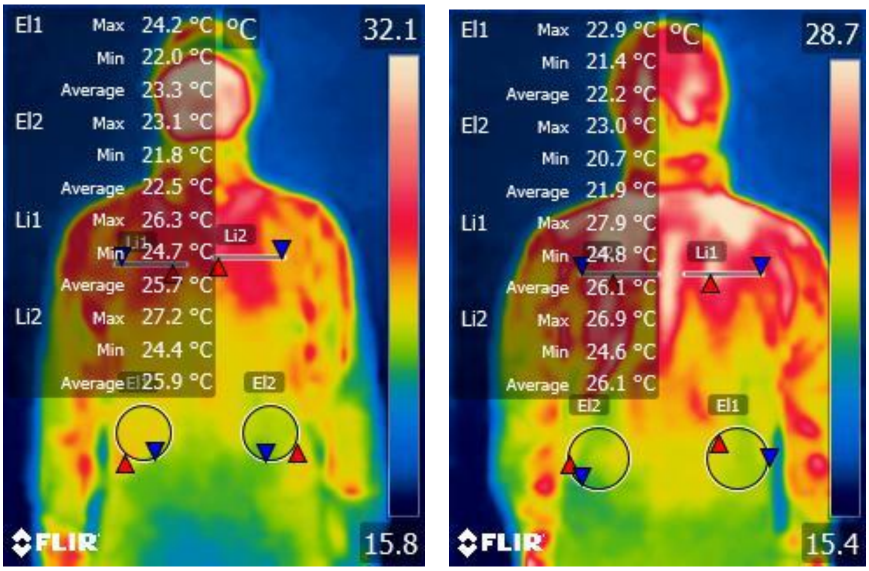


Figure 8.19: Subject three - Temperature difference (Δ*T*) between the two sides of the split jacket.

Table 8.7: Subject three - Temperature under the outer layer in dry conditions and simulated rain.

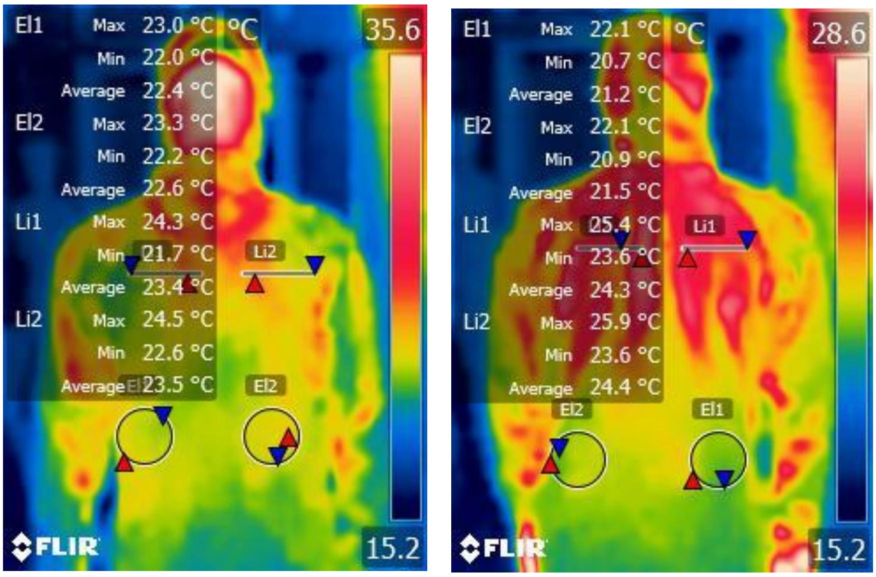
Sensor positioning	Temperature (ºC) at end of first stepping period	
	Dry	Simulated rain
A1	31	26
B1	33	28
C1	31	26
D1	26	23
E1	30	26
A2	30	26
B2	32	30
C2	30	27
D2	29	26
E2	32	28

Thermal imaging calculated a Δ*T* < 0.3 ºC between the two sides of the jacket after the first stepping period in dry conditions and under the simulated rain shower (Figure 8.20). The outer fabric face was calculated to be up to 2 ºC lower under simulated rain than in dry conditions (Figure 8.20). However, unlike data collected from the other subjects, this was not consistent across all calculated points.



(a)

ΔtA= +0.2 ºC; **Δ**tB = -0.8 ºC **Δ**tA= 0 ºC; **Δ**tB= -0.3 ºC



(b)

ΔtA= +0.1 ºC; **Δ**tB = +0.2 ºC **Δ**tA= +0.1 ºC; **Δ**tB = +0.3 ºC

Figure 8.20: Thermograms of subject three after (a) first stepping period in dry conditions and (b) after first stepping period under simulated rain.

In the simulated rain, relative humidity within the clothing microclimate was greater than in dry conditions after the first stepping period (Table 8.8). This, as with the other test subjects, was observed on both sides of the jacket due to the lower saturation vapour pressure due to the lower temperature and inhibited transfer of moisture vapour because of the high ambient water vapour concentration.

Table 8.8: Subject three - Relative humidity under the outer layer in dry conditions and simulated rain.

Sensor positioning	**RH (%) at end of first stepping period**	
	Dry	**Simulated rain**
A1	93	100
B1	84	94
C1	89	96
D1	68	86
E1	95	100
A2	91	100
B2	81	92
C2	83	94
D2	71	85
E2	95	99

The high ambient water vapour concentration during the simulated rain and increased moisture vapour within the clothing system resulted in a decreased driving force during the simulated rain testing period (Figure 8.21). The driving force on the untreated side of the jacket fluctuated greatly compared to the treated side of the jacket. This was ascertained to be due to the build-up of moisture vapour within the clothing after stepping periods with transfer to the environment inhibited by wet fabric.

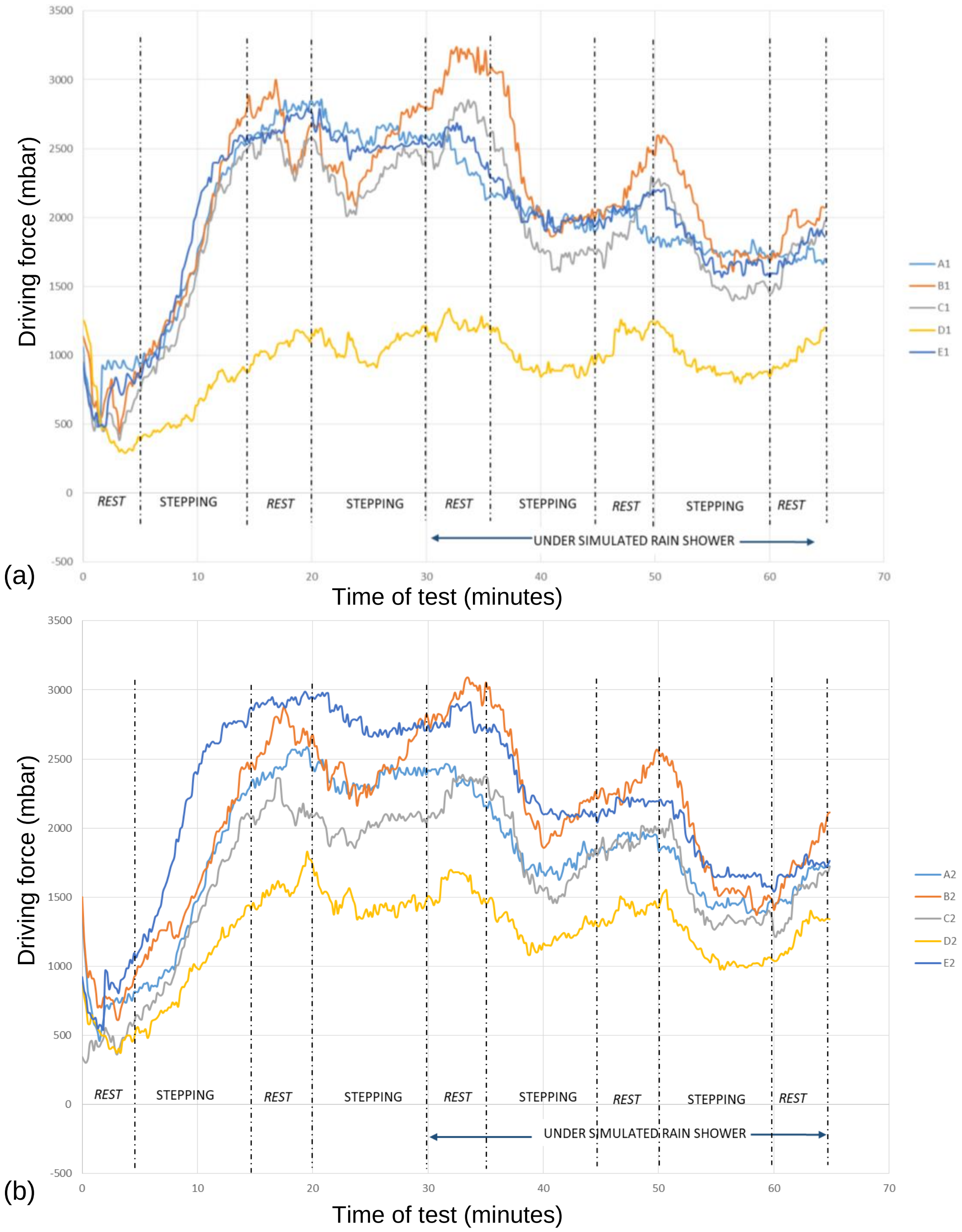


Figure 8.21: Subject three - Driving force across the outer layer: a) Untreated side of the jacket; b) Long SFP (C8) DWR side of the jacket.

8.3.4.6 Subject four

Temperature fluctuated with rest and stepping periods (Figure 8.22). Unlike subjects 1 and 2, the inner temperature between the two sides did not differ at most sensor positions. Only at sensor positioning C1/C2 was the temperature lower on the untreated side of the jacket compared to the treated side.

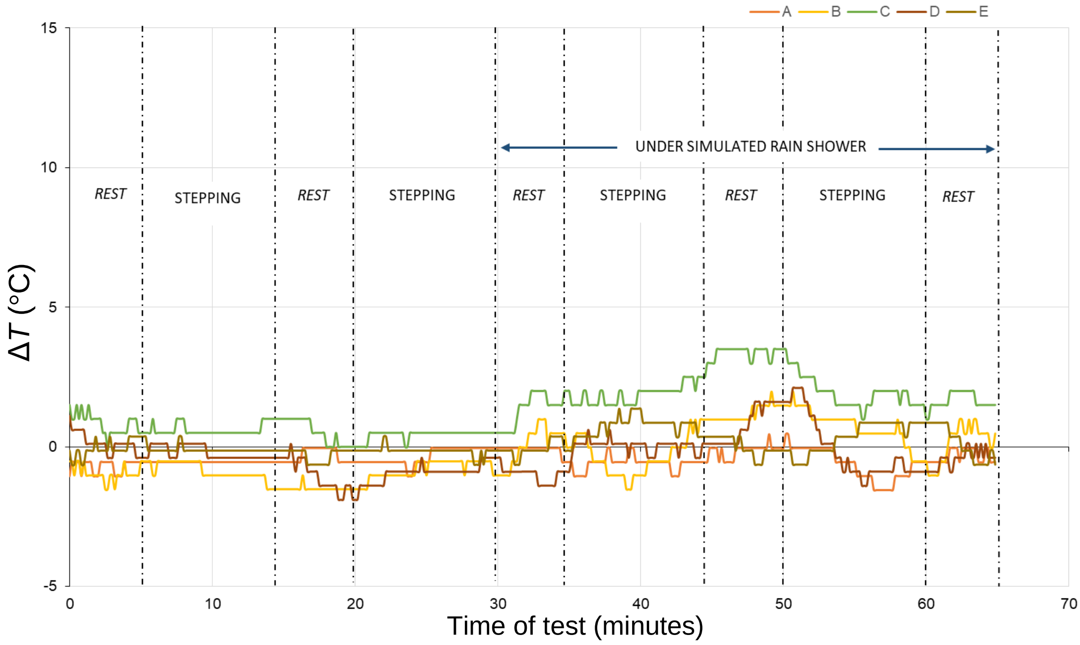


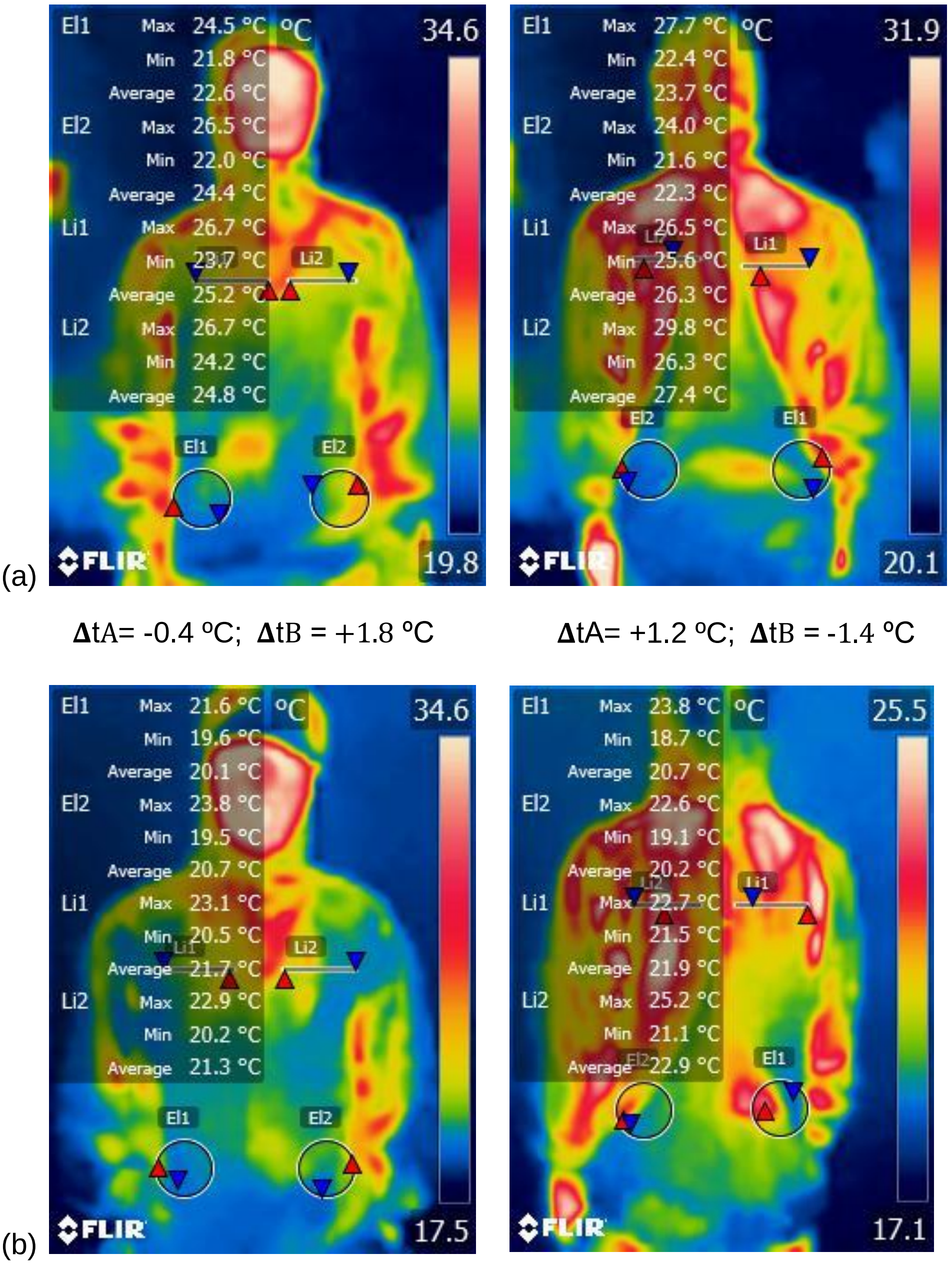
Figure 8.22: Subject four - Temperature difference (Δ*T*) between the two sides of the split jacket.

After the first stepping period, the temperature within the outer layer was lower in rain conditions than in dry conditions (Table 8.9). However, the temperature difference was less than observed from other test subjects' data.

Table 8.9: Subject four - Temperature under the outer layer in dry conditions and simulated rain.

Sensor positioning	Temperature (ºC) at end of first stepping period	
	Dry	Simulated rain
A1	32	29
B1	36	32
C1	33	30
D1	28	26
E1	31	28
A2	31	29
B2	34	33
C2	34	33
D2	28	26
E2	31	28

Thermal imaging showed little difference, ΔT ≤1.8 ºC, between the two sides of the split jacket, after first stepping period in dry conditions and under simulated rain (Figure 8.23). Temperature on the outer fabric decreased under rain conditions by 2.1-4.5 ºC (Figure 8.23).This was due to the wetting of the outer fabric face and accumulation of rain water cooling this side of the garment.



ΔtA= -0.4 ºC; **Δ**tB = +1.8 ºC

ΔtA= +1.2 ºC; **Δ**tB = -1.4 ºC

ΔtA= -0.4 ºC; **Δ**tB = +0.7 ºC

ΔtA=+1.0 ºC; **Δ**tB = -0.5 ºC

Figure 8.23: Thermograms of subject four after (a) first stepping period in dry conditions and (b) after first stepping period under simulated rain.

A greater relative humidity was observed within the outer layer under simulated rain than in dry conditions (Table 8.10). The RH values observed for this test subject were lower than for other test subjects. This and lower temperatures resulted in a lower water vapour pressure.

Table 8.10: Subject four - Relative humidity under the outer layer in dry conditions and simulated rain.

Sensor positioning	RH (%) at end of first stepping period	
	Dry	Simulated rain
A1	43	61
B1	39	68
C1	39	62
D1	50	67
E1	38	71
A2	42	59
B2	38	46
C2	38	47
D2	50	65
E2	44	63

Overall, the driving force was lower than observed for other test subjects (Figure 8.24). Unlike other test subjects, the driving force increased during wet conditions. This increased difference between the water vapour concentration in the ambient air and the water vapour concentration within the clothing system did not encourage the build-up of moisture vapour.

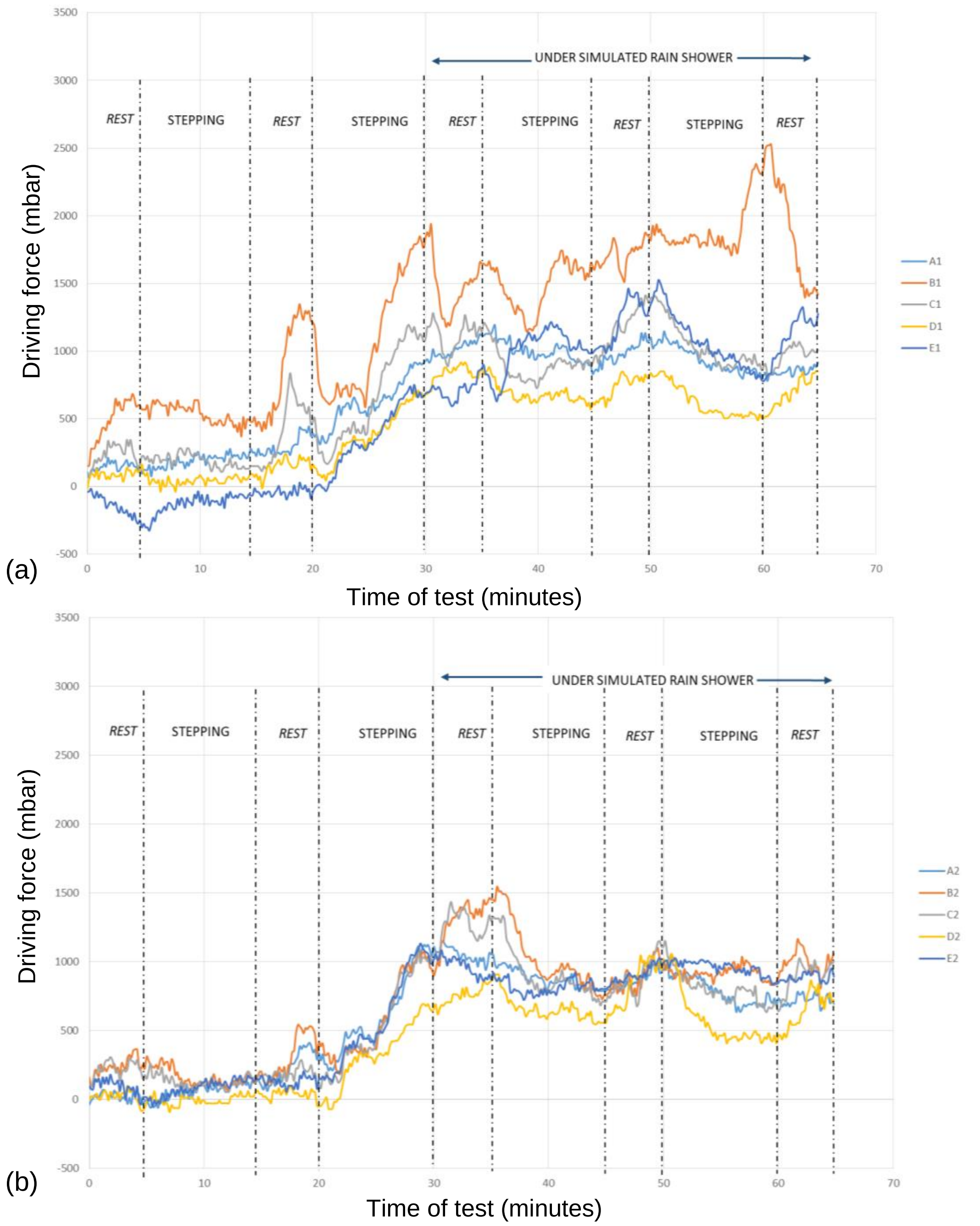


Figure 8.24: Subject four - Driving force across the outer layer: a) Untreated side of the jacket; b) Long SFP (C8) DWR side of the jacket.

8.3.5 Summary

Wearer trials under simulated rain allowed further testing to be carried out. Overall trends observed were the decreased temperature of the outer layer and a greater relative humidity underneath the outer layer under the rain conditions, compared to dry testing conditions [304]. This suggests that in simulated rain moisture vapour transfer rates fell due to the decreased driving force, seen on all subjects apart from subject 4, because of the increased water vapour concentration in the ambient environment [295].

The use of data logging sensors and thermal imaging allowed data collection by two methods; however further thermal imaging at frequent stages during testing could have further shown if heat loss was continuous over the testing period and at which point this change occurred.

8.4 Conclusions

Wearer trials in the field and under simulated rain have been carried out. Data from two test subjects in the initial field trials showed inconclusive trends on the effect of rainy conditions on the relationship between the DWR and moisture vapour transmission. The additional variable of wind is thought to have contributed to bellows ventilation affecting moisture vapour exchange within the clothing system to the environment. This forced convection is most likely to have been down the side of the jacket with arm movement affecting data.

Wearer trials under simulated rain allowed a greater number of test subjects and testing under conditions with less weather variables. Whilst differences between the two sides of the jacket were not seen, the wearer trials allowed a comparison between dry and rain conditions.

Overall observations were:

- A cold ‘wall’ was created at the outer fabric face by the simulated rain and accumulating rainfall. This in turn decreased the temperature under the outer layer compared to during dry conditions.
- Wet fabric leads to a build-up of moisture vapour within the clothing system which inhibits transfer through the fabric interstices. Therefore an efficient DWR prevents fabric wetting and this occurring [295].

- A difference in heat loss between the treated and untreated side could not be determined and therefore understanding the role of a DWR in terms of heat loss requires further research.
- A greater understanding of heat loss could be determined by calculating the next to skin temperature and therefore the driving force across the clothing system in its entirety.

8.5 Limitations

Split jackets are commonly used in field trials to assess the functionality of two fabrics simultaneously. However, for this study, this was the primary limitation as an equilibrium within the microclimate could not be established due to the split design. Is it thought that the microclimate between the base layer and outer jacket, where sensors were located, was never at a steady constant and there was interference between the untreated side of the jacket and the treated side of the jacket.

Further work would involve design and production of a number of testing jackets made from untreated fabric and DWR treated fabric separately. This would avoid the issue of the inconsistent microclimate and clarify testing.

A greater number of test subjects, collecting metabolic data, would have helped to understand the physiological impact on observations and data. In addition, a greater number of test hours would have led to a larger body of data and evaluation assessing whether observations seen within this study were consistent.

Chapter 9 - Conclusions and suggested further work

As discussed in the literature review, criticism and legislation on long SFP (C8) DWRs has driven a substitution process to shorter SFP (C6) DWRs and non-fluorinated DWR alternatives. Seeking alternative chemistries with equivalent functionality demonstrated by long side-chain fluorinated polymeric chemistries has been ongoing for almost a decade. DWRs are a formidable necessity for the shell category within outdoor clothing. Whilst this clothing category has been a focus within this work, it has also addressed the wider scope of DWRs, the application and durability of the chemistry within the textile and apparel sector.

Data collection from Chapter 2 highlighted the consumers use of liquid repellent outdoor apparel, environmental conditions it is worn within and consumer laundering practises. Water repellency was considered to be most important by respondents, followed by fit, breathability, durability and wind resistance. Stain resistance and dirt or oil repellency were not ranked as important by respondents. Chapter 3 showed varied information is given on product labelling and laundering advice from brands online. From both care labels and online information, a wash temperature of 30°C or 40°C was most commonly recommended. Whilst tumble drying and ironing were recommended, advice on heat setting or time was rarely given. Data from Chapter 2 and Chapter 3 was used to inform the variables within subsequent laboratory investigation.

Chapter 4 provided an assessment of repellent functionality provided by fluorinated and non-fluorinated DWR chemistries on outdoor apparel woven fabrics. Publication of this practise-led study was the first specifically addressing the use of fluorinated chemistries within the outdoor apparel and potential substitution chemistries [214]. The use of hydrocarbon hyper-branched structural chemistries is widely spread in non-fluorinated DWR alternatives and are being utilised by brands.

From this study, it was identified that the surface energy of DWR surfaces cited in literature differ when applied to textiles. With this, care should be taken when consulting information on non-fluorinated DWRs without subsequent testing to confirm repellent functionality. Non-fluorinated DWRs provide sufficient water repellency, but lesser than fluorinated DWRs, with no oil repellency. Whilst shorter SFP (C6) DWRs are a good equivalent substitution for the water, aqueous and oil repellency provided by long SFP (C8) DWRs, a move to non-fluorinated DWRs would need to considered case by case assessing the impact during garment manufacture and during end use, along with durability, as discussed in subsequent chapters.

Chapter 5 sought to evaluate the influence of washing and drying/heat application on the durability of DWR functionality. Data from Chapter 2 and Chapter 3 informed the washing variables used within the experimental method. For fluorinated DWRs, ironing is recommended as the optimal laundering practise to sustain liquid repellency, and the surface mechanisms attributing to this have been explained. For non-fluorinated DWRs, a specific laundering practise was not determined and longevity of repellency will decrease due to organisational differences in the chemical structure. Further understanding on the implications of heat on silicone-based DWRs is required along with evaluating other wash variables such as detergents, time and aftercare products.

AATCC 22-2014 (BS EN 4920:2012) spray test is used extensively to determine water repellency and is relied upon by the industry to comparatively evaluate non-fluorinated DWR functionality. Chapter 6 has addressed the limitations of the spray test by 1) using dynamic analytical determination of liquid repellency; 2) evaluating the Bundesmann rain-shower tester (BS EN 29865:1993/ISO 9865:1991) in relation to the spray test; and 3) modifying the existing spray test method. Whilst there is an increased interest, amongst the textile industry, in using the Bundesmann to determine water repellency, no correlation was determined between data from the Bundesmann and data from the spray test. It is recommended that the existing spray test method is extended in duration, as a cost effective modification to allow greater discrimination between DWR fabrics initially showing similar liquid repellency.

Chapter 7 has evaluated the durability of fluorinated and non-fluorinated DWRs to abrasion, simulating consumer end use with abrasives replicating consumer wear as discussed from consumer data in Chapter 2. Whilst a difference was not seen between fluorinated and non-fluorinated DWRs, abrasion to rocky terrain and adjacent rubbing to apparel have been evaluated as factors reducing liquid repellency during consumer use. Modification to the Martindale test method are proposed for future use subject to further work considering wet and cold environments and correlation to field trials.

Chapter 8 investigated the effect of a DWR on thermophysiological comfort. A difference between untreated fabric and treated long SFP (C8) DWR fabric was not determined. Within rainy conditions, moisture vapour was seen to increase within the clothing system with transfer inhibited due to the low driving force across the outer fabric.

Throughout this work, the mass increase, Δm, (g) has been calculated to determine the wetting of the fabric face by water quantitatively in the spray test method. This has allowed a greater discrimination between samples, particularly seen after the extended spray test (Chapter 6). It is recommended that this calculation is adopted when using the spray test to aid selection of non-fluorinated DWRs. Additionally, the AATCC 22-2014 rating scale has been modified and used throughout this work allowing greater discrimination during qualitative evaluation.

The main outcomes of this work are:

- Whilst alternatives to fluorinated DWR chemistries continue to be developed, due to the properties of carbon-fluorine chemistry and structural configuration, equivalent repellency from alternative chemistries have not be found.

- The important role that laundering and drying/heat application can play as an approach to maintain liquid functionality during consumer end use.
- The necessity to develop communication with the consumer on laundering and to further understand whether alternative DWR chemistries are sufficient for end-use.

9.1 Current outlook

Over the course of this research, concerns on sustainability issues within the manufacture of outdoor apparel industry have risen. The decline in visibility due to globalisation of the manufacturing supply chain has complicated visibility of production making chemical management difficult. Differing regional regulations on chemical use during manufacture as well as legislation for sale of goods have made chemical administration challenging. Problem shifting to different geographical areas, chemical management and chemical compliance are of key concern especially considering the time periods of seasonal clothing development, manufacture and sales drivers.

A period of change, awareness of corporate social responsibility and progressively open discussion has occurred, and continues. This dialogue and awareness has opened in response to legislation and development of both academic literature and publicity discussing sustainability within the textile and apparel industry as a whole. CSR reports from individual brands have become core foundations of business practise providing transparency and traceability on compliance and societal awareness. Chemical compliance is managed by production and manufacturing certification and restricted substances lists (RSLs) with due diligence of upmost importance as good working practise across all sectors. The concerns, criticism and substitution process of fluorinated repellent chemistries for textiles is one part of a larger issue on corporate social responsibility.

9.2 Suggested further work

This thesis has highlighted three main areas of further study:

1. Laundering of repellent fabrics to maintain functionality
2. Effect of repellency on breathability
3. Long-term functionality and life cycle of non-fluorinated DWR chemistries

1. The consumer laundering process includes a number of variables. This study has indicated further work should be carried out to determine the influence of different detergents, the effect of wash temperature and wash duration on repellent functionality over washing. Furthermore, further work could be carried out to understand the surface mechanisms of non-fluorinated DWR chemistries under differing drying/heat conditions.
   Use and application of reproofing products remains an area of further research. This would be a large-scale investigation considering the variety of reproofing formulations on the market and the comprehensive enquiry needed to understand the interaction between reproofing chemical products and the DWR remaining on the textile surface. However, this is greatly important to understand the potential binding of reproofing products on ‘new’ non-fluorinated DWR textile finishes to sustain repellent functionality during end-use.
2. The wearer trials have indicated the impact of a DWR in dry and rainy environments on moisture vapour transfer. Conclusive differences between the treated and untreated sides of the jacket were not determined in this study. Further work to determine the role of a DWR on thermoregulation and moisture vapour transfer is required, specifically considering the move to non-fluorinated DWRs in which there is currently no research on the potential effects on wearer comfort. Further comparative work to investigate potential differences between

fluorinated and non-fluorinated DWRs is essential to support the substitution to non-fluorinated chemistries by outdoor brands. Under high intensity activity in rainy conditions, an effective DWR is required to prevent wetting of the fabric face inhibiting moisture vapour transfer promoting build up and formation of condensation [295]. Therefore it is recommended that further research is carried out to evaluate the effect of changing DWR chemistry on wearer comfort and moisture vapour transfer.

3. Further work is required to establish the long term functionality of non-fluorinated repellent chemistries. This would provide further information to the outdoor industry aiding a substitution to non-fluorinated DWR chemistries. A thorough understanding on weathering, biodegradability and disposal, potential routes of degradation and emissions and life-cycle analysis of non-fluorinated repellent chemistries would provide information and comparative resources to brand substitution rather than further problem shifting.

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Appendix

A.1 Qualitative data from focus groups

Table A.1.1: Qualitative data from two focus groups. Focus group one was with the University of Leeds' Union Hiking Club and focus group two was with Leeds based hiking club 'Take a Hike'.

		Focus group one – qualitative comments	**Focus group two – qualitative comments**
Expectations of repellent apparel	Waterproofing	*Thinking about how long the waterproofing will last for.*	*Waterproofing I tend to just go for GoreTex so long as it says that on it I just assume that it's going to be relatively waterproof.*
	Affordability	*Go for the best I can afford.*	
The relationship between price and functionality		*...price reflects the quality. Cheap stuff that is waterproof but not breathable, effectively wearing a bin bag.*	*You get what you pay for. Something cheap is not going to be as good.*
		Are the treatments all the same anyway...is there a cheap to expensive DWR anyway or are they just all the same? If you got a £400 jacket I'd expect it to be treated with the same stuff as another one.	
Weather conditions		*Expect waterproof to just work; Depends on how windy it is; Always will get wet from sweat; Torrential rain - would not expect to come back absolutely dry; Wear a waterproof when it is raining, heavy rain, difference between drizzle and rain.*	*Get wet from perspiration; In really bad weather will get wet through the zip or down the arms; wear a waterproof jacket when it is cold.*
Technology and DWR chemistry		*There is not enough user information, and options. Different technology, lack of information.*	*Mud and staining would reduce the waterproofness.*
		GoreTex has the evidence to back it up. Based on recommendation.	*Each brand needs information, hydrostatic head rating about how waterproof it is and a*

			breathability rating so you can compare jackets together.
		GoreTex is more breathable.	*...they don't compare them by the same standards. There is nothing to do a direct comparison.*
		Not one place to compare fabrics and technology.	
		...your safe option is GoreTex.	
'Green' chemistry		*Chemicals killing off the environment.*	
Aftercare	Particular brand used	*I think it depends on the fabric. Whether it's been roughed up and then re-proofed.*	
		I like my waterproofs to bead, if they don't bead then they aren't waterproof.	
	The use of heat in laundering	*Have to check which garments can be subjected to heat. It's never been explained.*	*I'll try the radiator but I'm not going to take an iron to it.*
		Something about heat activation don't you, in a tumble drier..?	

A.2 Consumer survey questions

The following information was given on the first page of the online survey with questions asked following:

The survey will ask about your outdoor clothing, focusing on waterproof jackets. It aims to understand your preferences when buying water repellent clothing and to gain an insight into how you care and maintain your water repellent clothing. This survey will take approximately 10 minutes to complete. Participation is voluntary and can be withdrawn at any time by closing your web browser. By clicking 'next' you are agreeing to anonymously participate in this project and for the information you give to be used, and held, for the duration of this project and by the outdoor clothing sector.

Philippa Hill is a PhD student at the University of Leeds within the School of Design researching outdoor clothing. The project aims to understand your requirements for water repellent clothing and how these products can be developed sustainably. This research project is being supported by the European Outdoor Group who are seeking to improve the communication between brands and consumers, working in cooperation with brands and the outdoor industry to bring a cohesive approach to the sector. Data collected from this survey will be utilised by the industry to highlight your requirements and uses and to understand how best to communicate environmental issues to you. We are progressively aware of our environmental impact and this survey data will influence product development. Previous research work has suggested a communication gap between brands and consumers – this survey aims to bridge this.

Thank you for your interest and time in completing this survey. The following questions will ask about your recreational activities, your purchasing and care and maintenance of clothing.

Please only complete this survey once and please note you must be over 16 years of age to participate. Within the survey you will be asked about your waterproof jacket. This is occasionally referred to as a 'hard shell', 'cagoule' or 'anorak'. Please note that 'waterproof jacket' refers to all outer wear that is used to resist the rain and worn during outdoor recreational activity. For this study 'waterproof' will be defined as the ability of the jacket to resist rain, and water pressure, when you typically wear the jacket.

Table A.2.1: Consumer survey questions

Question no.	**Question**	**Answer selection**
1.	Country of residence	
1.	Please give your age (years)	
3.	Please state which you identify as:	Male; Female; Prefer not to disclose
4.	Where did you find out about this survey?	Through social media; Within store/retailer; Through word of mouth; Magazine; At a conference/presentation; Brand/organisation website; On a web blog; Directly from the researcher; Other
Participation		
5.	On a monthly basis how often do you participate in purposeful physical outdoor recreational activity, including casual weekend walks?	Not at all; Less than once per month; Once or twice per month; 3-5 times per month; 6-10 times per month; 11-20 times per month; 21-30 times per month; Everyday
6.	What would you consider to be your main recreational outdoor activity?	Walking, hiking, trekking, mountaineering, hill walking; Dog walking, casual activity, weekend stroll; Climbing, caving, bouldering; Cycling, running, trail running; Skiing, snowboarding; Sailing, canoeing, kayaking; Other; I do not participate in outdoor activity
7.	Do you belong to an outdoor recreational club, society or group? (excluding gym membership)	Yes; No
8.	How many waterproof jackets do you own?	I do not own a waterproof jacket; One jacket; Two-five jackets; Five-ten jackets; More than ten jackets
Weather conditions and your clothing		
9.	Choose the worst weather you are willing to go out in for recreational activities	Heavy rain; Light rain; Overcast but dry; Summer, warm conditions; Calm, dry weather; Heavy snow; Light snow
9a.	Please choose the weather conditions that you are typically out in for recreational activities	All weathers (including rain and snow); All conditions apart from heavy rain; All conditions apart from snow; Calm, dry weather; Summer, warm conditions

9b.	How many times per year are you doing outdoor recreational activities in the rain?	Not at all; Once or twice a year; Less than 5 times; 6-10 times; 11-15 times; 16-20 times; more than 20 times yearly
10.	The waterproof jacket that you currently use the most, how much did it cost?	Less than £50; £51-100; £101-150; £151-200; £201-250; £251-300; £301-350; £351-400; Over £401
10a.	Please give the brand of your jacket	
10b.	How long have you owned the jacket for?	Less than a month; 1-3 months; 4-6 months; 7-12 months; 1-2 years; 3-5 years; 6-10 years; 11-20 years; over 20 years
10c.	How long (hourly) per month do you wear your jacket?	0-2 hours; 3-8 hours; 9-15 hours; 16-25 hours; 26-35 hours; more than 36 hours
10d.	Do you usually wear a rucksack, climbing harness or similar on top of your jacket?	Yes rucksack; Yes harness; Yes other; Yes rucksack and harness; No
Purchasing		
11.	When purchasing a new waterproof jacket which factors do you consider to be important? Please rank the following properties using the scale where (1) is very important and (5) is unimportant	Weight; Colour; Fit; Water repellency; Stain resistance; Brand; GoreTex; the labelling; Price; Durability; Fabric technology; Wind resistance; Breathability; Dirt and oil repellency; The retailers' help/sale; Easy care properties; Reviews; The shop/retailers; Care and laundering procedure; Chemicals that are used
Aftercare		
12.	Have you ever asked for advice on caring and maintaining your waterproof jacket?	Yes; No
12a.	Where would you ask, or look, for information and advice on re-proofing and caring for your waterproof jacket?	Social media; Retailers; Clothing labels; Swing tags; Re-proofing brand websites; Friends; Brand websites; Other
13.	Do you clean your waterproof jacket?	Yes, in biological detergent; Yes, in non-biological detergent; Yes, but I do not know what with; No; Non-detergent cleaner/soap
13a.	Do you re-proof your jacket with a specialised re-proofing product?	Yes; No; I don't know
13ai.	What is the brand of the re-proofing treatment you use?	
13aii.	How often do you use the re-proofing product?	Once or more a month; A few times a year; Once a year; Less than once a year; Depending on use; Before a substantial amount of activity or trip

13aiii.	Do you follow the instructions on the re-proofing product and given by the re-proofing brand?	Yes, precisely; No, find advice on the Internet and blogs; No, follow advice from friends; No not at all; No, follow the advice given by the brand of the garment; Sometimes; Other
13b.	Do you use heat, for example tumble drying or ironing, after the wash process?	Yes ironing; Yes tumble drying; No; Sometimes
14.	Which factors do you consider important in an environmentally friendly waterproof jacket?	Low energy production; Price; Limited chemical use; Recycled materials; Repairable product; The brand; Colour; The water use; Ethically sourced; Non-toxic chemicals; Functionality to not be lessened

A.3 Fabric characterisation

Characterisation was completed as detailed within Chapter 4. The fabric samples supplied specifically for the study were samples C, M, V and Y. Fabrics Y and Z were untreated samples.

Table A.3.1: Characterisation of the repellent fabrics used within the study.

Sample ID	DWR: Long SFP (C8), shorter SFP (C6) or non-fluorinated	Specific chemistry (where known)	Mass (gsm)	Fabric thickness (mm)[a]			Fabric face structure	Warps and Wefts (per cm)	Fibre type	Yarn type	Number of layers	Membrane or laminate	Backing fabric structure	Warps and wefts (per cm)	Yarn type	Fibre type
				Under 2g cm^{-2} (T) pressure	Under 100 g cm^{-2} (T) pressure	Fabric surface thickness (ST)[b]										
A	C8	-	239.5	0.655	0.613	0.04	Plain weave	50 x 40	100% PA	Non-texturised	2	-	Jersey plain knit	30 x 19	Non-texturised	100% PES jersey
B	C8	-	146.8	0.310	0.287	0.023	Twill weave: 2 x 1	66 x 70	100% PA	Non-texturised	3	eVent membrane	Tricot warp knit	15 wales x 21 courses	-	100% PA
C[c]	C8	-	165.4	0.219	0.207	0.012	Twill weave: 2 x1	52 x 36	100% PES	Non-texturised	2.5	2.5 layer hydrophilic membrane	-			
D	C6	-	135.9	0.219	0.193	0.027	Plain weave	52 x 32	100% PA	Non-texturised	2	PU coating	-	-	-	-
E	C6	-	133.6	0.348	0.312	0.036	Plain weave	48 x 46	PA/elastane	Non-texturised	1	-	-	-	-	-

F	C6	-	47.1	0.085	0.075	0.009	Plain weave ripstop	60 x 64	100% PA	Non-texturised	1	Cire coating	-	-	-	-
G	C6	-	53.4	0.049	0.041	0.008	Plain weave ripstop	78 x 57	100% PA	Non-texturised	1	Acrylic coating	-	-	-	-
H	C6	-	50.2	0.036	0.030	0.006	Plain weave ripstop	50 x 50	100% PA	Non-texturised	1	Coating	-	-	-	-
J	C6	-	77.2	0.123	0.106	0.016	Plain weave ripstop	67 x 52	100% PA	Non-texturised	2	Membrane		-	-	-
K	C6	-	121.8	0.261	0.245	0.016	Plain weave	52 x 56	100% PA	Non-texturised	3	eVent membrane	Tricot warp knit	15 x 18	Non-texturised	Polyamide scrim
L	C6	-	193.3	0.380	0.358	0.021	Plain weave	82 x 42	96% PA 4% Elastane	Non-texturised	3	Membrane	Jersey plain knit	26 x 24	Non-texturised	
M[c]	C6	-	167.4	0.238	0.226	0.011	Twill weave: 2 x1	56 x 40	100% PES	Non-texturised	2.5	2.5 layer hydrophilic membrane	-			
N	Non-fluorinated	Fat modified resin	136.9	0.211	0.192	0.019	Plain weave	52 x 32	100% PA	Non-texturised	2	PU coating	-	-	-	-
O	Non-fluorinated	-	139.5	0.373	0.320	0.054	Plain weave	48 x 48	PA/elastane	Non-texturised	1	-	-	-	-	-
P	Non-fluorinated	Dendrimers with PU backbone	54.6	0.093	0.076	0.017	Plain weave	42 x 68	100% PA	Non-texturised	1	-	-	-	-	-
Q	Non-fluorinated	Dendrimers with PU backbone	121.5	0.250	0.221	0.029	Twill weave	37 x 51	100% PES	Non-texturised	2	PU membrane	-	-	-	-

R	Non-fluorinated	Dendrimers with PU backbone	138.5	0.190	0.176	0.014	Plain weave	30 x 40	65% PA, 35% PES	Non-texturised	2	PU coating	-	-	-	-
S	Non-fluorinated	Dendrimers with PU backbone	198.0	0.631	0.581	0.050	Plain weave	47 x 42	100% PES	Non-texturised	3	Membrane	Jersey plain knit	20 x 20	Non-texturised	
T	Non-fluorinated	Dendrimers with PU backbone	222.5	0.541	0.494	0.047	Plain weave ripstop	50 x 46	100% PA	Non-texturised	3	Membrane	warp knit	18 x 20	Non-texturised	
U	Non-fluorinated	Dendrimers with PU backbone	138.5	0.327	0.296	0.031	Plain weave	48 x 54	85% PA, 15% elastane	Non-texturised	1	-	-	-	-	-
V [c]	Non-fluorinated	Dendrimers	165.1	0.203	0.193	0.010	Twill weave: 2 x 1	58 x 36	100% PES	Non-texturised	2.5	2.5 layer hydrophilic membrane	-			
Y [c]	Untreated	-	169.4	0.190	0.175	0.015	Twill weave: 2 x 1	50 x 36	100% PES	Non-texturised	2.5	2.5 layer hydrophilic membrane				
Z	Untreated	-	114.6	0.179	0.171	0.008	Plain weave	30 x 24	100% PA	Non-texturised	1	-	-			

[a] Fabric thickness was calculated using a FAST-1 Compression meter under two fixed pressures. Value shown is the mean value of three different specimens measured. [b] Fabric surface thickness (mm) is calculated as the difference between the thickness of the fabric under a pressure of 2 g cm^{-2} and the thickness of the fabric under a pressure of 100 g cm^{-2}. [c] Fabrics *C*, *M*, *V* and *Y* were supplied specifically for the research study with the same fibre type and fabric construction (including number of layers). The only variable between them is the DWR type: *C* a long SFP (C8) DWR; *M* a shorter SFP (C6) DWR; *V* a non-fluorinated DWR; and *Y* an untreated fabric.

A.4 Differences in water repellency between fluorinated and non-fluorinated DWR chemistries

A one-way ANOVA was calculated for the Δ*m val*ues of samples *C, M* and *V* from Chapter 4 to determine the differences in DWR types. These fabric samples only differ in their DWR.

Using univariate analysis, the null hypothesis $H_{0:}$ $\mu_1 = \mu_2 = \mu_3$ that there are no differences among the mean Δ*m* values (mg cm^{-2}) where µ mean of $_1$ is sample *C* (long SFP (C8) DWR), $_2$ is sample *M* (shorter SFP (C6) DWR) and $_3$ is sample *V* (non-fluorinated DWR). The average value of the three specimens was used.

There is statistically significant difference at the 95% confidence level for the three DWR types. Despite this, the mean difference between the groups was small. Post-hoc tests using Tukey HSD test have indicated that the mean score for long SFP (C8) DWR was significantly different to non-fluorinated (Table A.4.3.). However, shorter SFP (C6) DWR was not significantly different from long SFP (C8) DWR (p=0.061) and non-fluorinated (p=0.127) (Table A.4.3.).

Table A.4.1: Descriptive statistics for mean (x̅) Δ*m* values

DWR type	**n**	**x̅**	**σ (Std. Dev)**	**Std. Error**	**95% Confidence Interval for Mean**		**Minimum**	**Maximum**
					Lower Bound	Upper Bound		
C8	3	0.019	0.004	0.002	0.009	0.030	0.016	0.024
C6	3	0.039	0.008	0.004	0.021	0.058	0.034	0.048
Non-fluorinated	3	0.055	0.012	0.007	0.026	0.084	0.042	0.064
Total	9	0.038	0.017	0.006	0.025	0.051	0.016	0.064

Table A.4.2: One-way ANOVA

	Sum of Squares	Error df	Mean Square	F	Sig.
Between Groups	0.002	2	0.001	13.811	0.006
Within Groups	0.000	6	0.000		
Total	0.002	8			

Table A.4.3: Post-hoc testing: Multiple Comparisons – Tukey HSD
Dependent Variable: Δ*m*

DWR type (I)	DWR type (J)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
C8	C6	-0.020	0.007	0.061	-0.041	0.001
	Non-fluorinated	-0.036*	0.007	0.005	-0.057	-0.015
C6	C8	0.020	0.007	0.061	-0.001	0.041
	Non-fluorinated	-0.016	0.007	0.127	-0.037	0.005
Non-fluorinated	C8	0.036*	0.007	0.005	0.015	0.057
	C6	0.016	0.007	0.127	-0.005	0.037

*. The mean difference is significant at the 0.05 level.

A.5 Measurement of iron temperature and tumble drier cycle temperature

The temperature of the iron was calculated as a minimum/maximum range of ten measurements (Table A.5.1) using a Jenway thermometer-model 2003 with thermocouple attachment. The temperature of the 40 minute tumble drier cycle was calculated using three DS1923 iButton hygrochron logger sensors at a 10 second recording interval. Three sensors were used and mean measurements calculated with standard deviation between the three repeat measurements (Figure A.5.1).

Table A.5.1: Temperature of the iron as a mean with minimum and maximum values

Measurements (ºC)	Mean (ºC)	Min/Max (ºC)
160, 137, 154, 135, 172, 170, 154, 180, 190, 168	162	135/190

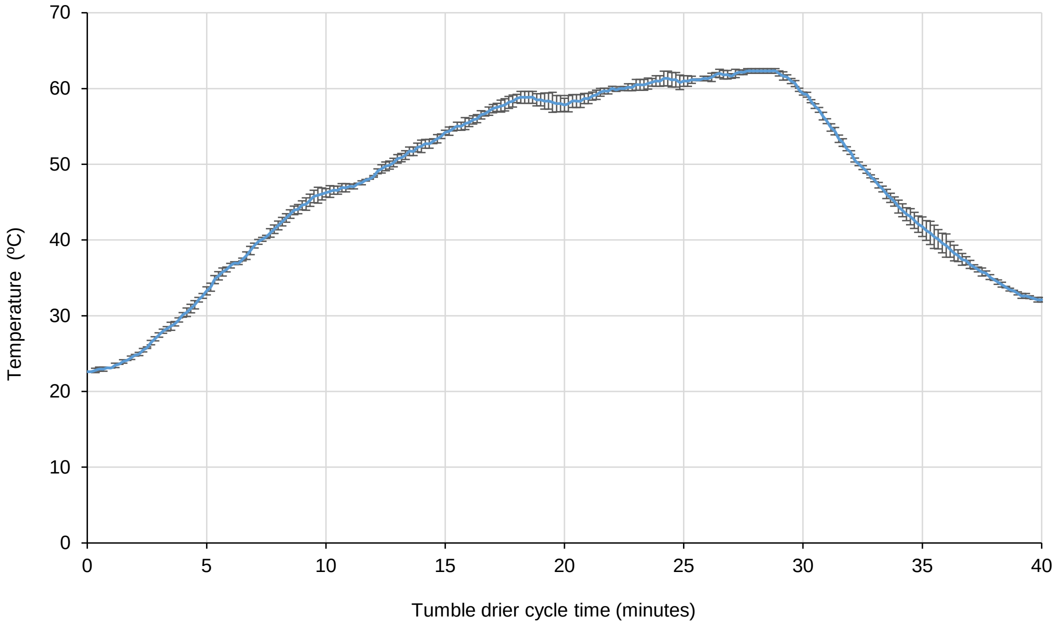

Figure A.5.1: Mean temperature measured over the 40 minute tumble drier cycle.

A.6 Effect of consumer laundering on liquid repellent functionality

Statistical testing was calculated for the weight increase per sample area, Δ*m,* values of samples *C, M* and *V* when washed with soapflakes, from Chapter 5*.* These fabric samples only differ in their DWR.

A.6.1 Repeated measures ANOVA: Δ*m* over ten wash cycles

A mixed between-within subjects repeated measures ANOVA was conducted on fabric samples *C, M,* and *V* at one wash cycle, three wash cycles, five wash cycles and ten wash cycles. This statistical testing was carried out to indicate if there is a statistically significant difference between the different DWRs and drying/heat application. The interaction effect was statistically significant (Sig. <0.0005; Wilks' Lambda). There was also a statistically significant effect for wash (p=0.00) with a very large effect size (partial η^2 = 0.96; Cohen's criterion). There was significantly difference in the Δ*m* between the groups (p<0.0005) with a very large effect size (partial η^2 = 0.72) (Table A.6.1.3).

Table A.6.1.1: Statistics for mean (x̅) Δ*m* values for DWR type and sample ID with drying/heat application. Standard deviation (σ) is for three sample repeats.

Washes	**DWR type**	**x̅ (n=3)**	**σ (n=3)**
One wash cycle	C8-AD	0.11	0.05
	C8-T	0.05	0.02
	C8-IR	0.04	0.02
	C6-AD	0.33	0.09
	C6-T	0.22	0.25
	C6-IR	0.77	0.02
	Non-fluorinated-AD	0.61	0.07
	Non-fluorinated-T	0.43	0.51
	Non-fluorinated-IR	0.12	0.03
	Total	0.22	0.25
Three wash cycles	C8-AD	0.50	0.14
	C8-T	0.10	0.03

	C8-IR	0.28	0.13
	C6-AD	0.48	0.07
	C6-T	0.19	0.13
	C6-IR	0.24	0.07
	Non-fluorinated-AD	0.76	0.09
	Non-fluorinated-T	0.19	0.03
	Non-fluorinated-IR	0.26	0.03
	Total	0.33	0.21
Five wash cycles	C8-AD	0.67	0.13
	C8-T	0.57	0.13
	C8-IR	0.53	0.06
	C6-AD	0.88	0.23
	C6-T	1.05	0.52
	C6-IR	0.54	0.09
	Non-fluorinated-AD	1.03	0.18
	Non-fluorinated-T	1.27	1.06
	Non-fluorinated-IR	0.76	0.22
	Total	0.81	0.43
Ten wash cycles	C8-AD	0.75	0.02
	C8-T	0.71	0.12
	C8-IR	0.65	0.10
	C6-AD	0.82	0.05
	C6-T	0.68	0.09
	C6-IR	0.65	0.04
	Non-fluorinated-AD	0.85	0.07
	Non-fluorinated-T	0.78	0.10
	Non-fluorinated-IR	0.76	0.05
	Total	0.74	0.09

Table A.6.1.2: Multivariate Tests

Effect		Value	F	Hypothesis df	Error df	Sig.	Partial η^2
wash	Pillai's Trace	0.96	120.67	3.0	16.0	0.00	0.96
	Wilks' Lambda	0.04	120.67	3.0	16.0	0.00	0.96
	Hotelling's Trace	22.63	120.67	3.0	16.0	0.00	0.96
	Roy's Largest Root	22.63	120.67	3.0	16.0	0.00	0.96
wash * DWR type	Pillai's Trace	1.33	1.80	24.0	54.0	0.037	0.44
	Wilks' Lambda	0.09	2.39	24.0	47.0	0.005	0.54
	Hotelling's Trace	4.90	3.00	24.0	44.0	0.001	0.62
	Roy's Largest Root	3.87	8.72	8.0	18.0	0.000	0.80

Table A.6.1.3: Tests of Between-Subjects Effects

Source	Type III Sum of Squares	Error df	Mean Square Error	F	Sig.	Partial η^2
Intercept	29.82	1	29.82	603.85	0.000	0.971
DWR type	2.25	8	0.28	5.69	0.001	0.717
Error	0.89	18	0.05			

A.6.2 Effect of drying/heat application on Δm

A two-way between-groups ANOVA was conducted to determine the effect of drying/heat application, Chapter 5. After one wash cycle with soapflakes there was a statistically significant main effect for drying/heat treatment (p=0.028) with large effect size (partial η^2 = 0.327; Cohen's criterion). Post-hoc tests using Tukey HSD indicated that the mean of Δm for air drying was significantly different to ironing (p=0.022), but not between air drying and tumble drying (p=0.393) nor between tumble drying and ironing (p=0.264) (Table A.6.2.3).

Table A.6.2.1: One wash cycle - Statistics for mean ($\bar{x}$) Δm values drying/heat application. Standard deviation (σ) is for three sample repeats.

Heat treatment	**DWR type**	**$\bar{x}$ (n=3)**	**σ (n=3)**
AD	C8	011	0.05
	C6	0.33	0.09
	Non-fluorinated	0.61	0.07
	Total	0.35	0.22
T	C8	0.03	0.01
	C6	0.22	0.25
	Non-fluorinated	0.43	0.51
	Total	0.23	0.33
IR	C8	0.04	0.02
	C6	0.08	0.02
	Non-fluorinated	0.12	0.03
	Total	0.08	0.04
Total	C8	0.06	0.05
	C6	0.21	0.17
	Non-fluorinated	0.38	0.33
	Total	0.22	0.25

Table A.6.2.2: One wash cycle - Tests of Between-Subjects Effects

Source	Type III Sum of Squares	Error df	Mean Square Error	F	Sig.	Partial η^2
Corrected Model	0.942[a]	8	0.118	3.137	0.021	0.582
Intercept	1.272	1	1.272	33.872	0.000	0.653
heat treatment	0.329	2	0.165	4.381	0.028	0.327
DWR type	0.469	2	0.234	6.241	0.009	0.409
heat treatment * DWR type	0.145	4	0.036	0.963	0.452	0.176
Error	0.676	18	0.038			
Total	2.890	27				
Corrected Total	1.618	26				

[a]R^2 = 0.582 (Adjusted R^2 = 0.397)

Table A.6.2.3: One wash cycle Post-hoc testing: Multiple Comparisons -Tukey HSD Dependent Variable: Δm

Heat treatment (I)	Heat treatment (J)	Mean difference (I-J)	Std. error	Sig.	95% Confidence interval	
					Lower bound	Upper bound
AD	T	0.122	0.091	0.393	-0.110	0.355
	IR	0.270*	0.091	0.022	0.037	0.503
T	AD	-0.122	0.091	0.393	-0.355	0.111
	IR	0.148	0.091	0.264	-0.085	0.381
IR	AD	-0.270*	0.091	0.022	-0.503	-0.037
	T	-0.148	0.091	0.264	-0.381	0.085

* The mean difference is significant at the 0.05 level.

After three wash cycles with soapflakes, there was a statistically significant main effect for drying/heat application ($p<0.05$) with large effect size (partial η^2 = 0.861; Cohen’s criterion). Post-hoc tests using Tukey HSD indicated that the Δm for air drying was significantly different to tumble drying ($p<0.05$) and ironing ($p<0.05$), at a 95% confidence level (Table A.6.2.6).

Table A.6.2.4: Three wash cycles - Statistics for mean ($\bar{x}$) Δ*m* values drying/heat application. Standard deviation (σ) is for three sample repeats.

Heat treatment	DWR type	$\bar{x}$ (n=3)	σ (n=3)
AD	C8	0.14	0.14
	C6	0.48	0.07
	Non-fluorinated	0.76	0.09
	Total	0.58	0.16
T	C8	0.10	0.03
	C6	0.19	0.13
	Non-fluorinated	0.19	0.03
	Total	0.16	0.08
IR	C8	0.28	0.13
	C6	0.24	0.03
	Non-fluorinated	0.26	0.03
	Total	0.26	0.07
Total	C8	0.30	0.20
	C6	0.31	0.15
	Non-fluorinated	0.40	0.28
	Total	0.33	0.21

Table A.6.2.5: Three wash cycles - Tests of Between-Subjects Effects

Source	Type III sum of squares	Error df	Mean Square Error	F	Sig.	Partial η^2
Corrected model	1.033[a]	8	0.129	16.426	0.000	0.880
Intercept	3.020	1	3.020	384.264	0.000	0.955
Heat treatment	0.873	2	0.436	55.528	0.000	0.861
DWR type	0.061	2	0.030	3.852	0.040	0.300
Heat treatment * DWR type	0.099	4	0.025	3.163	0.039	0.413
Error	0.141	18	0.008			
Total	4.194	27				
Corrected total	1.174	26				

[a] R^2 = 0.880 (Adjusted R^2 = 0.826)

Table A.6.2.6: Three wash cycles Post-hoc testing: Multiple Comparisons- Tukey HSD Dependent Variable: Δ*m*

Heat treatment (I)	**Heat treatment (J)**	**Mean difference (I-J)**	**Std. error**	**Sig.**	**95% Confidence interval**	
					Lower bound	**Upper bound**
AD	T	0.421*	0.042	0.000	0.314	0.528
	IR	0.322*	0.042	0.000	0.216	0.429
T	AD	-0.421*	0.042	0.000	-0.528	-0.314
	IR	-0.099	0.042	0.072	-0.206	0.007
IR	AD	-0.322*	0.042	0.000	-0.429	-0.216
	T	0.099	0.042	0.072	-0.008	0.206

*. The mean difference is significant at the 0.05 level.

After five wash cycles with soapflakes, a significant difference between the drying/heat application (air drying, tumble drying and ironing) was not indicated at a 95% confidence level (Table A.6.2.9).

Table A.6.2.7: Five wash cycles - Statistics for mean ($\bar{x}$) Δ*m* values drying/heat application. Standard deviation (σ) is for three sample repeats.

Heat treatment	**DWR type**	**$\bar{x}$ (n=3)**	**σ (n=3)**
AD	C8	0.67	0.13
	C6	0.88	0.23
	Non-fluorinated	1.03	0.18
	Total	0.86	0.22
T	C8	0.57	0.13
	C6	1.05	0.52
	Non-fluorinated	0.67	0.06
	Total	0.76	0.35
IR	C8	0.53	0.06
	C6	0.54	0.09
	Non-fluorinated	0.76	0.22
	Total	0.61	0.16
Total	C8	0.59	0.12
	C6	0.82	0.36
	Non-fluorinated	0.82	0.22
	Total	0.74	0.27

Table A.6.2.8: Five wash cycles - Tests of Between-Subjects Effects

Source	Type III sum of squares	Error df	Mean Square Error	F	Sig.	Partial η^2
Corrected model	0.957[a]	8	0.120	2.394	0.059	0.515
Intercept	14.948	1	14.948	299.080	0.000	0.943
Heat treatment	0.288	2	0.144	2.878	0.082	0.242
DWR type	0.321	2	0.160	3.208	0.064	0.263
Heat treatment * DWR type	0.349	4	0.087	1.745	0.184	0.279
Error	0.900	18	0.050			
Total	16.805	27				
Corrected total	1.857	26				

[a] R^2 = 0.515 (Adjusted R^2 = 0.300)

Table A.6.2.9: Five wash cycles Post-hoc testing: Multiple Comparisons- Tukey HSD Dependent Variable: Δm

Heat treatment (I)	Heat treatment (J)	Mean difference (I-J)	Std. error	Sig.	95% Confidence interval	
					Lower bound	Upper bound
AD	T	0.100	0.105	0.617	-0.169	0.369
	IR	0.251	0.105	0.070	-0.018	0.520
T	AD	-0.100	0.105	0.617	-0.369	0.169
	IR	0.151	0.105	0.345	-0.118	0.420
IR	AD	-0.251	0.105	0.070	-0.520	0.018
	T	-0.151	0.105	0.345	-0.420	0.118

After ten wash cycles with soapflakes there was a statistically significant main effect drying/heat application (p=0.003); with a large effect size (partial η^2 = 0.471; Cohen's criterion). Post-hoc tests using Tukey HSD test indicated that air drying was significantly different to ironing (p=0.003) at a 95% confidence level (Table A.6.2.12).

Table A.6.2.10: Ten wash cycles - Statistics for mean ($\bar{x}$) Δm values drying/heat application. Standard deviation (σ) is for three sample repeats.

Heat treatment	DWR type	$\bar{x}$ (n=3)	σ (n=3)
AD	C8	0.75	0.02
	C6	0.82	0.05
	Non-fluorinated	0.85	0.07
	Total	0.81	0.06
T	C8	0.71	0.12
	C6	0.68	0.09
	Non-fluorinated	0.78	0.10
	Total	0.72	0.10
IR	C8	0.62	0.04
	C6	0.65	0.04
	Non-fluorinated	0.76	0.05
	Total	0.67	0.07
Total	C8	0.69	0.09
	C6	0.71	0.09
	Non-fluorinated	0.80	0.08
	Total	0.73	0.09

Table A.6.2.11: Ten wash cycles - Tests of Between-Subjects Effects

Source	Type III sum of squares	Error df	Mean Square Error	F	Sig.	Partial η^2
Corrected model	0.143[a]	8	0.018	3.613	0.011	0.616
Intercept	14.549	1	14.549	2938.163	0.000	0.994
Heat treatment	0.079	2	0.040	8.002	0.003	0.471
DWR type	0.053	2	0.027	5.377	0.015	0.374
Heat treatment * DWR type	0.011	4	0.003	0.536	0.711	0.106
Error	0.089	18	0.005			
Total	14.782	27				
Corrected total	0.232	26				

[a] R^2 = 0.616 (Adjusted R^2 = 0.446)

Table A.6.2.12: Ten wash cycles Post-hoc testing: Multiple Comparisons – Tukey HSD Dependent Variable: Δ*m*

Heat treatment (I)	**Heat treatment (J)**	**Mean difference (I-J)**	**Std. error**	**Sig.**	**95% confidence interval**	
					Lower bound	**Upper bound**
AD	T	0.083	0.033	0.054	-0.001	0.168
	IR	0.131*	0.033	0.003	0.046	0.216
T	AD	-0.083	0.033	0.054	-0.168	0.001
	IR	0.048	0.033	0.342	-0.037	0.132
IR	AD	-0.131*	0.033	0.003	-0.216	-0.046
	T	-0.048	0.033	0.342	-0.132	0.037

*The mean difference is significant at the 0.05 level.

A.7 Correlation between the AATCC and BS EN ISO spray rating

The relationship between the spray ratings used within BS EN ISO 4920:2012 and the spray ratings used within AATCC 22-2014 was determined using Pearson correlation coefficient (Figure A.7.1). A strong positive correlation was determined (*r* = 0.93).

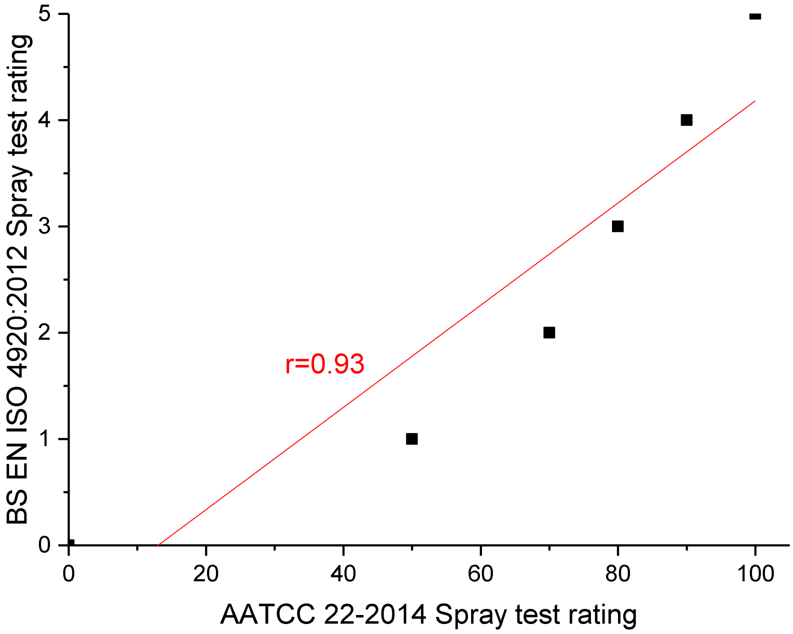

Figure A.7.1: Correlation between the BS EN ISO rating scale and the AATCC rating scale for the spray test method to determine water repellency

A.8 Pearson correlation coefficients between evaluation of wettability by roll off angle and the spray test

Wettability was determined using roll off angle (within the restricted range 0-90°) for samples initially and after one wash cycle, three wash cycles, five wash cycles and ten wash cycles (detailed within Chapter 5). The relationship between roll off angle and Δ*m* (evaluated using the spray test) was investigated using Pearson correlation coefficient. Due to the restricted range of roll off angle determined, roll off angle >90° was omitted from the dataset as an outlier.

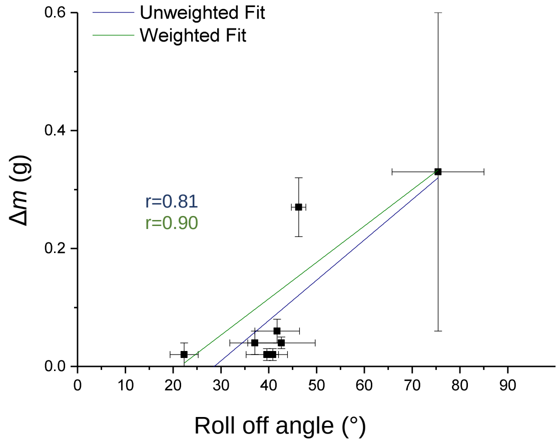

Figure A.8.1: Initial: Pearson correlation coefficient (*r*) between roll off angle and Δ*m* (n=8). Both weighted and unweighted coefficients are given.

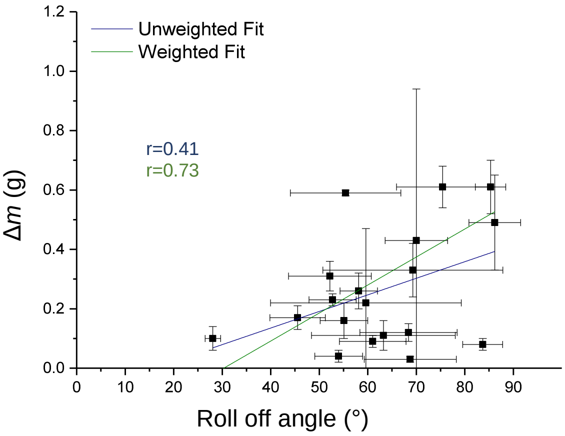

Figure A.8.2: One wash cycle: Pearson correlation coefficient (*r*) between roll off angle and Δ*m* (n=19). Both weighted and unweighted coefficients are given.

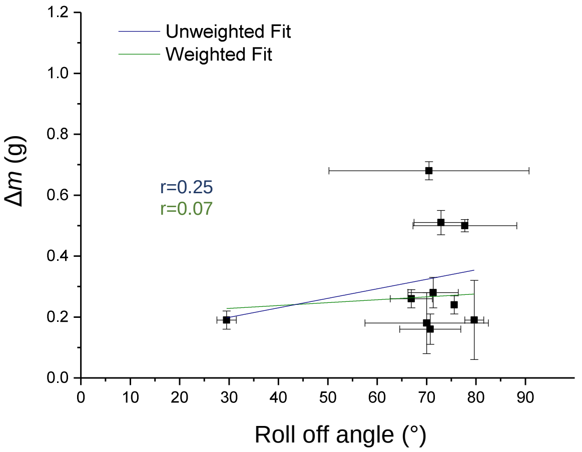

Figure A.8.3: Three wash cycles: Pearson correlation coefficient (*r*) between roll off angle and Δ*m* (n=9). Both weighted and unweighted coefficients are given.

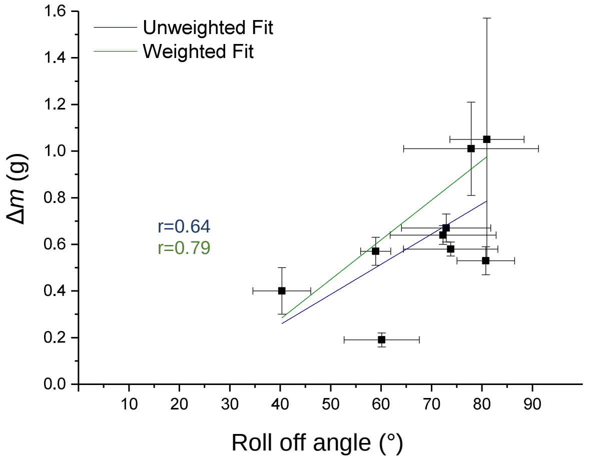

Figure A.8.4: Five wash cycles: Pearson correlation coefficient (*r*) between roll off angle and Δ*m* (n=9). Both weighted and unweighted coefficients are given.

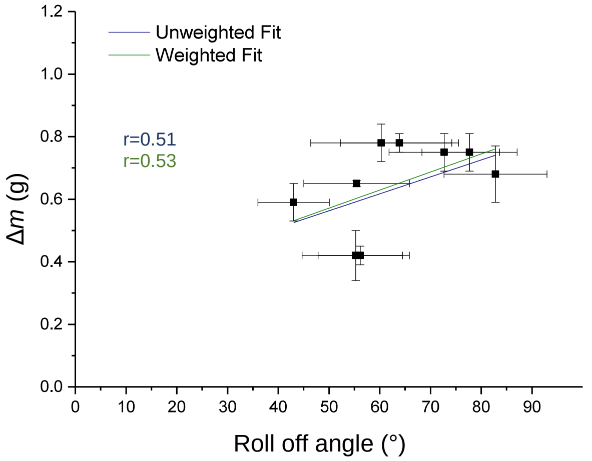

Figure A.8.5: Ten wash cycles: Pearson correlation coefficient (*r*) between roll off angle and Δ*m* (n=8). Both weighted and unweighted coefficients are given.

A.9 Bundesmann test data

Bundesmann testing was carried out by Intertek UK and the following data was supplied:

Table A.9.1: Data from Bundesmann test, carried out by Intertek UK

Sample Id	DWR type	Mean water absorption (%)	Mean visual grade	Wetting to underside	Penetration (ml)
C	C8	25.43	4	Yes	0
J	C6	26.36	2	No	0
M	C6	42.71	4	Yes	0
T	Non-fluorinated	31.87	5	No	0
V	Non-fluorinated	34.68	4	Yes	0

A.10 Effect of spray test shower duration on wettability of different DWR types

A one-way ANOVA was conducted at each spray test shower duration to assess the duration at which differences between the DWR types are significant at a 95% confidence level.

After the standard spray test duration, post-hoc tests using Tukey HSD indicated a statistically significant difference (p<005) between the long SFP (C8) DWR (sample *C*) with both the shorter SFP (C6) DWR (sample *M*) and the non-fluorinated DWR (sample *V*) (Table A.10.3). There was not a statistically significant difference (p=0.165) between the shorter SFP (C6) DWR (sample *M*) and the non-fluorinated DWR (sample *V)* (Tables A.10.3).

Table A.10.1: Standard spray test – Descriptive statistics for mean ($\bar{x}$) Δ*m* depending on DWR type. Standard deviation (σ) is for three sample repeats.

DWR type	**n**	**$\bar{x}$**	**σ (Std. Dev)**	**Std. Error**	**95% Confidence Interval for Mean**		**Minimum**	**Maximum**
					Lower Bound	Upper Bound		
C8	3	0.030	0.000	0.000	0.030	0.030	0.03	0.03
C6	3	0.070	0.010	0.006	0.045	0.095	0.06	0.06
Non-fluorinated	3	0.060	0.000	0.000	0.060	0.060	0.06	0.06
Total	9	0.053	0.019	0.006	0.039	0.068	0.03	0.03

Table A.10.2: One-way ANOVA

	Sum of Squares	**Error df**	**Mean Square**	**F**	**Sig.**
Between Groups	0.003	2	0.001	39.000	0.000
Within Groups	0.000	6	0.000		
Total	0.003	8			

Table A.10.3: Standard spray test Post-hoc testing: Multiple Comparisons - Tukey HSD. Dependent Variable: Δ*m*.

DWR type (I)	**DWR type (J)**	**Mean Difference (I-J)**	**Std. Error**	**Sig.**	**95% Confidence Interval**	
					Lower Bound	**Upper Bound**
C8	C6	-0.040*	0.005	0.000	-0.055	-0.026
	Non-fluorinated	-0.030*	0.005	0.002	-0.045	-0.016
C6	C8	0.040*	0.005	0.000	0.026	0.055
	Non-fluorinated	0.010	0.005	0.165	-0.005	0.025
Non-fluorinated	C8	0.030*	0.005	0.002	0.016	0.045
	C6	-0.010	0.005	0.165	-0.025	0.005

*. The mean difference is significant at the 0.05 level.

Following an extended 10 minute spray shower, a statistically significant difference was not indicated by ANOVA analysis at the 95% confidence level. This was further demonstrated by post-hoc tests using Tukey HSD where p>0.05 across all comparisons (Table A.10.6).

Table A.10.4: 10 minute extended spray test – Descriptive statistics for mean (x̅) Δ*m* depending on DWR type. Standard deviation (σ) is for three sample repeats.

DWR type	**n**	**x̅**	**σ (Std.Dev)**	**Std. Error**	**95% Confidence Interval for Mean**		**Minimum**	**Maximum**
					Lower Bound	**Upper Bound**		
C8	3	0.173	0.038	0.022	0.079	0.267	0.13	0.20
C6	3	0.213	0.032	0.019	0.134	0.293	0.19	0.25
Non-fluorinated	3	0.240	0.036	0.021	0.150	0.330	0.21	0.28
Total	9	0.209	0.042	0.014	0.176	0.241	0.13	0.28

Table A.10.5: 10 minute extended spray test – One-way ANOVA

	Sum of Squares	**Error df**	**Mean Square**	**F**	**Sig.**
Between Groups	0.007	2	0.003	2.690	0.147
Within Groups	0.008	6	0.001		
Total	0.014	8			

Table A.10.6: 10 minute extended spray test Post-hoc testing: Multiple Comparisons - Tukey HSD. Dependent Variable: Δ*m*.

DWR type (I)	DWR type (J)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
C8	C6	-0.040	0.029	0.407	-0.129	0.049
	Non-fluorinated	-0.067	0.029	0.131	-0.155	0.022
C6	C8	0.040	0.029	0.407	-0.049	0.129
	Non-fluorinated	-0.027	0.029	0.648	-0.115	0.062
Non-fluorinated	C8	0.067	0.029	0.131	-0.022	0.155
	C6	0.027	0.029	0.648	-0.062	0.115

After an extended spray shower of 60 minutes, ANOVA testing demonstrated a statistically significant difference between the DWR types with post-hoc tests using Tukey HSD indicating a statistically significant difference between the non-fluorinated DWR (sample *V*) with both the long SFP (C8) DWR (sample *C*) ($p<0.05$) and the shorter SFP (C6) DWR sample (sample *M*) ($p<0.05$). A statistically significant difference was not indicated between the long SFP (C8) DWR (sample *C*) and the shorter SFP (C6) DWR sample (sample *M*) where $p=0.467$ (Table A.10.9)

Table A.10.7: 60 minute extended spray test – Descriptive statistics for mean ($\bar{x}$) Δ*m* depending on DWR type. Standard deviation (σ) is for three sample repeats.

DWR type	n	$\bar{x}$	σ (Std. Dev)	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
C8	3	0.430	0.076	0.044	0.243	0.618	0.36	0.51
C6	3	0.510	0.036	0.021	0.420	0.600	0.47	0.54
Non-fluorinated	3	0.703	0.106	0.061	0.440	0.967	0.59	0.80
Total	9	0.548	0.139	0.046	0.441	0.655	0.36	0.80

Table A.10.8: 60 minute extended spray test- One-way ANOVA

	Sum of Squares	Error df	Mean Square	F	Sig.
Between Groups	0.118	2	0.059	9.748	0.013
Within Groups	0.036	6	0.006		
Total	0.155	8			

Table A.10.9: 60 minute extended spray test Post-hoc testing: Multiple Comparisons - Tukey HSD. Dependent Variable: Δ*m*.

DWR type (I)	DWR type (J)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
C8	C6	-0.080	0.064	0.467	-0.275	0.115
	Non-fluorinated	-0.273^{*}	0.064	0.012	-0.469	-0.078
C6	C8	0.080	0.064	0.467	-0.115	0.275
	Non-fluorinated	-0.193^{*}	0.064	0.052	-0.389	-0.002
Non-fluorinated	C8	0.273^{*}	0.064	0.012	0.078	0.469
	C6	0.193^{*}	0.064	0.052	0.002	0.389

*. The mean difference is significant at the 0.05 level.

After 120 minute extended spray test, ANOVA testing determined a statistically significant difference between the groups with post-hoc tests using Tukey HSD indicating this between the non-fluorinated DWR (sample *V*) with both the long SFP (C8) DWR (sample *C*) (p<0.05) and the shorter SFP (C6) DWR (sample *M*) (p<0.05). Post-hoc testing indicated there was not a statistically significant difference between the long SFP (C8) DWR (sample *C*) and the shorter SFP (C6) DWR (sample *M*) where p=0.372 (Table A.10.12).

Table A.10.10: 120 minute extended spray test – Descriptive statistics for mean ($\overline{x}$) Δ*m* depending on DWR type. Standard deviation (σ) is for three sample repeats.

DWR type	n	$\overline{x}$	σ (Std. Dev)	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
C8	3	0.627	0.124	0.071	0.318	0.935	0.55	0.77
C6	3	0.883	0.267	0.154	0.219	1.547	0.70	1.19
Non-fluorinated	3	1.997	0.228	0.132	1.430	2.563	1.86	2.26
Total	9	1.169	0.658	0.219	0.663	1.674	0.55	2.26

Table A.10.11: 120 minute extended spray test - One-way ANOVA

	Sum of Squares	Error df	Mean Square	F	Sig.
Between Groups	3.182	2	1.591	34.366	0.001
Within Groups	0.278	6	0.046		
Total	3.460	8			

Table A.10.12: 120 minute extended spray test Post-hoc testing: Multiple Comparisons – Tukey HSD. Dependent Variable: Δ*m*.

DWR type (I)	DWR type (J)	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
C8	C6	-0.257	0.176	0.372	-0.796	0.282
	Non-fluorinated	-1.370*	0.176	0.001	-1.909	-0.831
C6	C8	0.257	0.176	0.372	-0.282	0.796
	Non-fluorinated	-1.113*	0.176	0.002	-1.652	-0.574
Non-fluorinated	C8	1.370*	0.176	0.001	0.831	1.909
	C6	1.113*	0.176	0.002	0.574	1.652

*. The mean difference is significant at the 0.05 level.