Melamino migrants as breakdown products of applied amino resin cross-linked can coatings

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

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Abstract

This thesis consists of seven chapters. These are: (1) General introduction; (2) Preparation of reagents, characterisation of raw materials and calibration of the curing oven; (3) Formulation procedures, coating applications and curing procedures; (4) Analyses of liquid coatings, analyses of cured coatings and migration studies; (5) Epoxy-based coatings— study of the migration of melamine, the migration of benzoguanamine and the migration of formaldehyde; (6) Poly(ester)-based coatings— study of the release and migration of melamine, of benzoguanamine and of formaldehyde; (7) General discussion/summary.

In the work that was carried out, an investigation of the phenomena of migration of melamine, of benzoguanamine and of formaldehyde, primarily during the retorting of the coatings, was undertaken. Five coating systems were investigated; these were unpigmented epoxy-anhydride coatings, TiO_2 pigmented-epoxy anhydride coatings, epoxy-phenolic coatings, poly(ester)-urea coatings and poly(ester)-acrylic coatings. The coatings were applied through controlled repeatable procedures that were designed to represent industrial practices. The coatings were cured under controlled conditions relating to the temperature of curing and to the time over which the curing was performed. The curing oven was repeatedly calibrated to ensure that it was in a consistent and accurate working condition. This involved the need for a peak metal temperature (PMT), of 195 ^{o}C, maintained for 12 minutes and a PMT of 200 ^{o}C, held for 10 minutes, to be consistently achieved.

The raw material samples that comprised the samples and the coatings themselves were characterised/analysed for their compositional integrity. Several analytical techniques were used including NMR spectroscopy, FT-IR spectroscopy, mass spectrometry, scanning electron microscopy, UV-visible spectroscopy, fluorescence spectroscopy, liquid chromatography (UV detection) and gas chromatography (MS detection). Relevant application-based techniques that were used include rheometry, particle size analysis, surface wetting studies and hardness testing, each used as appropriate.

For the analyses of migrant species (melamine, benzoguanamine and formaldehyde) from the coatings, aqueous solutions of specified agents were used as food simulants (a simplified model food). These were used as food mimics, according to established European Commission standards. Elevated temperature treatments of cured coatings that were contained in the food simulants, in sealed containers, were carried out according to standard methods, to represent the effects of pressure cooking and the consequences of sterilisation of the canned foodstuffs during manufacture.

The effects of the cross-linker chemistry, the amount of cross-linker in the coatings, the curing conditions, the coating application procedures and the kinetics of the release processes were investigated as was the stability of the migrant species in retorted food stimulants and their potential for further reaction, after release.

Melamine, benzoguanamine and formaldehyde were not released from the coatings, at room temperature, after the cured coatings had come into contact with food simulants or with selected organic solvents, after a 24 hour exposure period. However, the migrant compounds were released from cured coatings that were retorted in the aqueous food simulants. The release was shown to be via the hydrolysis of the cross-linker components of the coatings. Such release was influenced by the 131 ^{o}C retorting temperature and the aqueous conditions. In all cases, the amounts of melamine, benzoguanamine and formaldehyde that were released and subsequently migrated into the food simulants were well within current limits, set by the European regulatory organisations.

The results show that increasing the amounts of the cross-linker compounds in the total coating formulations, up to 2% for epoxy coatings and up to 10% for poly(ester) coatings, does not always affect the hydrolysis of the cross-linking agents, although it leads to an increase in melamine release. Excluding the cross-linkers from formulation does not significantly affect thermal properties and the hardness of the coatings. As a consequence of this exclusion, melamine and benzoguanamine release and their subsequent migration should not occur. The results show that a substantial proportion (up to 90%, in unpigmented epoxy coatings) of the cross-linker suffers

hydrolysis to give melamine and yet the coatings still clearly perform their function when used commercially.

The influence of varying the curing time and the curing temperature were factors that affected the amount of melamine that was released from the various coatings. This influence was more severe with the selected epoxy coatings than with selected poly(ester) coatings. For the epoxy coatings, in certain instances, increasing the curing temperature, in stages, from 160 ^{o}C to 240 ^{o}C, reduced the extent of cross-linker hydrolysis by up to 60 %. The presence of the TiO_2 pigment particles in the epoxy anhydride coatings assisted in lowering the extent of melamine generation that would otherwise have occurred via hydrolysis. Also, the three grades of the TiO_2 pigments gave similar contributions with respect to the reduced melamine release from the epoxy coatings.

The results also indicate that melamine and formaldehyde are released during the curing of the coatings in the oven. Using various pigmented coating formulations that were allowed to stand under stated laboratory conditions, for specified time periods, resulted in wet ageing occurring. Such wet ageing significantly affected the amount of melamine that was released under hydrolytic conditions, leading to 20% more melamine being released after storage for 30 weeks.

Aims and Objectives of the research project

This PhD project was targeted towards the development of a comprehensive understanding of the factors that affect release and migration phenomena. Particular concerns related to the release and migration of melamine, the release and migration of benzoguanamine and the release and migration of formaldehyde from cured epoxy-based and poly(ester)-based can coating systems. The strategy involved carrying out detailed investigations, under controlled conditions, of the chemical breakdown of the coating systems and of the species generated. The studies encompassed different coating formulations, covering several melamino-based cross-linker options.

One objective was to provide an understanding of the inherent degradation mechanisms that occur within the coatings on processing and on storage. Thus, a strategy for minimising melamine generation was developed. Another objective was to establish why and how melamine was released, under the conditions in which the amino cross-linked can coatings were retorted using either acidic, aqueous simulants or non-acidic, aqueous simulants.

Factors related to the migration of the breakdown products, from within the coatings, towards the contents of the container were studied. The data were designed and used to establish a base-line for “safe practice” in the food can making industries.

Overall, this research is important because it provides a strategy for ensuring that no health and safety concerns should arise with respect to the release of melamine, benzoguanamine and formaldehyde as a result of the use of amino cross-linked can coatings when used in food contact applications.

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List of Abbreviations

ASTM	American Society for Testing and Materials
BDV	Benzoguanamine degradation value
BS	British Standard
COE	Council of Europe
DIN	Deutsche Institut für Normung
DBMB	Dibutoxymethyl benzoguanamine
DCSS	Double coat on the same side
DSC	Differential scanning calorimetry
EDX	Energy-dispersive X-ray spectroscopy
ETP	Electrolytic tinplate
EU	European Union
FCS	Food contact surface
FDV	Formaldehyde degradation value
FT-IR	Fourier transformed infrared spectroscopy
FWT	Film weight thickness
GC	Gas chromatography
GC/MS	Gas chromatography with mass spectrometry
g/g	Gram by gram
HBMM	Hexabutoxymethyl melamine
HMMM	Hexamethoxymethyl melamine

HPLC	High performance liquid chromatography
ISO	International Standards Organisation
LOD	Limit of detection
LOQ	Limit of quantification
mAU	Milliabsorbance unit
MDV	Melamine degradation value
MF	Melamine formaldehyde
MMTC	Methylol melamine-type cross-linker
MSDS	Materials safety data sheet
nm	Nanometre
NMR	Nuclear magnetic resonance spectroscopy
OML	Overall migration limit
ppm	Parts per million
PW1	Pigment White 1 (a grade of TiO_2 pigment)
PW2	Pigment White 2 (a grade of TiO_2 pigment)
PW3	Pigment White 3 (a grade of TiO_2 pigment)
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
TMTBM	Trimethylol tributoxymethyl melamine
SC	Single coat
SCES	Single coat on each side
SD	Standard deviation

SE	Standard error
SEM	Scanning electron microscopy
SML	Specific migration limit
TFS	Tin free steel
TGA	Thermogravimetric analysis
TiO_2	Titanium dioxide pigment
U.S. FDA	American Food and Drug Administration
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
VOC	Volatile organic compounds
v/v	Volume by volume
WM	Werner Mathis curing oven
%T	Percent transmittance

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Chapter 1: General Introduction

1.1. Concept of food canning

Canning is a process of packaging that is used for food preservation. Thus, cans are used for the container provision of a wide variety of complex fluids, mixed compositions and soft solids. It is the can as a package and the processing of the foodstuff that provides protection of the contents from spoilage and/or microbial activities, (Paine and Paine, 1992). Types of produce thus contained, include foodstuffs, oils, soft drinks, alcoholic beverages and so on. Almost every type of food product has at some time being contained in a metal can. Can coatings, as the name implies, are applied onto metallic substrates, (Breitbach et al., 2011). Many of these coated metals are used in food packaging applications, thereby providing a barrier between the food and the metallic components of the container, (Jackson and Shinn, 1979). Currently, in Europe, over nine billion food and beverage cans are sold and used each year. These cans are produced through fast production lines that are able to manufacture over a million cans per day, (Canmakers.co.uk). Figure 1.1-1 shows an example of canned food items.

Figure 1.1-1: Canned food items

Coatings are used in the can making industry to serve as barriers between the metal can and the can contents, thus protecting the contents from attack by the metal and also preventing the metal from attack by the contents, preventing spoilage of the food and limiting microbial activities, (Ho Lee et al., 2004). After can manufacture, including the application of the coatings onto the cans, the food contents are introduced into the cans. Sealing and then cooking, sterilisation or pasteurisation follow, (Muriana et al., 2002). In many cases, the sterilisation and/or cooking of the can contents takes place, under pressure, at greater than boiling water temperatures. In this context, it is important for the barrier coatings to possess adequate thermal, transport and mechanical properties.

Commercially available forms (shape-based) of metallic packaging materials include the following, (Yam, 2009):

- Drawn cans, as commonly used to package beverage materials
- Caps that are used for bottled products
- Closures, as used commonly with jars
- Drums, whose size can vary, used for foodstuff packaging
- Trays, used for food application purposes
- Lids, as used as seals for many packaging materials
- Ends as used as the base of cylindrical containers and boxes.

Cans have been developed in two major ways, as two-piece cans and as three-piece cans, (Stockdale, 1969, Ryuichi Eguchi et al., 1995). Two-piece can technology requires the use of metals that can be drawn from a metallic disc and then wall profiled or smoothed. In the drawing process, the disc is firmly held over a well of the required geometry while a punch is pressed onto the surface of the disc. The metal is stretched/drawn into the well. In this, the can wall thickness continuously decreases while the base maintains the original thickness, (Kubo et al., 2005). The lid is then sealed into place on the one-piece wall/base to complete the container. Figure 1.1-2 shows two-piece can packages.

Figure 1.1-2: Two-piece metal can

The components of a three-piece can usually undergo several processes including bending, cutting, forming/rolling, welding, flanging, end seaming, filling, capping, printing and transport, (Dunn and Morin, 2013). Soldering is no longer used in European can making. The finished product must be fit for service in the chosen application. The typical components of such a can include the metal/body component(s) (tinplate), the internal coatings, the opening system (ring pull, twist rod etc), inks and the external coatings and labels, (if used). Figure 1.1-3 shows three-piece can packages.

Figure 1.1-3: Three-piece metal can

Canned foodstuffs can be considered according to two broad classes, depending on the treatments that they undergo during processing. The two classes are the heat processed canned foodstuffs and the non-heat processed canned foodstuffs, (Nelson, 2010).

The substrate used in can formation, filing and sterilisation is in many cases printed, coated and formed prior to can formation. The printing stage includes text creation and image creation. The coatings/inks that are used for the external treatment of cans are therefore referred to as “non-food contact” coatings/inks. One or more of several printing processes can be employed to achieve the required objectives, (Ros, 1988).

1.2. Internal coatings for can packaging

Figure 1.2-1: Three-piece cans with internal "gold" coating

The term internal coating refers to those coatings that are applied to the inner surface of a material such as the interior of a can. Figure 1.2-1 shows metal cans that have been coated internally. With respect to coating choice and integrity, points of relevance include:

- **The content:** Cans that are designed to contain dry materials do not necessarily need to be coated internally. This statement applies to products such as diary powders and biscuits. There is a need to coat the internal surface of cans that are meant to carry liquid-based materials and semi-solids. These are especially important from health and safety points of view so that integrity of the contents is not affected by the metal can, (Embuscado and Huber, 2009a). Figure 1.2-2 represents examples of canned foodstuff.

Figure 1.2-2: Examples of typical canned food items

- **The metal can:** The coating to be applied needs to be formulated with respect to the metal to be coated. The number of coating layers that are applied to the internal face of the cans also depends on the properties of the metal and on any subsequent processing.

Coatings are expected, to provide the appropriate properties that are associated with expected application. These could include properties such as effective barrier provision, self sealing after damage, corrosion resistance, weather resistance, durability, ease of application/subsequent processing (drawing, bending), (Zhou et al., 2011, Paadture et al., 2002) and engineering processing compliance. When a coating is used to serve anti-corrosion purposes, it must prevent water and air from reaching the surface of the substrate, thus, preventing opportunities for corrosion to occur. The needs for effective barriers arise from the aggressive nature of many food items. Can coatings can be applied to the can's internal surface and/or the external surface, (Natarajan et al., 2009).

In internally coated cans, most of the coating treatments are thin. Thus, the properties of the substrate that was used in can construction remain unchanged. However, the lack of depth and uniformity of the subsequent coating could cause the underlying metal of the coated metal composite to be susceptible to unwanted attack, leading to compromise of the composition and to ultimate lack of “fitness for purpose”. Problems associated with the analysis of coated cans arise because of the complexities of the coating’s composition and the processes through which the coating has undergone before its ultimate use.

Here are addressed some of the issues that are associated with the coatings that are applied to cans that are intended to be used for food containment, with reduced attention being given to issues arising in the beverage can sector.

1.3. Composition of can coatings

Can coatings are often described in terms of the chemistry of their components, the interactions taking place between these components and the reactions that take place during the application and processing of the coatings (drying, curing), (Magami, 2013b).

Although the components of a coating may be many and varied, they can conveniently be placed into classes of polymeric binder, monomer(s) (for curable formulations), pigment(s), cross-linker(s) solvent(s) and additives.

1.3.1. Functions of polymeric binders

Several types of polymeric binders can be (and are) used in coating formulations (either singly or in combinations (blends)). This variety is due to many of the different requirements that coatings are expected to meet following their application onto the wide range of substrates that are to be coated, (Magami, 2013b).

Several different types of polymeric binder chemistries can be used in formulations of coating products. Specific examples include alkyd binders, vinylic binders, cellulosic binders, silyl binders, acrylic/acrylate binders, benzoguanamine-formaldehyde binders, alkyl-amino binders, amino-methylol binders, isocyanate binders, urea-formaldehyde binders, epoxy binders and so on (Dziczkowski and Soucek, 2010, Magami and Guthrie, 2012, Spirkova et al., 2010). However, not all of these are used in food can coatings. In the context of this thesis, examples of binders that are relevant to food can coating systems are considered below.

1.3.1.1. Epoxy-based polymeric binders

Epoxy-based polymeric binder systems are designed and used for interior can coating applications. Such binders and the parent coatings essentially possess good thermal properties and good barrier properties.

Epoxy polymeric binders provide a wide range of can coating based-applications. The epoxy functionality is very reactive, being capable of reacting with other functional groups during film formation. An example of epoxy pre-polymer is given in Figure 1.3-1. Epoxy compounds can be produced by the epoxidation of alkenes with peracids. Typical reactions can take place at 25 ^{o}C, (Hamerton, 1996).

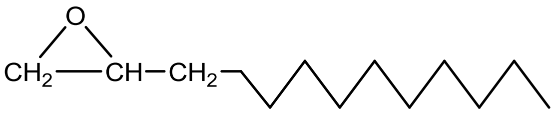


Figure 1.3-1: Schematic representation of an epoxy pre-polymer

Many epoxy-based can coatings are derived from 4,4'-(propane-2,2-diyl)-diphenol (known as Bisphenol A or BPA) monomers. BPA has been widely studied because of public concerns over its potential migration into food. Among many studies, the migration behaviour of BPA has been studied in canned vegetables, (Brotons et al., 1995) and in infant food, (Biles et al., 1997). The results from these two studies show that BPA is known to migrate from can coatings into food during retorting. However, in 2002, the relative safety of BPA was confirmed by a study carried out for the European Commission's Scientific Committee on Food, (EFSA, 2010a). Consequently, the potential risk for humans after exposure to BPA from can coatings is now considered to be minimal and not to endanger the consumer's health (US FDA, 2013a). BPA is shown in Figure 1.3-2. Figure 1.3-3 shows an idealised scheme for the creation of BPA-based, epoxy polymeric binder composition, (Hamerton, 1996).

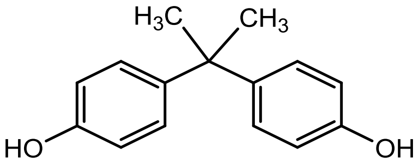


Figure 1.3-2: Bisphenol A

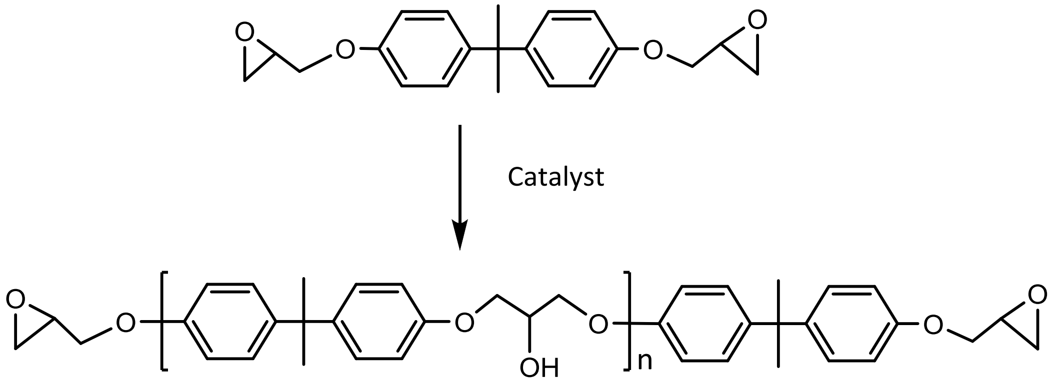


Figure 1.3-3: Scheme for the formation of a Bisphenol A diglycidyl ether epoxy polymer

1.3.1.2. Poly(ester)-based polymeric binders

Like epoxy binders, poly(ester) polymers possess good thermal properties, good mechanical properties and excellent barrier properties. Figure 1.3-4 represents a reaction scheme involved in the preparation of a poly(ester) polymer, based on a reaction between phthalic acid and neopentyl glycol, (Jiang, 2008).

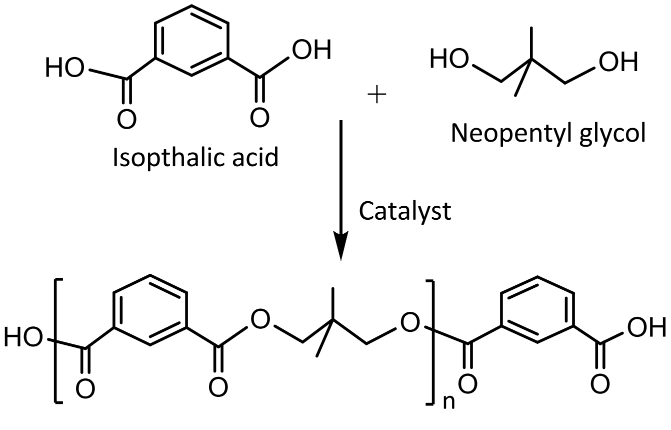


Figure 1.3-4: Poly(ester) polymer based on phthalic acid and neopentyl glycol

In contrast to epoxy coatings, where extensive studies aimed at understanding the migration potentials of the base polymer into food from coatings have been carried out, little has been done with regards to the potential for poly(ester)-based components to migrate into food. However, several studies have been carried on the theme of migration of poly(ester)-derived low molecular compounds from cookware into food, (Jiang, 2008).

In 1993, studies were carried out to monitor the migration, of styrene and styrene derivatives from polyester cookware into foodstuffs and into food stimulants, during normal cooking, (Jickells et al., 1993). Similar studies have also been carried out into the migration of ethylbenzene and styrene from poly(ester)-based plastics into pork, (Gramshaw and Vandenburg, 1995). Both studies confirmed the tendency of poly(ester) components to migrate from plastics into food. To be specific, styrene and ethylbenzene migrated into pork that was cooked in thermoset poly(ester) dishes for 1.5 hours, at 175 ^{o}C . This migration arose because of the thermal depolymerisation of the poly(ester)-based plastic at temperatures of 175 ^{o}C and above. In those materials studied (thermoset polyesters), styrene was used to cross-link unsaturated polyesters and ethyl benzene was an impurity in the styrene used.

1.3.1.3. Phenolic pre-polymers

Many phenolic polymer binders are manufactured from a condensation reaction between phenol or phenolic derivatives with formaldehyde. The reaction temperature, type of catalyst, pH and the ratio of phenol to formaldehyde are factors that affect the syntheses, (Astarloa-Aierbe et al., 1998). Phenol-based binders have wide application in can coatings owing to their outstanding cross-linking capabilities.

Amongst the phenolic binders that are widely used in the can coating industry are the cresols, (Zhang et al., 2011). Cresols (Figure 1.3-5) are vital intermediates in the synthesis of phenolic polymeric binders. Amongst the three isomers, p-cresol is the most widely used. Cresols can be made from a reaction of toluene with hydroxylamine in the presence of a suitable catalyst such as ammonium molybdate, (Otsuka et al., 1992). Figure 1.3-6 represents an idealised example of the synthesis of a p-cresol-based polymeric composition, (Chutayothin and Ishida, 2011).

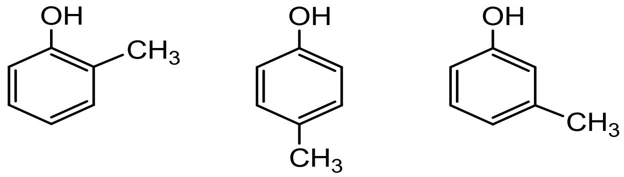


Figure 1.3-5: o-cresol, p-cresol and m-cresol

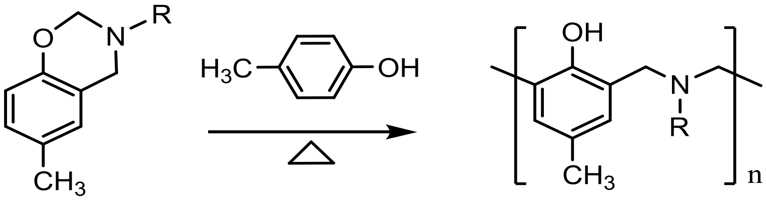


Figure 1.3-6: Idealised synthesis route for the formation of a p-cresol-based linear polymer composition

1.3.1.4. Epoxy-phenolic pre-polymers

As the term suggests, epoxy-phenolic compounds are made from combining epoxy starting materials and phenolic starting materials. A reaction scheme example is shown in Figure 1.3-9, (Jiang, 2008). Epoxy phenolic compounds have been used for decades as curing agents in can coating compositions because they give outstanding thermal, chemical and mechanical properties in the parent cured coating, (Tyberg et al., 2000).

Typical examples of epoxy-phenolic pre-polymers include the cresyl glycidyl ether (Figure 1.3-7) and the phenyl glycidyl ether, (Figure 1.3-8), (Hale et al., 1989). Both can be manufactured through a similar reaction method where in the former example, o-cresol is used and in the latter phenol is used as the starting phenolic compound. Many other products can be prepared based on Bisphenol A compounds, (Sunitha et al., 2013).

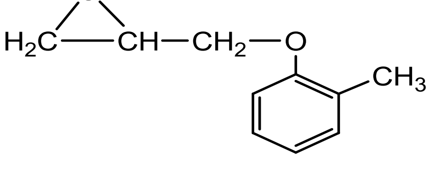


Figure 1.3-7: Cresyl glycidyl ether

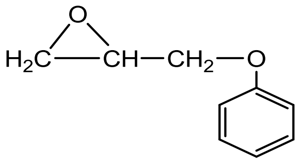


Figure 1.3-8: Phenyl glycidyl ether

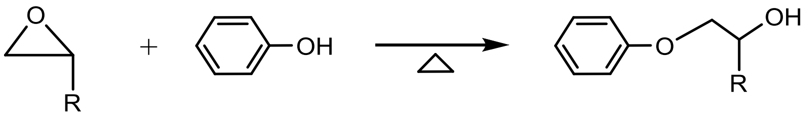


Figure 1.3-9: Idealised reaction between an epoxy compound and a phenolic compound

1.3.2. Functions of cross-linker compounds

Amino cross-linkers are used in can coatings because of their high functionality, being used as additives or as major components in the coating formulation. During curing, the cross-linkers functionally react with suitable polymeric binder species that are contained in the coating, in order to form a cross-linked network. The cross-linking process leads to higher molecular weight product formation and changes in physical and chemical properties through the interlocking of the non-volatile components in the coating, (Magami, 2013b).

1.3.2.1. Types of amino cross-linkers

The major groups of amino cross-linkers are based on melamine, urea, benzoguanamine and their derivatives. These derivatives are often the reaction products from their reaction with formaldehyde. In the context of this thesis, two broad classes of amino cross-linkers are considered. These are cross-linkers that are based on melamine and others that are based on benzoguanamine.

Melamine-based cross-linkers are produced via a controlled condensation reaction between melamine and formaldehyde, under acidic conditions or under basic conditions, (du Fresne von Hohenesche et al., 2008). This reaction leads to the formation of compounds containing the methylol functionality, the composition depending on the extent of the reaction. Subsequent alkylation reactions can occur when a suitable alcohol is used. This leads to the creation of alkylated cross-linkers. The degree of alkylation depends on the extent of the reaction and on the ratio of reagents used, (Cook et al., 2005).

Figure 1.3-10 and Figure 1.3-11 show reaction schemes that involve the formation of melamine-based cross-linkers.

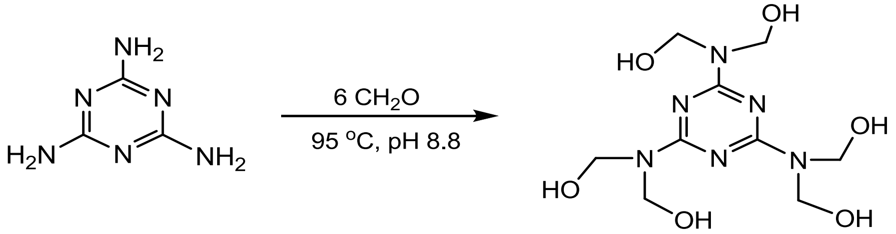


Figure 1.3-10: Idealised reaction scheme showing the formation of a completely methylolated melamine cross-linker composition

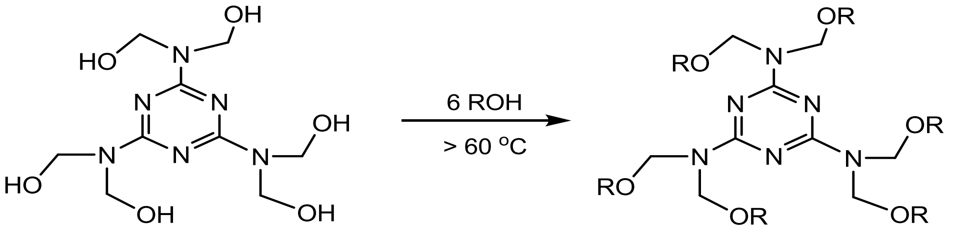


Figure 1.3-11: Idealised reaction scheme showing the formation of alkylated cross-linkers from their methylolated counterparts

From Figure 1.3-11, if R= CH_3 and n =6, the cross-linker compound that is formed is hexamethoxymethyl melamine (HMMM). However, if R= $(CH_2)_3CH_3$ and n =6, the cross-linker compound that is formed is hexabutoxymethyl melamine (HBMM). The alkylated cross-linkers, HMMM and HBMM are shown in Figure 1.3-12.

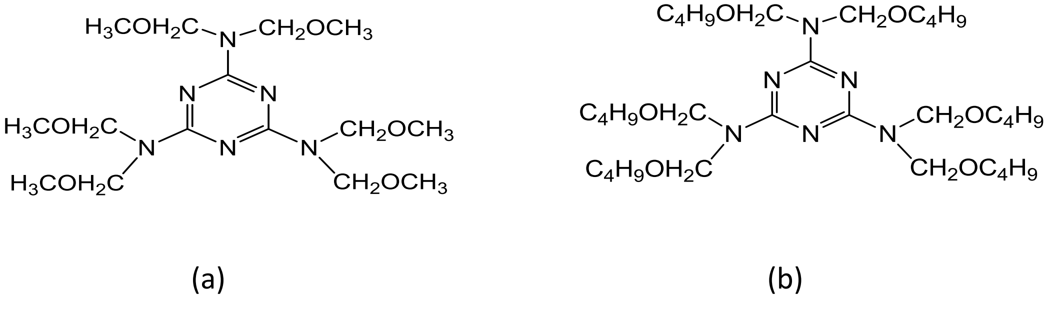

(a) (b)

Figure 1.3-12: Chemical structure of a: HMMM and b: HBMM

Benzoguanamine formaldehyde-based cross-linkers are formed by a reaction between benzoguanamine and formaldehyde. The reaction proceeds at >85 °C when a benzoguanamine to formaldehyde ratio of greater than 1:2 is used. Figure 1.3-13 shows a reaction scheme that involves the formation of a benzoguanamino cross-linker, (Alger, 1997).

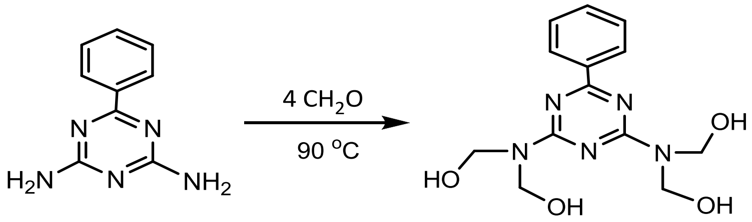


Figure 1.3-13: Idealised reaction scheme showing the formation of a benzoguanamino formaldehyde cross-linker

1.3.2.2. Functional groups in amino cross-linkers

Examples of the fundamental functional groups that are present in amino cross-linkers are shown in Table 1.3-1.

Table 1.3-1: Functional groups in amino cross-linker compositions

Functional group	Chemical representation
Alkoxyalkyl	$>N-CH_2OR$
Methylol	$>N-CH_2OH$
Imino	$>NH$
Amino	$-NH_2$
Methylol ether	$-CH_2-O-CH_2-$
Methylene amino	$>N-CH_2-N<$

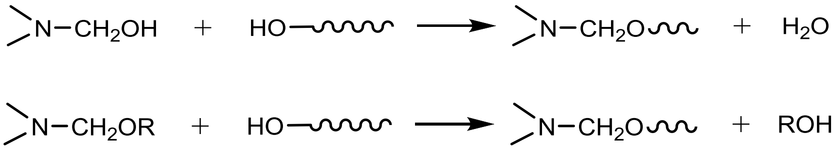
Amino cross-linkers can conveniently be grouped functionally according to:

- The nature of the amino compound used in formulations;

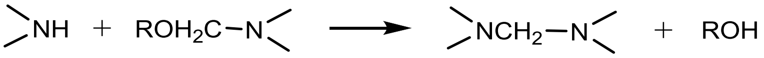
- The nature of the etherifying alcohol that is used during the alkylation reaction;

The degree of alkylation (full alkylation, partial alkylation, and so on), (Oldring and Tuck, 2001).

Many of the reactions that occur during the curing of amino cross-linked coatings depend on the specific functional groups that the cross-linkers possess. For example, both the alkoxyalkyl group and the imino group can readily react with an $-OH$ group from a suitable polymer backbone, during the curing of coatings, (Koleske, 1995b).



The imino groups, if present during the curing of the cross-linkers, usually are involved in co-condensation and self-condensation reactions. An example is given below, (Bann and Miller, 1958, Oldring and Nehring, 2007).



1.3.3. Functions of pigments in coatings

Pigments are aggregates of particles that are “insoluble” in the coating formulation, (Lomax, 2010). Pigments are generally classified as being organic or inorganic. Organic pigments are derived from synthetic organic compounds while their inorganic counterparts are usually obtained as processed minerals, though some are obtained by a precipitation (nucleation and growth) from solution. Inorganic pigment particles are often surface modified (coated) to improve their dispersion properties, particularly when they are used in non-aqueous solvents.

In coatings, pigments can provide UV resistance properties, (Liu et al., 2010). They contribute to the solid contents of the coatings, to the aesthetics (appearance), and usually to the durability of the coating, (Jiang et al., 2010), provided that the amount used is below the Critical Pigment Volume Concentration (CPVC). The CPVC is a point at which the characteristic properties of the coating change significantly. For example, at the CPVC, foams, voids and so on can be introduced into the coating films. The change in the durability that is provided by pigments is related to the role that pigments can play in either the degradation of the coating or conversely, the stability of the coating, (Wang et al., 2011). The average shape, shape distribution, size and size distribution of pigment particles play a role in the colour, the opacity, the overall appearance and even in the rheological characteristics of the final coating formulation, (Kumar et al., 2011).

1.3.3.1. Use of TiO_2 in can coatings

For can coatings, titanium dioxide (TiO_2) is the most widely used pigment. Its properties include its great opacity and its high refractive index. TiO_2 is produced in various particle size ranges. The particle size and the size distribution govern the industrial applications to which the pigment is applied, (Braun, 1997). TiO_2 is produced in two major crystal forms, termed the anatase form and the rutile form, the latter form having a greater opacity advantage, although both grades have can coating applications, (Yin et al., 2001).

For commercial coating applications, different quality grades/designs of TiO_2 exist. These are related to amount of the pigment that is required in the formulation, the dispersion quality needed, the particle size ranges, the durability, the presence of additives and so on. This is because the coating system will be designed to meet particular industrial needs. Thus, the application to which a TiO_2 pigmented coating would be subjected, for example its incorporation into an external coating/ink or into an internally applied coating, governs the grade choice, (Buxbaum, 2008).

The two major production pathways for TiO_2 are the sulphate process and the chloride process. The sulphate process generates titanium dioxide from a titanium-based slag as illustrated below, (Reck and Richards, 1997):

$$FeTiO_3 + 2H_2SO_4 \longrightarrow TiOSO_4 + FeSO_4 + 2H_2O$$

$$TiOSO_4 \xrightarrow{OH^-} TiO_2n(H_2O) + H_2SO_4$$

$$TiO_2n(H_2O) \xrightarrow[\Delta]{} TiO_2 + nH_2O$$

The chloride process depends on the production of TiO_2 from the impure mineral, rutile, according to the schemes below, (Reck and Richards, 1997).

$$TiO_2 \text{ (impure)} + 2Cl_2 + C \longrightarrow TiCl_4 + CO_2$$

$$TiCl_4 + O_2 \longrightarrow TiO_2 \text{ (pure)} + 2Cl_2$$

With regards to usage in coatings, the rutile grade is used more commonly than the anatase grade. This is because of its better scattering properties. In a polymer matrix, a stable dispersion of TiO_2 can be achieved with the aid of a suitable additive, (a dispersant). The size of the particles is controllable in the sub-micron range, with a narrow size and shape distribution, (Braun, 1997).

1.3.4. Functions of solvents in a coatings context

Solvents are used in coatings to dissolve other coating components such as the polymeric binders, cross-linker compounds and additives. They are often used in attempts to achieve the desired rheological characteristics. For many coating formulations, a combination of solvents may be used, (Koleske, 1995b).

Solvents, including water in this context, are technically the volatile components of a coating. This is because they are removed during the processing, application and curing of the coating. Complete solvent evaporation from the coating is usually desirable after solid state creation to prevent pin-holing that can otherwise occur during the drying of coating film, thereby allowing a uniform film to be achieved. The evaporation rate and solvency power of solvents are vital characteristics that a coating chemist considers in formulating solvent-based coatings. This is because the solvency and evaporation character of the solvents or the mixed solvents govern the setting time of the coatings. The solvents are needed to remain in the coatings long enough to allow for desired properties to be achieved. These properties include adhesion, levelling, gloss and flow, (Sward, 1972). Examples of solvents that are widely used in can coatings are shown in Table 1.3-2.

Table 1.3-2: Physical properties of solvents-relevant to can coating application

Solvent	Boling temperature/ ^{o}C	Evaporation rate *
Acetone	56	1160
Methyl ethyl ketone	80	570
Isobutyl acetate	115	145
Methoxypropyl acetate	146	>33
Ethylene glycol monomethyl ether	125	56
Dimethoxyethane	85	-
Isobutanol	107	70
2-Ethylhexanol	182	<1
Hexane	69	1500
Cyclohexane	81	1000
Toluene	110	180
m-Xylene	139	70

* Evaporation rate based on n-butyl acetate = 100, (Koleske, 1995a)

In certain instances, in coating manufacture, the use of mixed solvents (solvent blends) might be necessary. The reason for this practice might depend on several factors, such as when a particular solvent cannot dissolve certain coating components, when it has a low evaporation rate and when there are miscibility/solvency concerns. The solvent blend will therefore be designed to enhance practically and refine the total solvent character of the coating, (Koleske, 1995b).

1.3.5. Functions of “additives” in composite materials

Several kinds of additives can be incorporated (and are incorporated) into a coating formulation. Additives of interest include flow modifiers, lubricants, waxes, dispersants and wetting agents, used to give desired characteristics to the coating material in formulation, application and longer term stability. Many of these additives are used in small quantities, usually less than 5% of the total formulation, (Bieleman, 2000). Several are based on surfactant-type properties. Some examples are considered below:

- **Flow modifiers:** These additives are used to eliminate rheological and surface defects. Examples of flow modifiers include benzoguanamine-formaldehyde polymers and poly(urethane) polymers, (Abel and Memmer, 1985).

- **Wetting agents:** These are used to improve the spreading and penetrating properties of liquids by lowering the surface tension. When they are used in coatings, they can improve levelling, wetting and adhesion of the applied coating, especially on low energy surfaces. Examples of wetting agents include phosphate esters and nonylphenol phenol ethoxylates, (Kohli and Mittal, 2010).

- **Lubricants:** These are used to reduce localised friction in formulation and to aid the transportation of pigment particles in the coatings (if required). They promote the lubrication of the liquid coatings and can give an improvement of their flow behaviour. Typical examples are based on aliphatic greases and on siloxane surfactant compounds, (Robb, 1997).

- **De-foamers:** These are used to reduce or to hinder the formation of foams in coating formulations. Foams can be problematic in coatings and are usually formed during the mixing, agitation or stirring of the coatings. Many de-foamers are based on surfactant structures. Examples include alkyl phenol ethoxylate compounds, (Wicks et al., 2007).

- **Dispersing agents:** These are used to promote the conversion of polymer components into a “solution” state. In water borne coatings, water can be used to act as a solvent or as a dispersing agent, (Ulrich, 2008).

1.4. Coatings application and curing/drying (physical and chemical events)

In can coatings, the thermal curing process converts the wet coating film, applied onto a substrate, into a cured film, through chemical reactions. More commonly, as the coating is cured, volatile solvent components of the coating are lost through evaporation. In order to control solvent evaporation, solvent(s) need to be chosen on the basis of their solvency and their evaporation rate, (Stout, 1998). An alternative approach involves the curing of formulations containing reactive monomers in which one or more of the monomers act as a reactive “solvent”. This solvent becomes part of the cured system, leading to the concept of the 100% solids system, as encountered in uv curing/thermal combinations, (Vigneron et al., 1994).

During the curing of melamino cross-linked coatings, two general chemical reactions occur, those which form melamino-polymer links and those which form melamino-melamino links. These reactions depend on the functionality of the cross-linkers and on the functional groups that are present in a reacting polymeric binder(s), (Magami, 2013a).

1.4.1. Cross-linking reactions between binders and cross-linkers

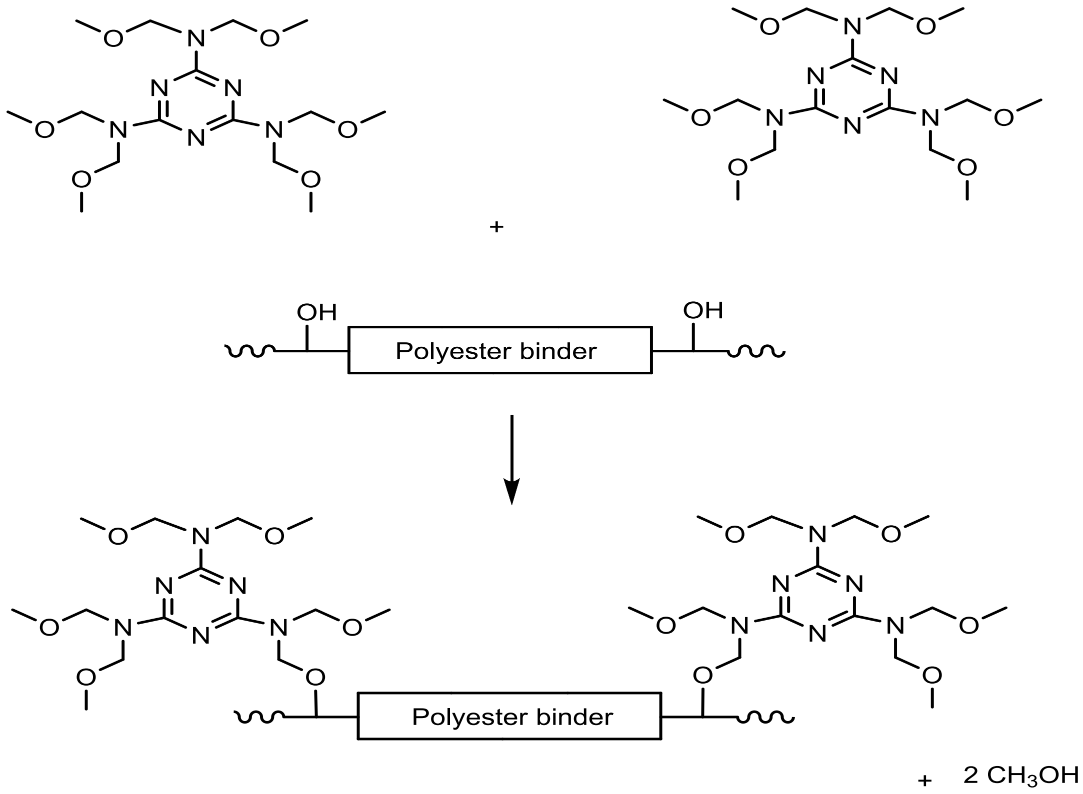


Figure 1.4-1: Schematic representation of the mechanism of reaction during the curing of a polyester/HMMM-based coating

In a melamino cross-linked coating system, due to the high degree of functionality, the pre-polymer composition can react functionally with other resin precursors in the medium during the curing process, (Weiss, 1997). A simplified, model cross-linking reaction between a melamino cross-linker and a poly(ester) binder component is represented by Figure 1.4-1.

1.4.2. Self-condensation reactions of amino-based cross-linkers

Amino cross-linker compounds can self-cure. The reactions can take place even at lower temperatures. These reactions are dependent on the reactivity of the functional groups that are present. Usually, the presence of catalysts (acidic or basic) is required. On this note, a detailed comparison between the different types of groups that self-condense in MF resin, including their reactivity, have been published, (Jonesa et al., 1994). Figure 1.4-2 shows a self-curing reaction in a melamine-based cross-linker system.

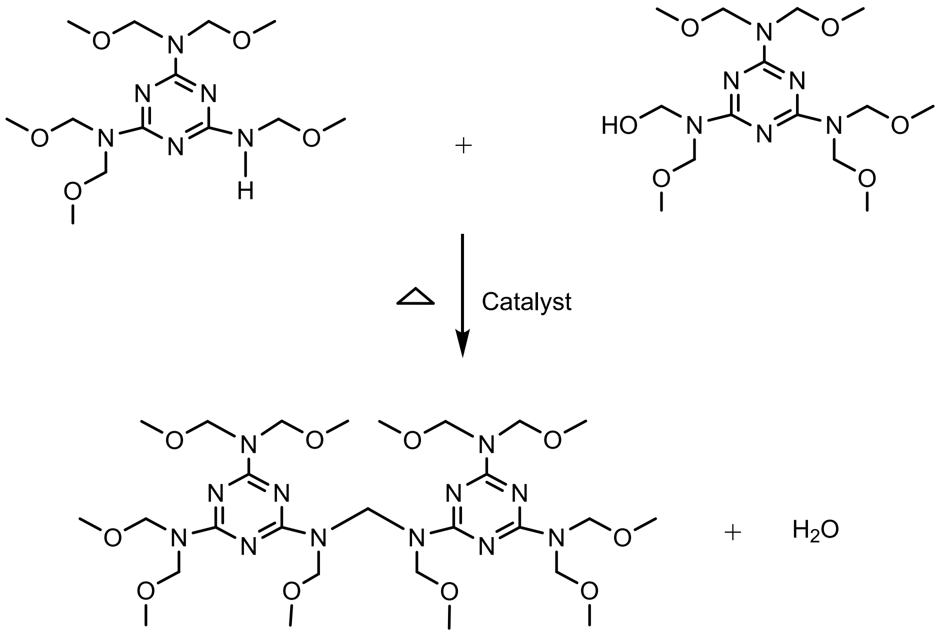


Figure 1.4-2: Acid catalysed self-curing reaction in a melamino-based, amino resin creation

1.5. Physical-chemical aspects of can coatings use

In formulations that contain components that are volatile at the application temperature and during other processing operations, the subsequent evaporation (solvent, additives) from the coating enables the composition to be converted from the wet state into the dry state, with the diffusion of solvent molecules, of by-products molecules and of other components through the continually changing coating film, (Jiang, 2008). The operating temperature, the curing oven air velocity and the volatility of the by-products and other components affect the rate at which volatiles are removed from the coating into the immediate environment, (Goldschmidt and Streitberger, 2003).

As the solvent evaporates from a coating during application and curing, the mobility of the oligomer/polymer chains in the system decreases (Kiil, 2010). This mobility is reduced to a minimum when all of the solvent and the volatile by-product molecules that were in the system have been removed. During these processes, interlocking of the polymer chains in the coating occurs, (Goldschmidt and Streitberger, 2003). Such interlocking is especially important for food contact can coatings since, in such coatings, it is vital that the coating components are prevented from migrating into the can contents, (Jiang, 2008).

1.6. Substrates used for food canning

The metals that are generally used as a component of can packaging include aluminium and steels of various compositions. Alloys based on aluminium-transition metal combinations are also used, (Davis, 1994).

1.6.1. Tinplated steel

Electrolytic tinplate (ETP) substrate, is fabricated as a deposition of tin onto steel, (Yfantis et al., 2000). ETP is the most common material for tins and cans, (Johnsen, 2009). In some instances, the tin surface may be replaced by a very thin chromium surface or an aluminium surface. Using such combinations, a variety of different shapes and subtle colour combinations can be created.

1.6.2. Tin-free steel

Tin-free steel (TFS) has been replacing ETP for some applications. Another form of TFS is Electro-Chromium Coated Steel (ECCS). Both have similar performance properties. TFS is more resistant to retort conditions, (Oldring and Tuck, 2001). TFS is manufactured through a procedure where chromic acid treatments are applied onto steel sheets. Unlike ETP which is used for food cans, TFS is used for beverage applications and, as the name implies, it does not contain tin, (Paine, 1991). There are moves to find alternatives to chromic acid treatment because of environmental concerns over the use of Cr(VI).

1.6.3. Aluminium

Aluminium is widely used for beverage cans and for some food cans (e.g. fish). If uncoated, aluminium is susceptible to attack by mineral acids or organic acids. The widespread use of aluminium is attributed to its compatibility with many foodstuff, its corrosion resistance and the fact that is does not cause coloration of food or beverages, (Davis, 1994).

1.7. Ageing phenomena in can coatings

Internal coatings and external coatings that are used on cans should be stable for the "lifetime" of the can. Ageing is a property of the overall coating composition, in which the polymeric binder(s) play(s) a major role. Due to the conditions encountered during service, the quality, the performance of material coatings and the nature of the polymers that they contain erode with time, (Fernando, 2011). This deterioration of the coatings eventually affects the viability of the can-coating composition.

Many of the factors that influence the ageing of coatings are related to the polymeric binders from which the coatings originate. In the lifetime of the coating material, conditions such as the weather, light/radiation, temperature and humidity have an influence. If a flexible polymer is used in the coating and this experiences exposure changes that are in the glass transition region, there can be a significant influence on the performance of the coating/print, (Schulz, 2009).

Formulation strategies can be used to improve or complement the performance of binder compositions. One option is the incorporation of polymeric modifier additives into the coating. For example, oligomeric siloxanes are known to act as good durability modifiers for epoxy resins, (Kumar et al., 2001).

For can coatings, the durability or the service life that the coating is able to provide can be estimated, (Shreepathi et al., 2011). According to coating experts, electrical resistance values of around $10^7 \Omega \text{ cm}^{-2}$ are a determining factor in whether or not a coating is fit for its intended protection purpose. A coating possessing a value that is greater than $10^7 \Omega \text{ cm}^{-2}$ can be considered to offer protection to an applied surface, (Leidheiser, 1991). For can coatings, electrochemical impedance spectroscopy (EIS) can be used, to predict the remaining service life of the coating and also the amount of coating that is present on the can, (Kern et al., 1999).

1.7.1. Time dependent ageing

Time dependent ageing studies are important with regards to coatings, because they can help in assessing the long term performance properties of the coatings. These properties could include durability, polymer degradation, chemical resistance and mechanical strength. Successful tests would then need to be interpreted in order for the performance of the coatings during testing, to represent the performance in service.

Gravimetric techniques can be used in time dependent ageing studies that involve monitoring the weight loss of the coating over time. During this period, polymer degradation could occur leading to the release/loss of small volatile species as the polymer chains are broken, (Aguirre, 2010).

1.7.2. Temperature dependent ageing

The ageing of coatings can also be studied by monitoring a change in the chemical and physical characteristics of the components of the coating, as a function of the temperature, under controlled conditions. Evaluations can be carried out by measuring one of several of the performance properties of the coatings as they are being subjected to various thermal conditions. Analyses involving one or more of microscopy, spectroscopy and thermogravimetry could be carried out to monitor signs of deterioration in the coating films, (Martín et al., 2012). Approaches based on the use of the Arrhenius equation could also be used during attempts to monitor the kinetics of the degradation process or other changes, (Aguirre, 2010).

1.8. Testing and performance attributes of can coatings

The behavioural properties of coatings can be monitored in either their solid state or their liquid state. In addition to the flow tests that are usually carried out on wet coatings, solid state coatings are also characterised. A broader classification for the testing of solid coatings concerns their mechanical properties, their physical properties and their chemical properties.

1.8.1. Testing of liquid coatings– emphasis on can coatings

1.8.1.1. Flow time estimation

Flow time estimation procedures are straight forward techniques that a coating chemist can use. The test procedures are generally highly practical in nature. They should not be considered ideal as measures of “true” viscosity and rheological properties. They serve a quality control purpose. One approach involves allowing a known volume of coating to flow through the orifice (located at the bottom) of a cup-shaped container, (Shah, 2007). The cups can vary in shape and size. Typical example of cups include Zahn cups, Ford cups, ISO cups, DIN cup, ASTM cup, and ANFOR cups, (Sheeninstruments.com). The relevant tests are based on ASTM D4212-10 and on ISO 2431.

1.8.1.2. Solids content estimation

The measurements involve the determination of total solids (dry, non-volatile components) in the coatings. The methods are based on gravimetric analysis, where a known mass of a coating sample is dried (cured for can coatings) by the application of heat, in an oven, in order to remove the volatile/solvent components. Other energy sources may also be used (UV curing, electron beam curing). Equation 1.8-1 represents the % solids equation, (Jiang, 2008).

$$\textbf{\% Solids} = \frac{W_3 - W_1}{W_2 - W_1} \times 100\%$$

Equation 1.8-1: Solids content equation

Here, W_1 = weight of the uncoated metal substrate (g)

W_2 = weight of the metal and the fluid coating (g)

W_3 = weight of the metal and the cured coating (g)

Care needs to be taken to ensure that a consistent weight is achieved during the drying/curing process and after the drying of the coating before the sample is reweighed. For the tests, a thoroughly mixed sample, a reliable oven, suitable vessels and an accurate weighing balance are needed, (Koleske, 1995b). Test guidelines are also provided by ASTM D2974 standards.

1.8.1.3. Thermal analytical studies

Thermogravimetric analysis (TGA), thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) are important tools in the analysis and the characterisation of liquid coatings. These techniques can be comprehensively and conveniently used to study the various thermally induced transitions that arise in the coatings on heating/curing. They can also be used to monitor the thermal decomposition behaviour of coatings. With suitable controls, thermal analysis techniques can also be used to monitor the kinetics of the breakdown processes, (Tracton, 2006).

1.8.1.4. Rheological studies

Rheological techniques are often used to characterise the flow behaviour of liquid coatings. In these, it is important to monitor the flow patterns of coating materials under highly controlled conditions relating to the applied shear stress, shear strain rate and temperature. The general flow behaviour of surface coating materials including inks, paints, etc is given in Figure 1.8-1, (Guthrie and Lin, 1994):

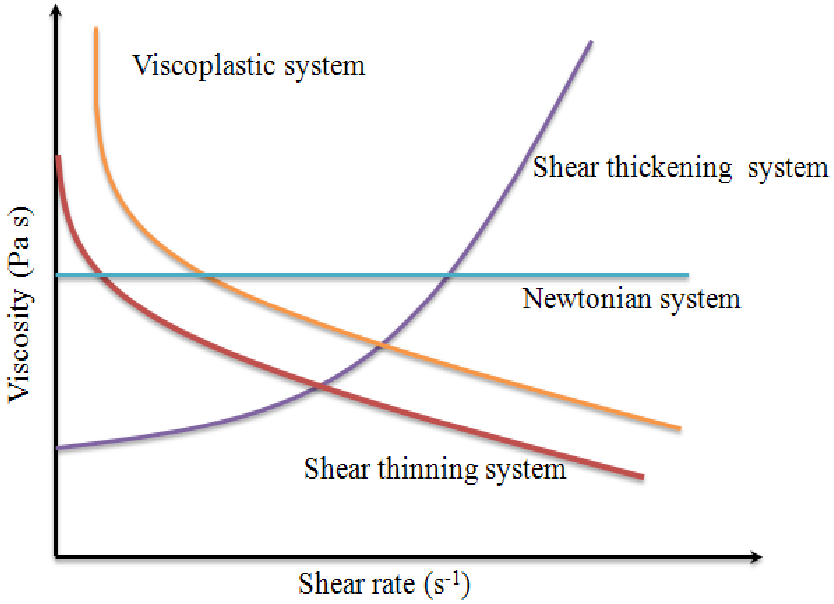


Figure 1.8-1: Flow behaviour of common fluid systems

Can coatings generally exhibit shear thinning behaviour. This means that the viscosity of the coating fluid decreases with increase in the shear rate and the shear stress. Also, the viscosity of shear thinning coatings usually decreases with increase in the temperature, provided the composition of the coating remains unchanged, (Magami, 2013b). Relevant to can coatings, both Newtonian fluids and shear thinning fluids are defined as follows:

Newtonian fluids exhibit linear flow curve, i.e. a linear plot of shear stress against shear rate. This means that such a fluid exhibits a constant viscosity when the amount of shear force is changed. In contrast, a non-Newtonian fluid exhibits a viscosity that changes with change in the applied shear force, (Malkin and Isayev, 2012).

Shear thinning or pseudo-plastic fluids exhibit an apparent viscosity that decreases when the shear rate is increased. At very low shear rate values and at very high shear rate values, most shear thinning fluids exhibit Newtonian flow character, (Chhabra and Richardson, 2008).

1.8.1.5. Kinetic aspects of rheological studies

The values for the activation energy of flow of coatings can be calculated using modified versions of the Arrhenius equation, Equation 1.8-2. The procedures are well documented and described in the literature, (Schoff and Kamarchik, 2005). Such approaches treat flow in a kinetic sense, as a function of the prevailing temperature. The yield stress point and infinite sheer viscosity values can be obtained using experimental approaches based on Equation 1.8-3, Equation 1.8-4 and Equation 1.8-5. Equation 1.8-3 represents the Casson-Asbeck relationship whereas Equation 1.8-4 and Equation 1.8-5 are the rheological forms of the Arrhenius equation, (Hong et al., 2010).

$$k = A\, e^{\frac{-Ea}{RT}}$$

Equation 1.8-2: Arrhenius equation

Here, k is the rate of flow constant, Ea is the activation energy of flow (the minimum amount of energy required initiate flow), A is the Arrhenius parameter (collision frequency factor), R is the molar gas constant and T is the Kelvin temperature.

$$\eta^{1/2} = \eta_{\infty}^{1/2} + \sigma_{o}^{1/2}\ \gamma^{-1/2}$$

Equation 1.8-3: Casson-Asbeck equation

$$\eta = A\, e^{\frac{-E_{af}}{RT}}$$

Equation 1.8-4: Arrhenius equation (rheological form 1)

$$\ln \eta = \frac{-E_{af}}{RT} + \ln A$$

Equation 1.8-5: Arrhenius equation (rheological form 2)

Here, η is the dynamic viscosity, η_{∞} is the infinite shear viscosity, σ_{o} is the yield stress point, γ is the shear strain rate, E_{af} is the activation energy of flow, *R* is the molar gas constant and *T* is the Kelvin temperature.

The yield stress point can also be obtained by extrapolating a graph of shear rate vs. shear stress to the point where the line intercepts the shear stress axis, (Zhu et al., 2005). This point of interception is the yield stress and is defined as the force at which a fluid that is being mixed/stirred begins to flow or deform. Although an understanding of the yield point can be of great benefit to understanding the fluid characteristics, the existence of the yield stress is still debatable, (Deshpande et al., 2010). One indication that such a point does not exist is that the transition of a fluid from rest (zero flow) to a flow moment cannot be considered to be a single defined event.

1.8.2. Testing of cured coatings– emphasis on can coatings

1.8.2.1. Film weight thickness evaluation

The weight thickness (FWT) of a cured coating film can be evaluated using gravimetric analysis. For can coatings, the method often involves removing the coating from a known area of the cured coated, metal substrate by removal in acetone, (often with the aid of NaCl). After removal of the coating, the plate is then re-weighed, (Wagner, 2008). Equation 1.8-6 summarises the procedure.

$$\mathrm{FWT} = \frac{W_1 - W_2}{A}$$

Equation 1.8-6: Film weight thickness equation

Here, FWT (gm^{-2}) is the film weight deposited per unit area (m^2), W_1 is the weight of the coated substrate (g), W_2 is the weight of the corresponding substrate without the coating (g) and A is the area of the weighed substrate (m^2).

The thickness of the liquid coating layer that is applied to the substrate is dependent upon the applicator that is used. For application of can coatings using K-bar coaters, Table 1.8-1 provides information on the relationship between the K-bar choice and wet film thickness, (Largoab.se).

Table 1.8-1: K-bar coater specifications

K-bar number	K-bar wire diameter	Wet film thickness
1	0.08 mm	6 µm
2	0.15 mm	12 µm
3	0.31 mm	24 µm
4	0.51 mm	40 µm
5	0.64 mm	50 µm
6	0.76 mm	60 µm

1.8.2.2. Flexibility testing

Can coatings are expected to possess the appropriate flexibility properties for them to withstand the stress conditions that they undergo during processing, shelf-life and use. Standard methods exist for testing the flexibility of can coatings, (Miguel-phil.en). ASTM D4145 describes such a method. Such a method tests the severity of bending of a coated panel needed to cause failure in the coating as seen by cracking. Other popular tests are impact, wedge bend, T-bends, and conical mandrel flexibility test. A “simple” procedure involves bending or folding the coated panel after which an assessment of the coating’s flexibility is carried out, (Koleske, 1995b).

1.8.2.3. Surface wetting studies

Contact angle studies can be used in an attempt at determining the critical wetting tension of a substrate or a surface, (such as a coated, cured coating). The contact angle, (ϴ), gives a useful guide to the extent to which a solid can be wet by a liquid. A value of zero in contact angle depicts perfect wetting. The critical wetting tension (also known as critical surface tension) is usually obtained by conducting measurements of contact angles provided by a range of pure liquids or selected blends of liquids, deposited on the surface of a substrate in a sessile fashion. A plot of the cosine of ϴ against the surface tension of the fluids is formed. At $\cos \Theta = 1$, $\Theta = 0^{o}$. The importance of the critical wetting tension parameter is that any liquid with a surface tension that is less than the critical surface tension should have the capacity to wet the substrate, (Mark, 2003). Tests are usually based on ASTM D 179 and ASTM D 1331. In Figure 1.8-2, a low wetting surface is shown as providing a high contact angle, (droplet A), while a highly wetting surface is shown to provide a low contact angle, (droplet B).

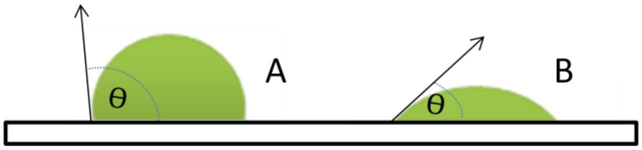


Figure 1.8-2: Surface tension illustration

1.8.2.4. Surface reflectance studies

A coating's surface reflection characteristics in the visible region of the electromagnetic spectrum (400–700 nm) can be measured using a reflectance spectrophotometer. The appearance (colour, reflectance, transmittance, etc) of the surface is measured using this device with an integrating sphere that is capable of including or excluding the specular surface reflection from measurements. The data are usually represented as a graph of the reflectance (on a scale of 0 to 100%) against the wavelength (nm). The devices, the procedures and the conditions of measurement are covered in the international standard CIE 1986 related to ASTM, 1985b and ISO, 1984, (Blum, 1997).

1.8.2.5. Adhesion testing

One of the more common adhesion tests is the T-peel test, (Zumelzu and Gipoulou, 2002). Other adhesion tests are based on surface spectroscopy and surface microscopy. The objective principle of the T-peel test is to gain an understanding or an estimation of the strength of adhesion that exists between a coating and the substrate. The test is commonly applied to can coatings as a means of monitoring their adhesion strength, any detachment and the occurrence of adhesion failure.

In the peel testing routine, an adhesive tape is applied onto the coated cured substrate and the extent of coating detachment is observed. The test procedures are governed by ASTM D1876 and BS-5350 part C12/19940.

1.8.2.6. Hardness testing

Most hardness testing procedures are based on an indentation approach, where a pointed or spherical, hard object is brought into contact with the surface of the coating for a specified time period. The level of indentation and the area of indentation can be used as a measure of the coating's hardness, (Fink-Jensen, 1964) as can the energy involved in achieving the indentation. Many of the test procedures are governed by DIN 53 157 and ISO 1522.

1.9. Migration phenomena in can coatings

Migration tests are applied to can coatings, as required, so that one can monitor the performance of a coating and its ability to comply with health, safety and other regulations. Depending on the composition of the coating, the can-containment conditions and the interaction of the can substrate with the dried coating, the movement of small molecules into the can food contents, through physical processes, might/will occur.

1.10. Use of food simulants to test for migration into/from food-contact coatings

Food simulants are media that are conveniently used to mimic the chemical/physical behaviour of foodstuffs. They can be used in place of food, in food analysis, in order to give understanding of the amount of coating material that is transferred into food as a result of exposure during manufacture or use. Examples of standard food simulants are given in Table 1.10-1, (European Commission, 1985).

Table 1.10-1: Examples of approved food simulant compositions

Food simulant	The food that the simulant mimics
Acetic acid 3% w/w in aqueous solution	Foodstuff with high acidity levels, pH<4.5
Ethanol 10% w/w in aqueous solution	Alcoholic beverages aqueous foods with a solubilising power higher than plain water
Olive oil or Sunflower oil	Fatty foodstuffs

1.10.1. Melamino migrants/ release products from coatings into food

In melamino cross-linked coatings that are used in can packaging there is a tendency for more mobile melamino compounds to be created, during the sterilisation processes or the pasteurisation processes that the canned foods undergo during manufacture, (Bradley et al., 2008). This means, that from the public/consumer safety point of view, the foods and the coatings should/must be tested in order for any compound that might be created and that might have subsequently migrated into food/food stimulants to be quantified. Any migration limit should be compared with the standard/stated/required Overall Migration Limit (OML) and the Specific Migration Limit (SML), each of which is set by regulatory agencies, (Barcelo, 2008). Such comparisons are designed to ensure that any migration arising from the processing, the application and the storage is quantified and that the resulting data are rigorously interpreted with respect to food health and safety issues, (Grob et al., 2007).

1.10.2. Concern regarding potential food contamination by melamine and melamine derivatives

In 2008, in China, there was a severe food adulteration incident following the deliberate addition of melamine to infant milk formula. The incident resulted in the deaths and/or hospitalisation of many babies after consumption of the food, (Zhou et al., 2010). In addition to global condemnation of the incident, many governmental and non-governmental agencies voiced the need to establish standard methods and procedures for the detection and quantification of melamine and its analogous compounds, (Han et al., 2009, Lund and Petersen, 2006). This incident brought melamine and related compounds into the spotlight and has resulted in considerable attention/awareness being activated with regards to melamine and its hydrolysis products.

The Chinese incident was not a migration issue. However, following the incident, there has been continuing interest from consumer advocacy groups in understanding the migration characteristics of components of amino cross-linked coatings, since these are used in food contact based applications.

Melamine has an SML (specific migration limit) of 2.5 mg/kg (equivalent to 2.5 ppm) of food or food simulant (European Union, 2011b). Prior to January 2012, (when Regulation EU 2011b came into force), melamine had a higher SML of 30 mg/kg based on a tolerable daily intake (TDI) value of 0.2 mg/kg body weight (b.w.) for this substance. The restrictions were drafted and communicated by the European Food Safety Authority (EFSA) for the European Commission (EC) of the European Union (EFSA, 2010b). As a result of a recent re-evaluation of melamine by EFSA, including a consideration of exposure from sources other than food contact materials, it was concluded that the migration limit for melamine should be reduced and the migration limit of 2.5 mg/kg food was the result (European Union, 2011b).

Figure 1.10-1 shows that from 2008, most probably because of the "Chinese melamine issue", the number of related journal articles rose to a maximum before tailing off somewhat.

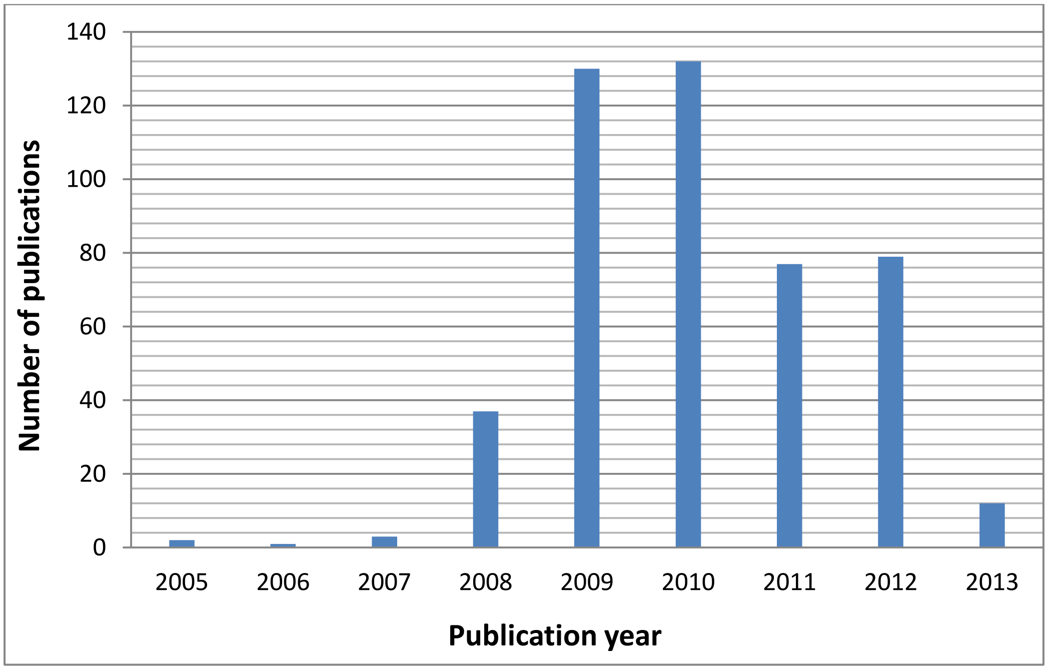


Figure 1.10-1: Number of articles published each year from 2005 to 31/07/2013 on the topic of "melamine food contamination", using SciFinder scholar search gateway

1.10.3. Potential migrants in food contact amino-based coatings

In amino cross-linked can coatings that are intended for food contact applications, the key potential migrant compounds that need to investigated are melamine, benzoguanamine, cyanuric acid, formaldehyde and related low molar mass derivatives.

1.10.3.1. Melamine

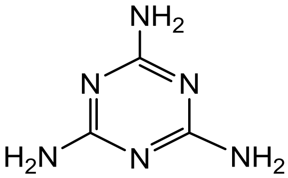


Figure 1.10-2: Melamine, (2,4,6-triamine 1,3,5-triazine)

Melamine is a 6-membered, heterocyclic compound, (Shimadzu, 2010), belonging to a group of compounds known as the *s*-triazines, composed of three carbon atoms and three nitrogen atoms in the ring, (Katritzky et al., 2008). Melamine has a solubility value (in water) of 3.3 g dm^{-3}, a molecular weight of 126 g/mol and a melting point of 345 ^{o}C, (Bann and Miller, 1958). The chemical structure of melamine is shown in Figure 1.10-2.

It was mentioned in Section 1.10.2 that European Union legislators have allowed the use of melamine as a monomer in the manufacture of plastic articles and have established a specific migration limit (SML) of 2.5 mg/kg for its use, (European Commission, 2005b, European Union, 2011b).

1.10.3.1.1. Melamine and its hydrolysis products

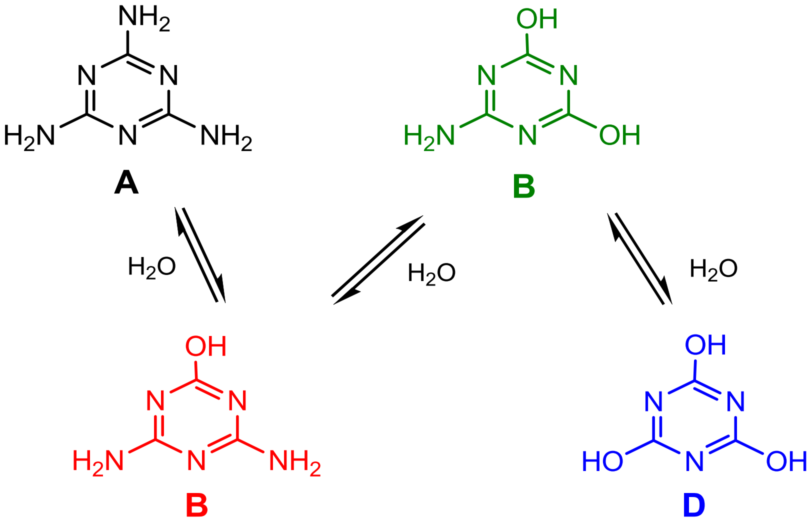


Figure 1.10-3: A: melamine, B: ammeline, C: ammelide and D: cyanuric acid

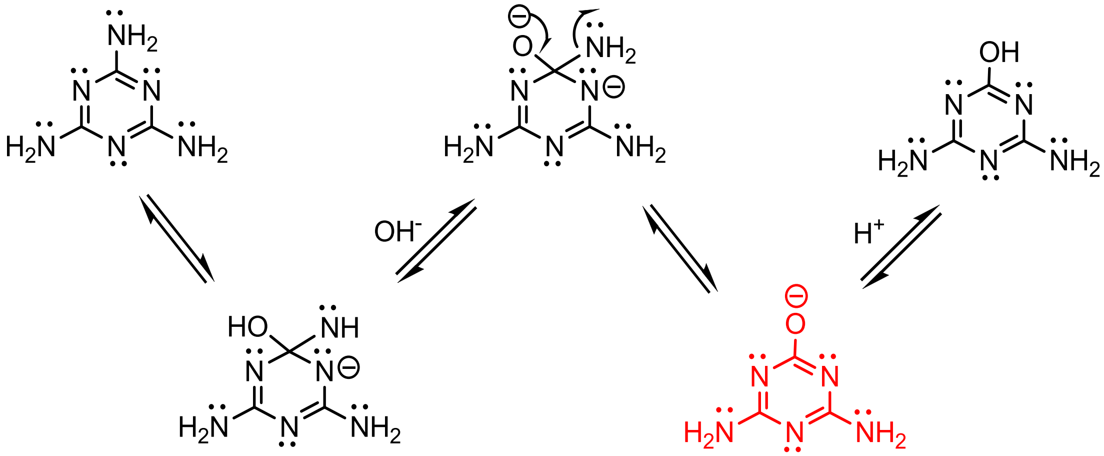


Figure 1.10-4: Mechanistic pathway showing the hydrolysis of melamine to ammeline

The hydrolysis of melamine in a mineral acid or in a basic medium generates ammeline, ammelide and cyanuric acid, one step after the other with cyanuric acid being the end product of the hydrolysis, (George et al., 2006). This hydrolysis pathway is shown in Figure 1.10-3. The reaction mechanism for the conversion of melamine to ammeline is shown in Figure 1.10-4.

When melamine and cyanuric acid co-exist in a matrix, there is a tendency for the formation of "melamine stones" or a melamine-cyanuric acid complex, formed through H-bonding interactions between the melamine and cyanuric acid. The self-assembled "supramolecular complex" is represented in Figure 1.10-5, (Sun et al., 2010, Katritzky et al., 2008, Litzau et al., 2008). The main problem posed by this complex is its relative insolubility compared to the solubility of the individual compounds, melamine and cyanuric acid. This means that the complex can precipitate from the urine and form kidney stones, causing renal damage.

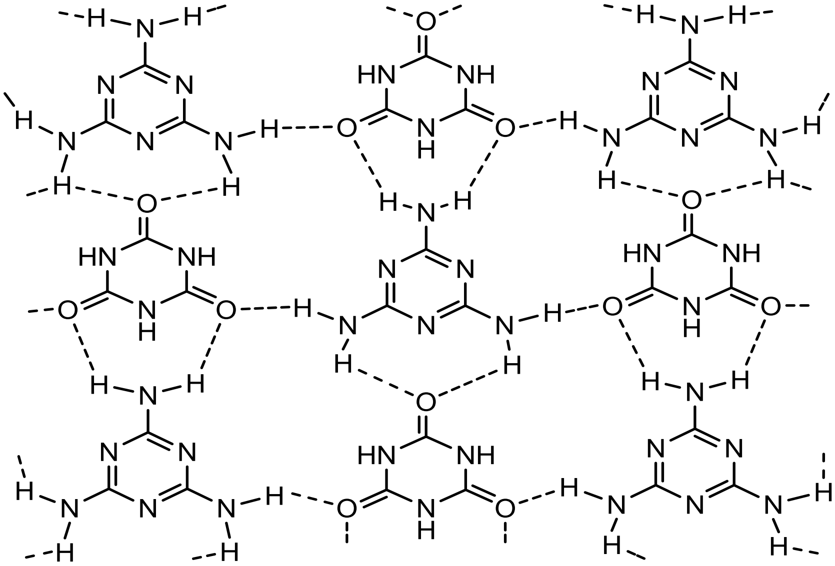


Figure 1.10-5: Melamine-cyanuric acid complex, also termed melamine stones

1.10.3.2. The migration of melamine from coatings

Chromatographic techniques are important in the analysis of melamino migrants from coatings into food or into food simulants. The techniques can separate individual compounds from a mixture, even when these compounds are very similar, (Wagner, 2008). These techniques include liquid chromatography (LC), gas chromatography (GC) and inverse gas chromatography (IGC) together with associated hybrid techniques (GC-MS, LC-MS and so on – the symbol “MS” denotes mass spectrometry).

To obtain an efficient separation system that can be used prior to determining the melamine loading in migration-based studies, several columns and extraction media have been cited and are available, (Chan et al., 2009). For each column used, the limits of quantification were recorded. MALDI-MS (matrix assisted laser desorption ionisation) has also been successfully used in the analysis of melamino compounds, several matrices having been employed, (Campbell et al., 2007). For the LC quantification of melamino migrants, the use of “isotope-labelled” calibration standards has been reported, (Bradley et al., 2011).

During the analysis of melamine, as a migrant from coating systems, any formation of the melamine-cyanuric acid complex could pose a problem because of the relative insolubility of the complex in a large number of solvents, compared to the solubility of the individual compounds, melamine and cyanuric acid. In practice, the addition of diethylamine can lead to this complex being dissociated, a procedure that helps significantly to dissolve any ammeline and ammelide, both of which have limited solubility in some solvents, (Litzau et al., 2008).

1.10.3.3. Benzoguanamine

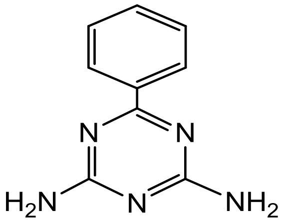


Figure 1.10-6: Benzoguanamine

Benzoguanamine is a member of the triazine family. The chemical structure of benzoguanamine is shown in Figure 1.10-6. It is less functional than melamine as it contains only two amino groups. It is used as a monomer in amino resin systems.

Benzoguanamine, as supplied, may contain up to 2% melamine, either as an impurity or as an additive. The melamine impurity can therefore compete with the benzoguanamine in reactions, including those occurring during the preparation of cross-linker compounds, (Inchem.org, 2001). Benzoguanamine forms a cross-linked network when reacted with other resin precursors, (Mark, 2003). Various cross-linkers that are based on benzoguanamine are used in coating formulations along with other resin precursors to achieve superior performance characteristics. These characteristics include good mechanical properties, good barrier properties and good chemical resistance, (Christensen, 1977).

The specific migration limit (SML) of benzoguanamine is 5 mg/kg (European Union, 2011b). For both melamine and benzoguanamine, the legislation establishing migration limits relates only to plastics. None-the-less, in the absence of legislation, harmonised at the EU level specifically for can coatings, these migration limits are often taken as presumptive standards for non-plastics too, (European Union, 2011b).

1.10.3.4. Formaldehyde

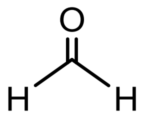


Figure 1.10-7: Formaldehyde

Formaldehyde is a difunctional organic compound that is usually supplied in aqueous solution, stabilised with methanol because of its tendency to polymerise. It is stable in alcoholic solutions, in closed container systems, (Lewis, 1989). The chemical structure of formaldehyde is shown in Figure 1.10-7.

European Union legislations have established a specific migration limit (SML) of 15 mg/kg for the use of formaldehyde in plastics and in food contact materials, (European Commission, 2005b).

1.10.3.4.1. Paraformaldehyde

Paraformaldehyde is an oxygen-containing polyacetal compound which is formed through the addition polymerisation of formaldehyde, a reaction that takes place as an aqueous solution of formaldehyde is concentrated. This addition polymerisation is only slightly exothermic. As a result, paraformaldehyde undergoes depolymerisation in water, reforming formaldehyde. In certain instances, paraformaldehyde is used to manufacture amino resins in an alternative approach to using formaldehyde, (Fox and Whitesell, 2004). A schematic representation of paraformaldehyde is shown in Figure 1.10-8. Figure 1.10-9 shows a reaction scheme for the formation of paraformaldehyde.

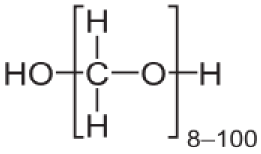


Figure 1.10-8: Paraformaldehyde

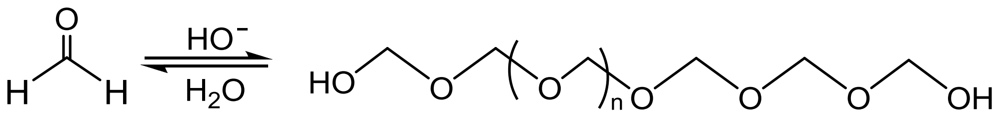


Figure 1.10-9: Formation of paraformaldehyde

1.11. Health, safety and environmental aspects of can coatings

In reality, coatings may (will) contain one or more of each of the following, pigments, residual components, and additives. It is, therefore, in line with health and safety protocols, that the Council of Europe (COE) has provided a list of chemicals, including monomers that can be used in coatings manufacture and application, with respect to can coatings, (Council of Europe, 1996, Council of Europe, 2002). These provisions are intended to reduce the risks that are associated with the handling of the “raw material” chemicals and the derived products.

Many of the solvents and polymeric binders that are used in coating formulations are required to meet established environmental standards. These standards are updated regularly on the basis of acquired exposure data that are related to the volatility, to the emission of environmentally unfriendly compounds and to the effects of such compounds on test specimens, (Alidedeoglu et al., 2011). It is also for environmental reasons that many waterborne, functional polymers are increasingly preferred over their solvent-borne counterparts, when these are used in coating formulations, (Zhu and Hu, 2011). Similarly, the curing of a coating by radiation, (UV radiation for example), is considered by many to be environmentally friendlier than curing/drying that involves the removal of solvents and other volatile organic components (VOC), (Gozzelino et al., 2010). The following four options can be regarded as formulation strategies that could be aimed at reducing volatile emissions from coatings. These are routes to the formulation of powder-based coatings, the formulation of water-based coatings, the formulation of low VOC coatings and the employing radiation curing procedures.

Several solventless coatings, (100% curing formulations and powder coatings), are available commercially. Because these do not contain any solvent, when they are used in can coating formulations, they can be expected to offer good barrier characteristics by preventing/reducing the occurrence of those bulk defects and surface defects that arise from the migration of the solvent through the coating, (cissing, bubble formation, trapped voids). Such defects can supply a route whereby “unwanted” reactants are able to reach the metal substrate surface by either chemical processes or physical processes and possibly cause corrosion, (Weinmann, 1998).

1.12. Regulations for can coatings

Regulatory measures that relate to can coatings, if adopted successfully, ensure that sustainably defined coating manufacturing routes are in place, that good formulation strategies are followed, that the appropriate coating materials are supplied and that such materials are stored appropriately. The regulatory measures also govern whether or not the appropriate application methods have been/are used. The effect of legislation that relates to the coatings industry is seen in the classification of labelling, in market restrictions, in VOC controls, in the need for notification of the use of new chemicals, in the assessment of existing chemicals and in the maintenance of regulations covering the exposure limits of the substances, (Jotischky, 2001).

The Registration, Evaluation, Authorization and Restriction of Chemicals directive (REACH), is a product of the European Commission for enterprise and industry. This directive is designed to ensure that chemicals are handled properly to ensure human and environmental protection. In its part, REACH legislates that manufacturers must communicate with downstream users. This means also that in situations where a product is identified as being inappropriate, this information should be communicated to the users, (European Comission, 2007).

Although the REACH directive exempts most polymers from registration and evaluation, the regulation/responsibility of safety that is contained in the legislation that has been laid down applies to coating manufacturers, since many coating starting materials are affected. This responsibility, by implication, means that there is a need to provide, to transporters, suppliers and the end user, information that relates to the “chemical” materials to ensure that health and safety issues are addressed. Also, risk assessments on hazardous materials are required as is the substitution of such materials with safer alternatives to ensure health and safety compliance.

Table 1.12-1 shows examples of regulations that are relevant to coatings and the “coatings” industries that relate to safety and environmental issues.

Table 1.12-1: Regulations relevant to coatings that relate to safety and environmental issues

Regulation	Regulatory Organisation	Description	Reference
VOC Solvent emission directive	*European Commission*	Aims at reducing the emission of volatile organic solvents including from coatings.	(European Commission, 1993)
TiO_2 production regulation	*European Commission*	Applies to production and waste disposal of TiO_2	(European Commission, 1992)
AP (96) resolution on surface coatings intended to come into contact with foodstuffs	*Council of Europe*	Contains specifications on coatings' manufacture based on health and safety. Global and specific migration limits of monomers and additives that are used in food contact coatings.	(Council of Europe, 1996)
Test procedures for resinous materials used in food contact coatings	*US FDA*	Descriptions of allowed levels of chemicals including monomers, solvents etc. that can be used in food contact coatings.	(US FDA, 2011a)
Risk assessment procedures	*US FDA*	Detectable limits of melamine that can cause health effects.	(Newstrack, 2010)

Directive 94/62/EC	*European Commission*	This relates to procedures to reduce packaging waste problems through recycling and other methods.	(Oldring and Nehring, 2007)
Dangerous preparations directive	*European Commission*	Directive that includes the formulation and supply of mixtures such as paints, inks etc.	(European Commission, 1994)
Resolution on inks for use in food packaging materials	*Council of Europe*	Resolution on standardisation based on risk assessments and safety evaluations on inks applied to non-food contact areas of food packaging materials.	(Council of Europe, 2005)
Regulation on articles to come into contact with food	*European Parliament*	Not specifically on can coatings or inks, but a general regulation on the design, composition, measures, labelling and safety assessment of materials that are intended to come into direct contact with food.	(European Union, 2004)
Regulation/restriction on the use of certain epoxies in food contact applications	*European Commission*	This relates to the restriction of certain epoxy chemistries for us as binders, monomers in coatings for	(European Commission, 2005a)

		safety reasons.	
Directive on coated cellulose materials in food contact applications	*European Commission*	Includes directives on certain monomers/solvents that are allowed or restricted for use in coatings that are applied onto cellulosic substrates.	(European Comission, 2004)
Directive on simulants that can be used in testing migration of plastic components into food	*European Commission*	This primarily relates to plastic materials. However, it is adopted as a method of testing migration from can coatings.	(European Commission, 1985)
Produce safety: safe handling of raw produce	*US FDA*	Directives on the use of wax coatings on farm produce. Producer, shippers and supermarkets need to comply with.	(US FDA, 2011b)
Regulations for polymers and resin-based coating materials	*US FDA*	Provides a list of allowed coating raw materials, conditions of testing coatings and relevant migration limits.	(US FDA, 2013b)

Chapter 2: Preparation of reagents, characterisation of raw materials and calibration of the curing oven

2.1. Introduction

It is important to follow established and repeatable procedures in the preparation and use of laboratory reagents. It is also important to document the procedures that have been followed. In the preparation of chemical reagents and of chemical samples, methods can vary in terms of the nature of the materials to be used, their concentration, their measurement and the volumes that are required. Good laboratory practice involves following safety precautions, using appropriate safety devices, (such as fume cupboards, spectacles, hand gloves and glove boxes) and following advice from Material Safety Data Sheets (MSDS).

The effective characterisation of materials is vital to effective coating science and technology. This is because the data that are obtained provide information related to the material's composition, properties and structure. Knowledge that is obtained from the characterisation and testing of a sample material helps one to understand its interaction with other components and with itself when it is used in complex formulations. For the characterisation of pigments, particle size analysis, zeta potential analysis and optical and/or electron microscopy are useful techniques. With regards to polymers or pre-polymers, techniques such as the various forms of thermal analysis, spectroscopy, spectrometry, residual analysis and microscopy have an important part to play.

Many can coatings are applied to the metal substrate as liquids. The liquids are then converted into dry films by curing in the oven, for specific curing periods at required temperatures. The ovens are simply heating chambers that can be of different sizes, depending on the curing needs. The ovens need to possess good temperature control, good air flow, often being fitted with conveyor belts to transport substrates during the curing.

In this chapter, details concerning the purity of chemicals, grades of pigments and so on are provided. In addition, the chemical nature of polymers and of cross-linkers, the equipment that was used and the procedures that were followed in the characterisation of TiO_2 pigments and of amino cross-linker compounds are given. The procedures that were used to calibrate the curing oven are described. Relevant results are also discussed.

2.2. Materials

In the preparation of required aqueous solution of the chemicals, doubly-distilled, deionised water, discharged from an Elga, 18 Ω, Purelab-flex-Velolia distiller, was employed (Elgalabwater.com). Table 2.2-1 provides a list of the chemical reagents that were used in the study, details of the supplier and the purity and grade of each of the chemicals. For each chemical, MSDS advice was followed. An example of MSDS information presentation is given in Appendix 1.

In the calibration of the Werner Mathis curing oven, an electronic thermometer, Comark, type 1602, was used, (Comarkusa.com). Tin-plated sheets were used as substrates in the studies. These were provided by Valspar, (Valspar UK, 2011). They were manufactured by Arcelor Mittal, with specifications of 2.8/2.8 TH415 - 0.21mm, (Arcelormittal.com).

The different grades of the TiO_2 pigment are shown in Table 2.2-2. The three grades of the pigment differ from one another in the average particle size and in the multilayer inorganic treatment that has been applied over the TiO_2 core. Each pigment's surface was treated with aluminium oxide in order to enhance the pigment particle's stability in the coating formulations.

The various amino cross-linker compounds are shown in Table 2.2-3. Each class of amino cross-linker differs from another class on the basis of the chemical composition, the solids content, the viscosity, the coating compatibility, the water solubility and the cost, (OCCA, 1993). The cross-linkers in each particular group differ from one another in their composition, their degree of alkylation, their degree of methylolation, their water solubility and their viscosity, (Valspar UK, 2011).

Table 2.2-1: Inventory of chemical reagents used

Chemical	Supplier	Purity
1-methyl propanone	Aldrich	99%
2-butoxy ethanol	Acros Organic	98%
Acetic acid	Aldrich	Glacial
Ammonium acetate	Aldrich	97%
Benzoguanamine	Aldrich	97%
Chromotropic acid, disodium salt dehydrate	Aldrich	99%
Cyclohexanone	Alfa Aesar	99%
Formaldehyde	Aldrich	37%
Melamine	Aldrich	99%
Naphtha-light aromatic™ (Aromatic 100)	Valspar	99%
Propylene glycol monomethyl ether acetate	Aldrich	96%
Sodium dihydrogen phosphate monohydrate	Alfa Aesar	97%
Sodium thiosulphate pentahydrate	Alfa Aesar	99%
Surfynol® CT-324	Air Products	99%
Xylene	Vickers	97%

Table 2.2-2: Different grades of TiO_2 pigments

Acronym	Av. particle size	Zeta potential	Surface treatment	Supplier
PW1	318 nm	-54 mV	Alumina	Valspar
PW2	310 nm	-49 mV	Alumina	Valspar
PW3	355 nm	-46 mV	Alumina	Valspar

Table 2.2-3: Various melamino cross-linking compounds

Acronym	Chemistry	Supplier
HMMM-1	Hexamethoxymethyl melamine	Cytec
HMMM-2	Hexamethoxymethyl melamine	Valspar
HMMM-3	Hexamethoxymethyl melamine	Valspar
HBMM-1	Hexabutoxymethyl melamine	Cytec
HBMM-2	Hexabutoxymethyl melamine	Cytec
HBMM-3	Hexabutoxymethyl melamine	Valspar
MMTC-1 (TMTBM)	Methylol melamine type cross-linker	Valspar
MMTC-2	Trimethylol tributoxymethyl melamine	Valspar
MMTC-3	Methylol melamine type cross-linker	Valspar
MMTC-4	Methylol melamine type cross-linker	Valspar
DBMB	Dibutoxymethyl benzoguanamine	Valspar

2.3. Preparation of chemical reagents— as aqueous solutions, unless otherwise stated

2.3.1. 10% (v/v) ethanol solution, 1.72M

100 mL of ethanol was placed into a 1 L volumetric flask. The volume of the ethanolic solution was achieved by making up to 1 L with doubly-distilled deionised water.

2.3.2. 3% (v/v) acetic acid solution, 0.5M

30 mL of acetic acid were weighed and transferred into a 1 L volumetric flask. The volume of the aqueous solution was achieved by making up to 1 L with doubly-distilled deionised water.

2.3.3. Phosphate buffer, 5mM

0.69 g of sodium dihydrogen phosphate monohydrate were weighed and dissolved in approximately 900 mL of distilled water. The pH was adjusted to 6.5 ± pH 0.2 by adding small aliquots of an aqueous (10% g/g) sodium hydroxide solution. The volume was made up to 1 L with doubly distilled water.

2.3.4. Chromotropic acid salt solution, 14mM

0.5 g of chromotropic acid disodium salt were weighed and dissolved in 100 mL of doubly distilled water, in a volumetric flask. This solution was prepared on each day of analysis due to stability concerns.

2.3.5. 75% (v/v) sulphuric acid solution, 14M

125 mL of doubly distilled water were measured into a 500 mL volumetric flask. The volume of the flask was then made up to 500 mL by adding sulphuric acid, in portions, in a fume cupboard. This solution heats up considerably during preparation and therefore the flask was kept under ice during the dilution.

2.3.6. Melamine calibration solutions

2.3.6.1. UV-Vis calibration solutions

5 mg of melamine were weighed into a 50 mL volumetric flask. The volume was made up to the mark with a 3% (v/v) aqueous acetic acid solution. The procedure was repeated. Thus, a second stock solution was obtained.

Calibration solutions were prepared by measuring 0.25 mL, 0.5 mL, 2 mL, 4 mL, and 8 mL of the melamine stock solution, respectively into a series of 20 mL volumetric flasks. The volumes of the flasks were then made up to the mark with a 3% (v/v) aqueous acetic acid solution.

2.3.7. Benzoguanamine calibration solutions

A stock solution of benzoguanamine was prepared by weighing 0.05 g of benzoguanamine into a 500 mL volumetric flask. The volume of the flask was made up to mark with a 10% (v/v) aqueous ethanol solution.

Calibration solutions were prepared from the stock solution. Into a series of 10 mL volumetric flaks, 0 µL, 10 µL, 50 µL, 100 µL, 500 µL, 1 mL, 2 mL, 4 mL and 8 mL of the benzoguanamine stock solution were pipetted. The volume of each flask was made up to the 10 mL mark with a 10% (v/v) aqueous ethanol solution.

2.3.8. Formaldehyde calibration solutions

A stock solution of formaldehyde was prepared by weighing 0.8 g of formalin into a 200 mL volumetric flask. The volume of the flask was made up to mark with a 10% (v/v) aqueous ethanol solution. The procedure was repeated and a second stock solution was obtained. Both solutions were then kept in a refrigerator at 5 ^{o}C.

Into a series of 25 mL volumetric flaks, 0 µL, 15 µL, 50 µL, 100 µL, 200 µL, 300 µL and 500 µL of the formaldehyde stock solution were pipetted. The volume of each flask was made up to the 25 mL mark with a 10% (v/v) aqueous ethanol solution. The procedure was repeated using the second stock solution that was prepared. All of the calibration standard solutions were kept in a refrigerator at 5 ^{o}C, prior to being analysed for formaldehyde content using the procedure described in Section 4.4.6.1.

2.4. Characterisation of cross-linker compounds

The various amino cross-linkers compounds are shown in Table 2.2-3.

2.4.1. NMR characterisation

NMR spectra were recorded using a Bruker Avance (^{1}H= 500 MHz) spectrophotometer (Bruker.com), with dimethyl sulfoxide (DMSO) as the solvent, at 25 ^{o}C. Small portions of each sample were dissolved in approximately 2 mL of DMSO. These were then shaken thoroughly before analysis. The amino cross-linkers were characterised by NMR to observe the presence or absence of –NH and NH_2 peaks in the spectra, at 7.2 − 7.4 ppm and 5.8 − 6.2 ppm respectively. Such analyses were undertaken to establish whether or not there was any detectable melamine (residual or that generated during hydrolysis) in the samples.

2.4.2. FT-IR characterisation

The melamino cross-linker samples were characterised using FT-IR spectroscopy, using a Perkin-Elmer spectrophotometer, Spectrum One, (Perkinelmer.com). The instrument was operated under an attenuated total reflectance (ATR) mode, at room temperature. Prior to sample analysis, a background run was carried out, which was then subtracted from subsequent spectra to produce the sample spectra. After mounting a drop of each sample, on the diamond, spectra were recorded by carrying out 100 scans at 4 cm^{-1} resolution.

2.4.3. Mass spectrometric analyses

Each melamino cross-linker was evaluated for its molecular weight and mass/charge ratio using a Bruker micOTOF mass spectrometer, (Bruker.com). The spectrometer was operated under the electro-spray method (positive ionisation mode) and was equipped with a time of flight (TOF) detector. The samples were prepared by dissolving small portions of the cross-linkers in approximately 2 mL of methanol.

2.4.4. CHN elemental analyses

The CHN analysis was carried out using a Thermo Flash EA 1112, (Thermo.com). Approximately 2mg of each cross-linker were weighed into a tin capsule. This was then placed into the auto-sampler and was subsequently moved into the reactor chamber. This sample was flushed with excess oxygen at 900^{o}C. This triggers an exothermic reaction and subsequent combustion, producing CO_2, NO_2 and H_2O. These gases were moved by a helium carrier gas. The resulting mixture was separated in a chromatography column. Through this procedure, the elemental distribution, as a percentage in each of the cross-linkers, was recorded. Oxygen was calculated by difference (i.e. 100% minus (C+H+N)).

2.4.5. Residual melamine analysis

1 g of each cross-linker sample was weighed and dissolved in 50 mL of methanol, in a volumetric flask. Portions were then taken for analysis, by HPLC, for any residual melamine that might be present. The HPLC conditions that were used are described below, (Smith et al., 2003).

Column: *Hypersil C18, N 5 µm, 2.1 mm x 300 mm,* (Chromtech.com)

Column temperature: *25 °C*

Injection volume: *10 µL*

Detection: *UV, 230 nm*

Eluent A*: 100% acetonitrile*

Eluent B: *5mM phosphate buffer, pH 6.5*

Flow rate: *1 mL/ min*

Run time: *10 minutes*

Method: *Isocratic (10% Eluent A and 90% Eluent B)*

2.4.6. Residual benzoguanamine analysis

1 g of each cross-linker sample was weighed and dissolved in 50 mL of methanol, in a volumetric flask. Portions were then taken for analysis, by HPLC, for any residual benzoguanamine that might be present. The HPLC conditions that were used are described below:

Column: *SiELC Obelisc N, 5 µm, 100 Å, 2.1 mm x 150 mm,* (Sielc.com)

Column temperature: *30 °C*

Injection volume: *10 µL*

Detection: *UV, 248 nm*

Eluent A: *100% acetonitrile*

Eluent B: *ammonium acetate+ 0.1% (v/v) acetic acid*

Flow rate: *0.5 mL/ min*

Run time: *15 minutes*

Run time: *Gradient*

The HPLC procedure was used as described in the literature, (Bradley et al., 2010). The procedure was modified to account for some differences in the approach to sample preparation. Such modifications were necessary because of the samples to be analysed and the food simulants that were used. The conditions of the linear gradient method are shown in Table 2.4-1.

Table 2.4-1: HPLC method, gradient conditions

Time/min	% Eluent A	% Eluent B
0	5	95
5.0	50	50
9.0	50	50
9.5	5	95
14.5	5	95
15.0	5	95

2.4.7. Thermogravimetric analyses

The thermal decomposition profiles of the cross-linking compounds were recorded using a TA Universal Instruments (V4.1D) (Tainstruments.com), over a temperature range of 25 − 500^{o}C, with a heating rate of 10^{o}C/min. Small quantities of the samples, (approximately 5 mg), were used in each analysis.

2.4.8. Differential scanning calorimetric analyses

DSC analyses of the cross-linker samples were carried out using TA Instruments (Q10) (Tainstruments.com). The samples were heated from 30^{o}C to 500^{o}C using a 20^{o}C/min heating rate, during which endothermic and exothermic transitions were recorded.

2.4.9. Rheological studies

2.4.9.1. Shear ramp studies

Rheological evaluations were carried out using a TA−Instruments (ARES-G2) (Tainstruments.com). The evaluations were run under a continuous shear stress ramp mode at 25 ^{o}C. A steel parallel plate, with a 40mm diameter and a truncation gap of 50 µm, was used.

In each case, enough of the cross-linker sample was poured onto the rheometer-base-plate to cover the parallel plate. Excess sample was then removed after the plate had made contact with the sample. The shear stress rate was increased from 1 Pa to 1000 Pa. Seventy viscosity value points were collected during a total run time of 5 minutes.

2.4.9.2. Temperature ramp studies

The temperature gradient ramp tests were carried out using the TA−Instruments (ARES-G2) (Tainstruments.com), equipped with a 1° angle aluminium cone, having a 60mm diameter, using a truncation gap of 33 µm. The cross-linker samples were evaluated at a constant shear stress rate of 5.00 s^{-1} over a controlled range of temperatures between 25 ^{o}C and 50 ^{o}C. In each case, the change in viscosity (flow behaviour) was observed as the temperature rose.

Flow recovery tests on selected cross-linkers were carried out, employing three peak hold steps. Step 1 was a low shear step where values of viscosity were recorded at 0.1 Pa s shear. In Step 2, a high shear stress of 1000 Pa s was applied and the viscosity response was monitored. In the final step, Step 3, a low shear stress of 0.1 Pa s was applied to allow for observations of any flow recovery of the tested compositions.

Flow kinetic parameters were calculated based on the Arrhenius equation, using the procedures and the equations that were described in Section 1.8.1.5.

2.5. Characterisation of the polymeric binders

2.5.1. Thermal analyses

For the TGA characterisation of the polymeric binders and of pre-polymer solutions, the procedures that were described in Section 2.4.7 to 2.4.8 were used.

2.5.2. Solids content estimation

A known weight of each cross-linker sample (typically 1g) was applied onto a metal substrate of defined area and was then heated in an oven at 200 ^{o}C for 30 minutes or until a consistent weight was achieved. The evaluation is represented by Equation 1.8-1, in Section 1.8.1.2.

2.5.3. Free-melamine analysis

Approximately, 1g of each melamine-based cross-linker was measured into a 50 mL volumetric flask. 50 mL of methanol were then added to the flask. The contents were shaken thoroughly. Portions were then taken for analysis, by HPLC (Section 2.4.5), for any residual melamine that might be present.

2.6. Characterisation of the TiO_2 pigments

The three different grades of the TiO_2 pigment are shown in Table 2.2-2. The three grades of the pigment differ from one another on the basis of average particle size, mono disperse size distribution and on the basis of multilayer inorganic treatment over the TiO_2 core.

2.6.1. Particle size analysis

For this aspect of study, a Malvern Instruments Zetasizer (Nano-ZS) was used, (Malvern.com). For each of three pigment grades, the following procedure was adopted. Approximately, 1g of each pigment was weighed and transferred into a beaker. 1 mL of Surfynol CT-324 was added to act as a dispersant/wetting agent, before mixing, until a paste was formed. 40 mL of doubly-distilled water were then added into the beaker. The mixture was stirred and ultrasonicated for 5 minutes, after which time a suspension was formed. 15 drops of the formed suspension were then added into a beaker containing 25 mL of doubly-distilled water. This mixture was then shaken and stirred. Portions were then transferred into plastic cuvettes for particle size measurement.

The technique used in the particle size analysis procedure is based on dynamic light scattering (DLS), (Syvitski, 1991). During the analysis of each dilute sample, particles in the sample that are in a state of Brownian motions are illuminated by a laser beam. The light scattered by the particles is collected and measured with a photomultiplier. Light fluctuations in the detector are also caused by the moving particles. The extent of the fluctuation depends on the size of the individual particles, with larger particles causing a more rapid fluctuation at the detector than smaller particles. The intensity of the fluctuations is computed to provide an intensity correlation function, whose analysis provides the diffusion coefficient of the particles (also known as diffusion constant), as represented by Equation 2.6-1.

$$D = {}^{\mathrm{kT}}/_{6\pi \mathrm{R}\eta}$$

Equation 2.6-1: Stokes-Einstein equation

Here, D is the diffusion coefficient, R is the radius of the particle, k is the Boltzmann-constant, T is the temperature and η is the viscosity.

2.6.2. Zeta potential measurements

For the zeta potential measurements, a portion of each of the samples that was prepared according to Section 2.6.1 was taken and transferred into “zeta” capillary cells for zeta potential measurement, using the Malvern Instruments Zetasizer (Nano-ZS) (Malvern.com).

2.6.3. Hydrophilicity testing of the pigments

The hydrophilic nature of each the three grades of TiO_2 pigment particles was estimated because of the need to know the ability of the different grades of the pigment to retain moisture.

1 g of each pigment grade was mixed with 1 mL of distilled water until a pigment paste was formed. Each paste was applied onto a watch glass and allowed to dry in a fume cupboard for 24 hours. Portions of the samples were taken and studied using TGA. The thermograms were recorded using a TA Universal Instrument V4.1D, (Tainstruments.com), over a temperature range of 0–500^{o}C, using a temperature increase rate of 10^{o}C/min. Small quantities (approximately 10 mg) of each sample were used for each evaluation.

2.6.4. Scanning electron microscopic evaluations

In order to observe the morphology of the three grades of pigment particles in each of the TiO_2 pigment grades, a JOEL JSM-6610LV, Oxford Instruments INCA-X-Max 80 EDS was used, (Jeolusa.com). For the SEM analyses, small portions of each pigment grade were used. Each sample was mounted on a brass stub and then pre-treated to a uniform 30 nm gold film deposition, using a Bio-Rad diode sputter coating unit, (Bio-Rad House, Hertfordshire, UK), before being evaluated by SEM.

The metal atom contents and the metal atom ratio in the pigment samples were evaluated using the EDX components of the JOEL JSM-6610LV, Oxford SEM Instruments, (Jeolusa.com). 100 frames of data were collected for each sample using an accelerating voltage of 15kV under the aperture 3 mode of operation. In each case, an elemental distribution for a selected microscopic area was monitored.

2.7. Calibration of the curing oven

2.7.1. Curing oven geometry

The Werner Mathis Oven unit, Model—KTF4099 (Mathisag.com), was used, (Jiang et al., 2008), (schematically represented in Figure 2.7-1). This unit was chosen to ensure consistency and control were provided during the curing of the coatings and that the conditions of a commercial oven were replicated. The oven was calibrated, periodically, in order to ensure that it was consistently fit for the intended purposes/studies.

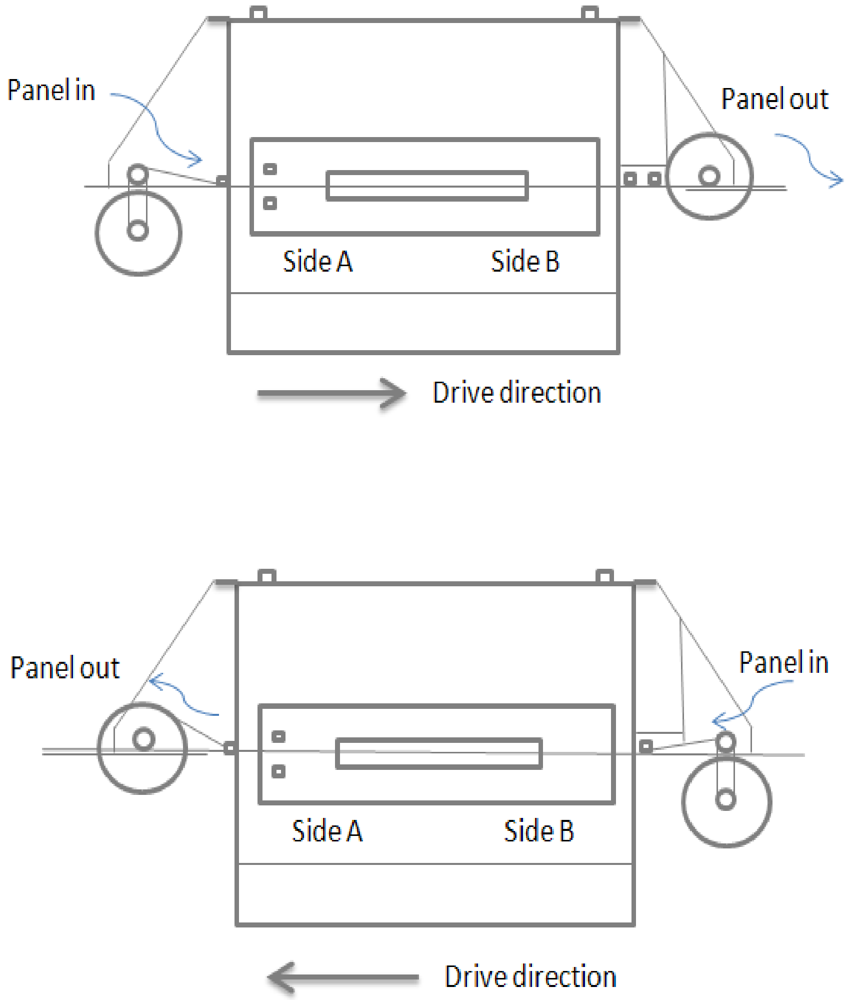


Figure 2.7-1: Schematic diagram of the Werner Mathis oven system

The unit operates via two optional fan settings that govern the exhaust of species and air exchange in the oven. These are fan 1 settings and fan 2 settings. A coated metal panel can be introduced into the oven, for curing of the coatings, either through side A or through side B of the oven.

2.7.2. Isothermal calibration

This procedure was carried out to monitor the temperature profile of the coated tinplate samples while the coating underwent curing in the oven. This point is especially important if one is to ascertain whether or not a peak metal temperature (PMT) can be achieved while a coated panel is being cured.

For the isothermal calibration, the Fan 1 setting and side A of the oven were used. The thermocouple was physically attached onto a tinplate substrate. The coating was an epoxy-anhydride formulation. The oven was switched on and was allowed to reach 200 ^{o}C. The heating rate was 3 ^{o}C/minute. The coated metal panel that had the thermocouple attached to it was then introduced into the oven. Temperature readings on both the oven and the thermocouple were recorded during the 12 minutes period over which the coating was cured in the oven.

2.7.3. Temperature ramp calibration

In the temperature ramp calibration, the Fan 1 setting and side A of the oven were used. The thermocouple was then inserted into the oven. The oven was switched on and the heating proceeded from room temperature until 200 ^{o}C was achieved. Temperature readings on both the oven and the thermocouple were recorded as a function of the heating time.

2.7.4. Cooling behaviour and cooling rate studies

Here, the cooling behaviour of the oven was monitored, from 200 ^{o}C to 100 ^{o}C. The heating switch in the oven was turned off after a thermocouple had been inserted into the oven chamber. As the oven was cooling down, the temperature readings on both the oven dial and the thermocouple were monitored. These measurements were the basis upon which the cooling rate of the oven was established.

2.7.5. Calibrating the oven’s two components

For this procedure, a thermocouple was inserted into side A of the oven. The oven was turned on and was set to heat up to 200 ^{o}C. After the heating switch had been activated, temperature readings on both the thermocouple and the oven display board were recorded. The measurements were carried out for 30 minutes and readings were taken after each 2 minute interval. The same procedure was repeated by recording the temperature readings when the thermocouple was inserted into side B of the oven.

2.7.6. Calibrating the oven's two fan settings

Oven side A was used to monitor the performance of the unit at the two different fan control speeds that the oven possessed. The thermocouple was inserted into the oven, side A. Based on a Fan 1 setting, the oven was heated from room temperature to 200 ^{o}C. The thermocouple temperature reading and the oven temperature reading were recorded at each 2 minute interval, for a total period of 30 minutes. The same procedure was repeated based on the Fan 2 setting of the oven.

2.8. Discussion of results

In each case, reference to the specific test procedure is recommended.

2.8.1. Calibration graphs

Figure 2.8-1 shows UV absorption details for solutions of the melamine calibration standard where the UV absorbance increased with an increase in the concentration of melamine in the standard solutions that were employed. Figure 2.8-2 shows a calibration trace for the absorption that occurs at a wavelength near 235 nm, (Han et al., 2009). In the figure, the UV absorption increased with an increase in the concentration of melamine in the standard solutions that were employed.

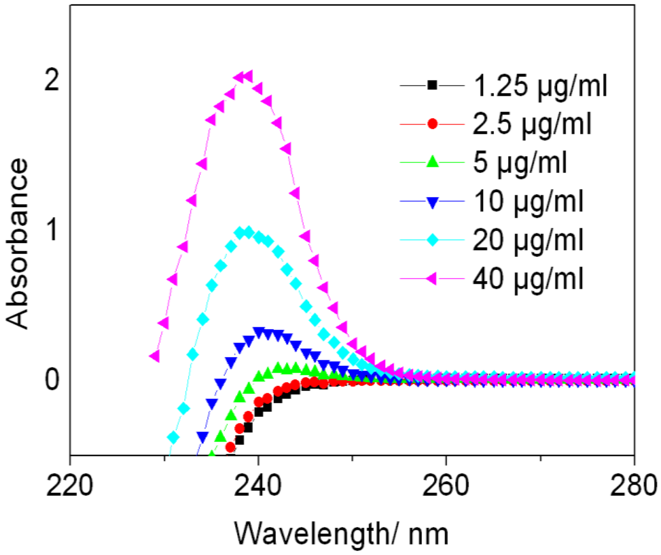


Figure 2.8-1: UV absorption-variation in absorbance with wavelengths for melamine standard calibration solutions

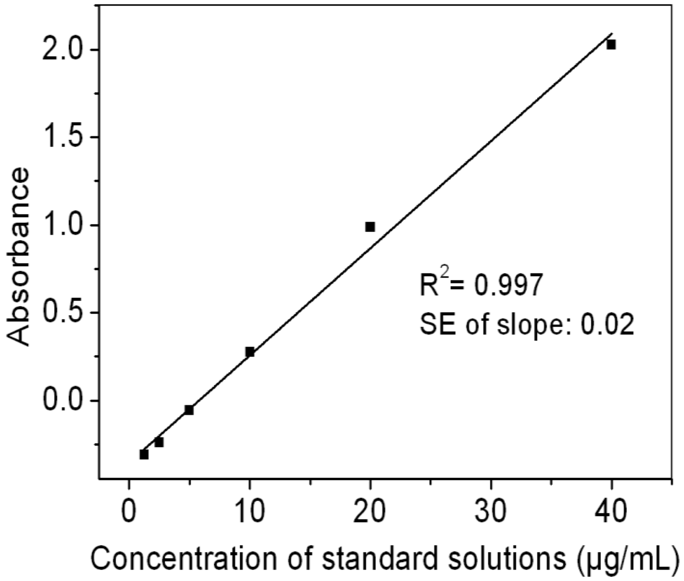


Figure 2.8-2: UV calibration trace for melamine standard solutions, at 238 nm

Figure 2.8-3 shows a HPLC chromatogram with melamine peak at 3.03 min, during the analysis of a 40 μg/mL standard solution. Both the melamine peak's lower characteristic broadening and the clear separation of the peak from adjacent peaks indicate the efficiency of the column that was used and the method that was developed.

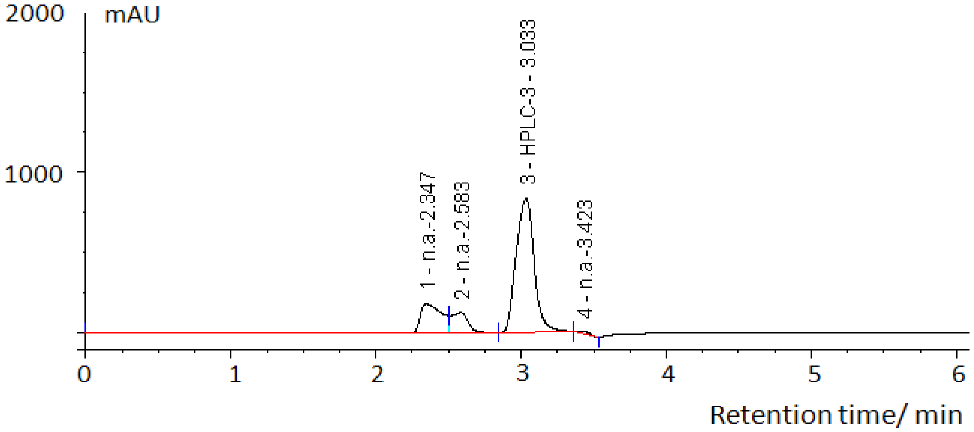


Figure 2.8-3: HPLC chromatogram showing melamine peak at 3.03 min, during the analysis of a 40 μg/mL standard solution

Figure 2.8-4 shows HPLC calibration traces for melamine. In the figure, for each set of calibration solutions, the peak area increases linearly with an increase in the concentration of melamine in the standard solutions. The results show the good repeatability and reliability of the technique and signify the relevance of employing UV detectors for melamine content-related studies.

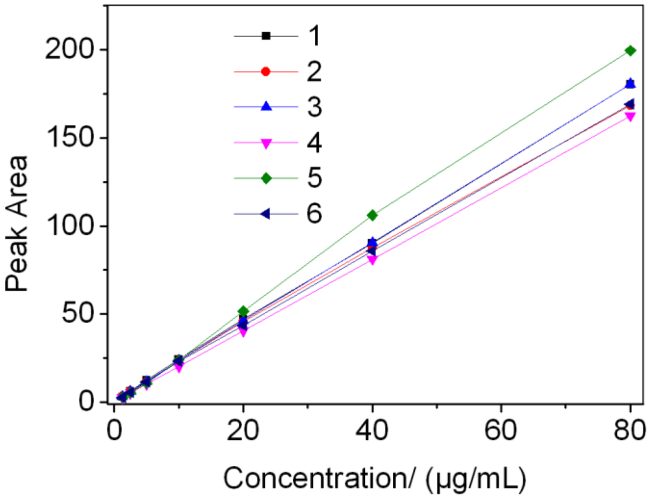


Figure 2.8-4: HPLC calibration traces for melamine standard solutions. The numbers represent calibration solutions that were repeated and developed periodically

Figure 2.8-5 shows the UV absorption by the benzoguanamine calibration standard and Figure 2.8-6 shows a calibration traces for the absorption that occurs at a wavelength close to 248 nm. Like melamine, the benzoguanamine UV absorption increased linearly with an increase in the concentration of benzoguanamine in the standard solutions that were used. The results signify the relevance of employing UV detectors for the analysis of benzoguanamine.

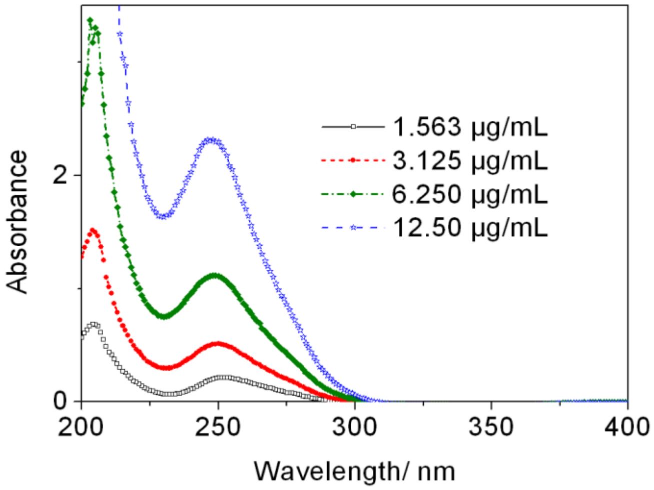


Figure 2.8-5: UV absorption-variation in absorbance with wavelength for benzoguanamine standard solutions

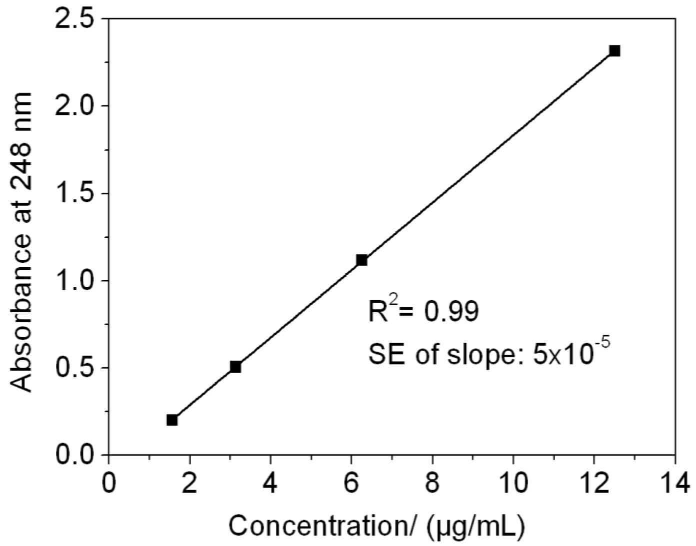


Figure 2.8-6: UV calibration trace for benzoguanamine standard solutions

In Figure 2.8-7, HPLC-based calibration traces of benzoguanamine solutions are shown. The figure shows that when the concentration of benzoguanamine in the standard solutions is increased, both the corresponding benzoguanamine peak height and the benzoguanamine peak area increase accordingly. Thus, in each case, a linear plot is achieved. Again, the results signify the relevance of employing HPLC-based techniques and UV detectors for the analysis of benzoguanamine in migration related studies.

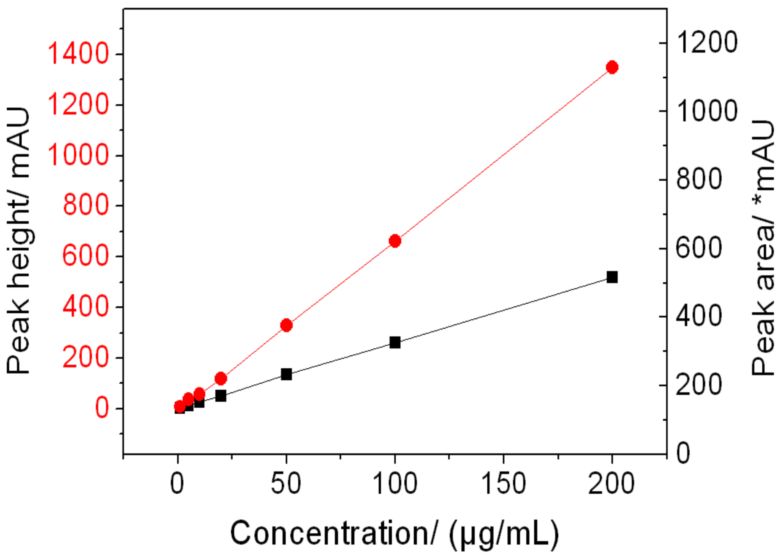


Figure 2.8-7: HPLC calibration traces- peak height and peak area versus concentration, for benzoguanamine standard solutions

Figure 2.8-8 shows a HPLC chromatogram with benzoguanamine peak at 2.657 min, during the analysis of 6.250 µg/mL standard solution. The benzoguanamine peak exhibits lower characteristic broadening and good separation. This indicates the efficiency of the column used and the method developed, for the analysis and separation of benzoguanamine in migration related studies.

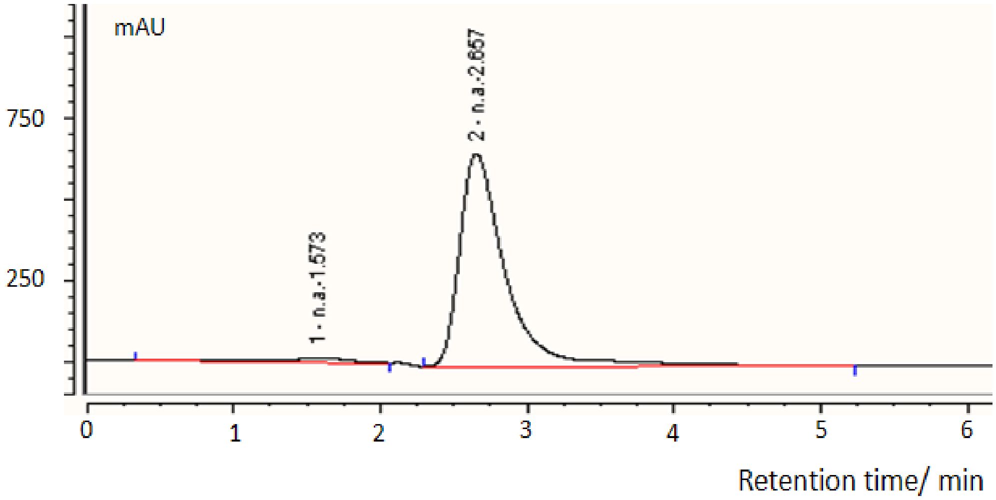


Figure 2.8-8: HPLC chromatogram showing a benzoguanamine peak at 2.657 min, during the analysis of a 6.250 µg/mL standard solution

Figure 2.8-9 shows that UV-visible spectrophotometry can be used for the analysis of formaldehyde. In Figure 2.8-7, formaldehyde standard solutions were shown to absorb visible radiation at 475 nm and the absorption increased linearly with an increase in the concentration of formaldehyde in the solutions. The absorption at 475 nm was a consequence of the formation of a formaldehyde-chromotropic acid complex. The 75% sulphuric acid used during the analysis, (Section 4.4.6.1) acts as a dehydrant and also as an oxidant. During the process, sulphuric acid is reduced to sulphurous acid, (Hudlicky, 1990). The mechanism through which the formaldehyde-chromotropic acid complex is formed is well documented, (Fagnani et al., 2003). The structure of the complex is shown in Figure 2.8-10.

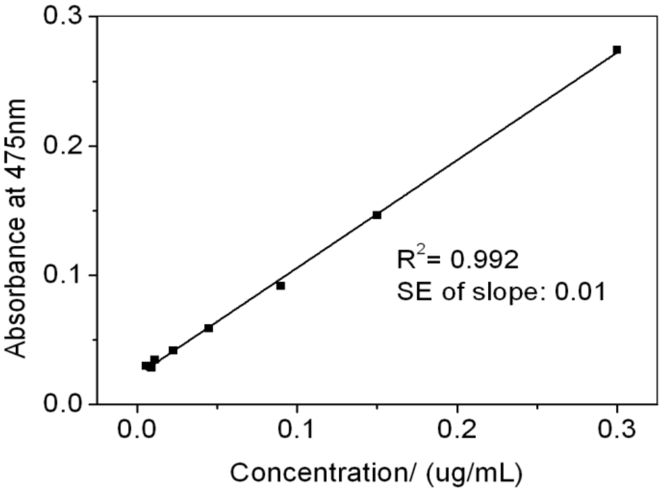


Figure 2.8-9: UV calibration traces for formaldehyde standard solutions

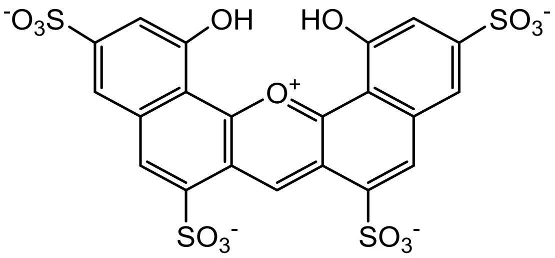


Figure 2.8-10: Formaldehyde-chromotropic acid complex

2.8.2. Chemical composition of the amino cross-linkers

The IR plots obtained from investigations of the cross-linker samples are shown in Figure 2.8-11 to Figure 2.8-14. These are seen as changes in the % transmission as a function of the wavenumber, (cm^{-1}).

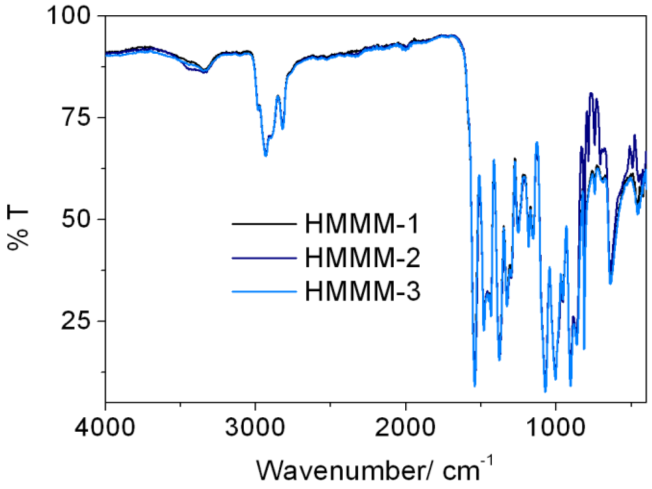


Figure 2.8-11: FT-IR spectra of the hexamethoxymethyl melamine (HMMM) cross-linkers

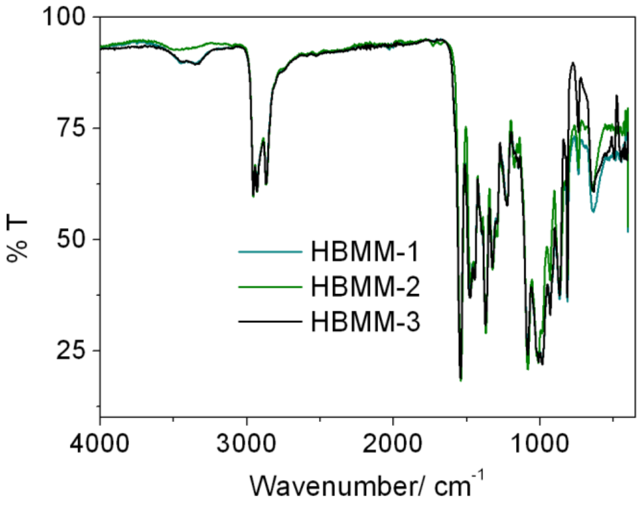


Figure 2.8-12: FT-IR spectra of the hexabutoxymethyl melamine (HBMM) cross-linkers

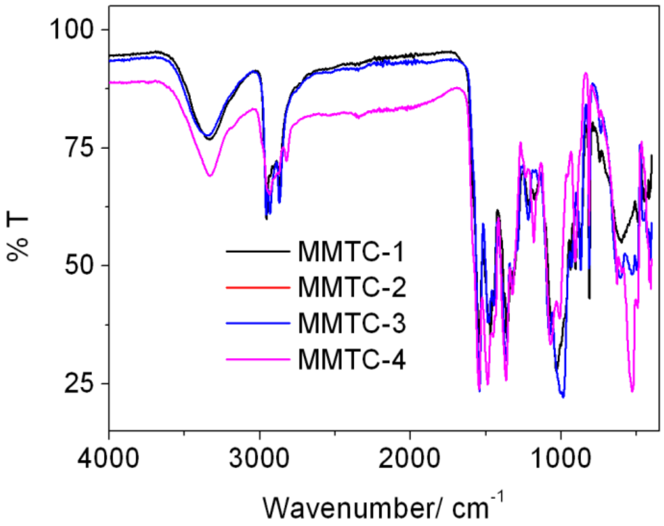


Figure 2.8-13: FT-IR spectra of the methylol melamine-type cross-linkers (MMTC)

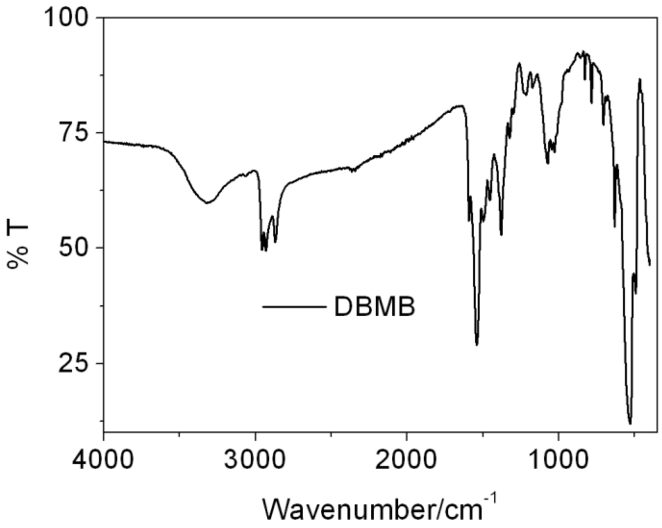


Figure 2.8-14: FT-IR spectrum of the dibutoxymethyl benzoguanamine (DBMB) cross-linker

The band for the hydroxyl functionality in the methylol (–CH_2OH) group is visible in the spectra of the methylol-type cross-linkers (Figure 2.8-13 and Figure 2.8-14), at a wavelength position of approximately 3300 cm^{-1}, (Socrates, 2001). This observation clearly distinguishes the methylolated cross-linkers from their alkylated counterparts Figure 2.8-11 and Figure 2.8-12, from the stand point of the presence of methylolation. The results also provide evidence for the presence of methylene (–CH_2–) functionality in the cross-linkers, at wavenumber position of 2900 cm^{-1}. The results do not show any evidence of the amino –NH_2 stretching band, at 3500 cm^{-1}, indicating the absence of any residual melamine and/or any generated melamine in the cross-linker samples, within this level of sensitivity.

The results obtained from the NMR studies on the cross-linkers (analysed as supplied) are represented in Figure 2.8-15 to Figure 2.8-18. The NMR peak assignments were carried out based on literature reports, (Barrett, 1996, Bauer, 1986).

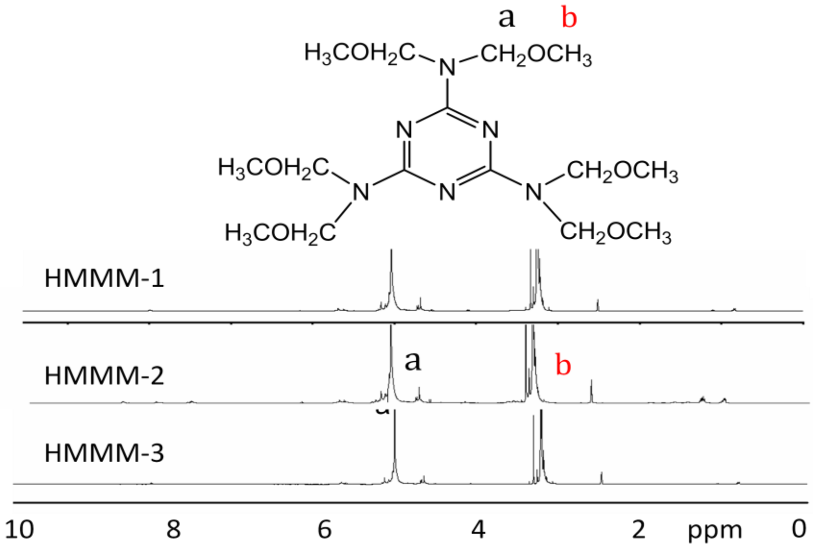


Figure 2.8-15: ^{1}NMR spectra of the hexamethoxymethyl melamine (HMMM) cross-linkers

The hexamethoxymethyl melamine (HMMM) cross-linkers are clearly identified in Figure 2.8-15. The peak near 5.2 ppm is a characteristic of the –CH_2 protons while the peak near 3.4 ppm is a characteristic of the –CH_3 (methyl) protons. The NMR data do not show evidence of the melamino –NH proton peaks and NH_2 proton peaks, at 7.2 − 7.4 ppm and

5.8 − 6.2 ppm, respectively. The absence of both –NH$_2$ and –NH functional groups could indicate the limitations of the technique for the analysis of residual melamino derivatives in the cross-linkers.

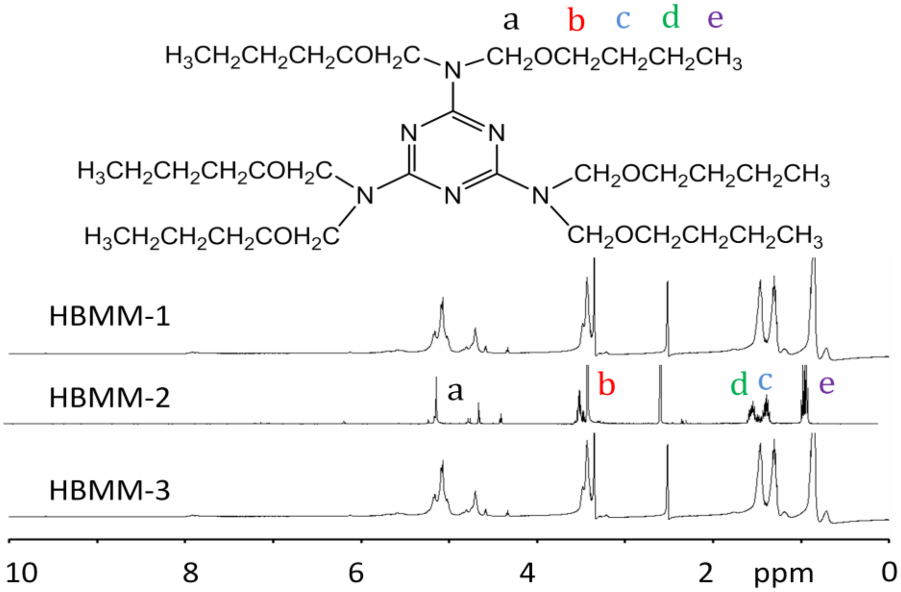


Figure 2.8-16: ^{1}NMR spectra of the hexabutoxymethyl melamine (HBMM) cross-linkers

The hexabutoxymethyl melamine (HBMM) cross-linkers are clearly identified in Figure 2.8-16. The peaks near 5.2 ppm are a characteristic of the first –CH$_2$ protons (a) while the multiple peaks near 3.4 ppm are a characteristic of the second –CH$_2$ protons (b). The third –CH$_2$ protons peaks (c) are shown near 1.3 ppm, the fourth –CH$_2$ protons (d) are shown near 3.4 ppm. The –CH$_3$ methyl protons (e) are shown near 0.8 ppm. The NMR data do not show evidence of the melamino –NH proton peaks and NH$_2$ proton peaks, at 7.2 − 7.4 ppm and 5.8 − 6.2 ppm, respectively. The absence of both melamino functional groups indicates the limitations of the technique for the analysis of residual melamino derivatives in the cross-linkers.

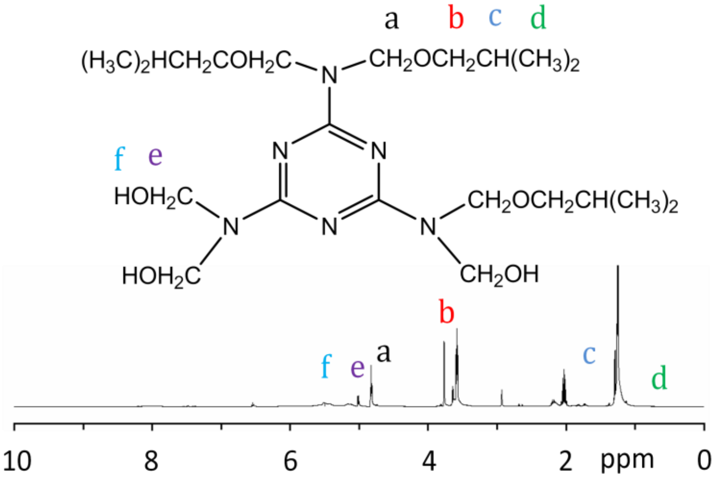


Figure 2.8-17: ^{1}NMR spectra of the methylol melamine-type cross-linker, MMTC-1, (methoxymethyl melamine-1) cross-linker

Figure 2.8-17 shows the NMR spectra of MMTC-1, the methoxymethyl melamine-type cross-linker. Clearly, the cross-linker has a different chemistry in comparison to the chemistry of the HMMMs and the HBMMs. The major difference is the presence of hydroxyl proton of the methylol group. The NMR data do not show evidence of the melamino –NH proton peaks and NH_2 proton peaks, at 7.2 − 7.4 ppm and 5.8 − 6.2 ppm, respectively.

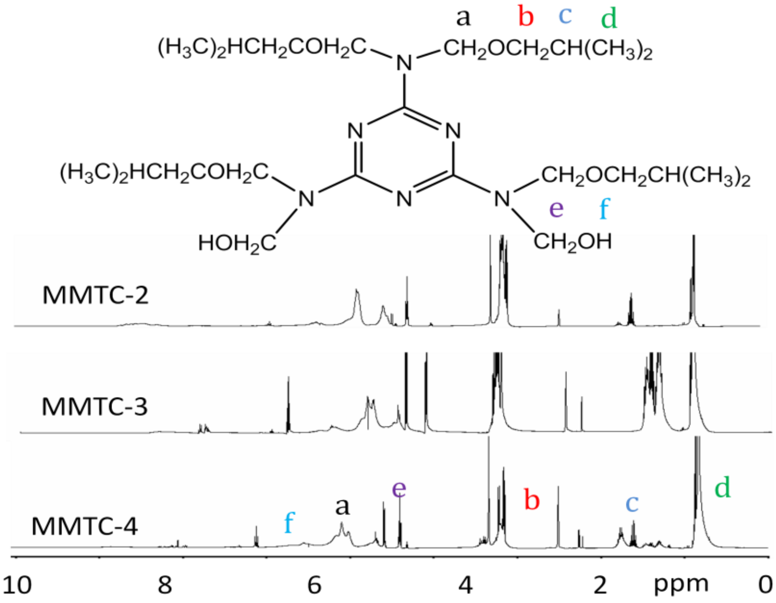


Figure 2.8-18: ^{1}NMR spectra of the methoxymethyl melamine cross-linkers (MMTC-2, MMTC-3 and MMTC-4)

The three methylol melamine-type cross-linkers MMTC-2, MMTC-3 and MMTC-4, exhibit very similar NMR characterisation data, as shown in Figure 2.8-18. The presence of methylol functionality in the cross-linkers, shown by the NMR data, agrees with the FT-IR results, Figure 2.8-13. Both the NMR data and the FT-IR data do not show any evidence of residual melamine, as seen in the absence of $-NH_2$ stretching band, at 3500 − 3100 cm^{-1}, and the absence of any peak for '$-NH_2$ deformations', at 1680 − 1640 cm^{-1}, from the FT-IR data. Similarly, the NMR results do not show evidence of the melamino –NH proton peaks and NH_2 proton peaks, at 7.2 − 7.4 ppm and 5.8 − 6.2 ppm, respectively.

There were minor differences between the NMR and the FT-IR data that were obtained for the different methylol melamine-type cross-linkers. Other minor differences can also be seen from the data shown in Table 2.8-1 and Table 2.8-2. These disparities arise because of differences in the extents of reaction and differences in the levels of methylolation that are thought to arise during synthesis and also as a result of manufacturing conditions. The results are relevant to appreciating the categorisation/differentiation of the cross-linker classes. Clearly, there were sensitivity and detection limits associated with the NMR and the FT-IR techniques that were employed, as indicated by the HPLC data that showed the presence of trace residual melamine species in the cross-linker samples.

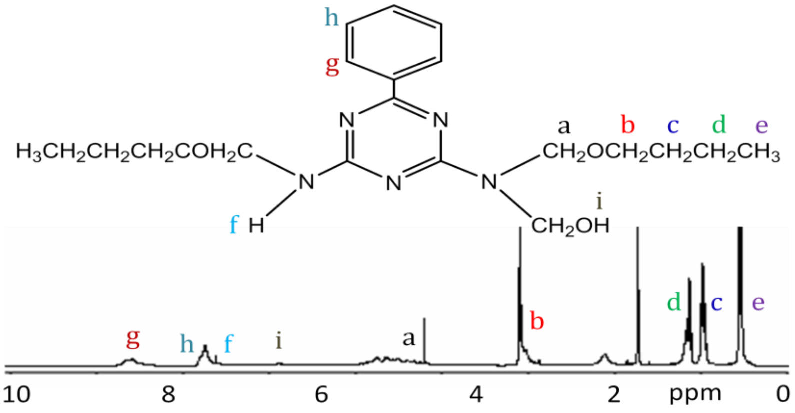


Figure 2.8-19: ^{1}NMR spectra of the dibutoxymethyl benzoguanamine (DBMB) cross-linker

Figure 2.8-19 shows the NMR structure elucidation of the dibutoxymethyl benzoguanamine (DBMB) cross-linker. The peaks near 5.2 ppm are a characteristic of the first –CH_2 protons (a) while the multiple peaks near 3.4 ppm are a characteristic of the second –CH_2 protons (b). The third –CH_2 protons peaks (c) are shown near 1.3 ppm, the fourth –CH_2 protons (d) are shown near 1.4 ppm. The –CH_3 methyl protons (e) are shown near 0.9 ppm. The melamine –NH proton peak (f) is shown near 7.3 ppm. The aromatic protons (g and h) are shown near 7.5 − 8.5 ppm. The methylol proton (i) is shown at 6.4 ppm. Again, the absence of the melamine NH_2 proton groups indicates the limitations of the technique for the analysis of residual melamino derivatives in the cross-linker.

The mass spectrometric data and the rheological data that were obtained from the cross-linker characterisation studies are presented in Table 2.8-1, allowing consistent interpretation to be made. The base peak values and the compound identification for the HMMM and the HBMM compounds were found to be consistent with literature reports, (Chang, 1994).

2.8.3. Physical-chemical behaviour of the cross-linkers

The overall cross-linker characterisation results that were obtained from CHN analysis, from residual melamine analyses, from mass spectrometric studies and from rheometric evaluations are summarised in Table 2.8-1.

The values of molecular weight, represented in Table 2.8-1, indicate the "molecular ion" of each cross-linker type, as provided by the mass spectrum, in each case. The table also shows results from the residual melamine studies that were undertaken. The results indicate that each of the amino cross-linker compounds contained residual melamine. The values obtained for each cross-linker were different from the other values. These differences arise because of differences in chemical composition which are thought to arise during synthesis and also as a result of manufacturing conditions. The results are relevant to appreciating the significance of the melamine that is present in the compositions. This provides a basis for correlations to be made between the residual melamine and the melamine that the cross-linkers generate after the retorting of the cross-linked, cured coatings.

The results obtained from the CHN elemental analyses, carried out on the cross-linker samples, as supplied, are shown in Table 2.8-2.

Table 2.8-1: Cross-linker characterisation. Physical-chemical data, obtained from several studies i.e. HMMM (hexamethoxymethyl melamine, HBMM (hexabutoxymethyl melamine, MMTC (methylol melamine type) and DBMB (dibutoxymethyl benzoguanamine)

S/N	Cross-linker	Molecular peak (g/mol)	Residual melamine (%)	Viscosity (Pa s)	Yield point (10^{-4} Pa)	Flow activation energy (kJ/mol)	Infinite shear viscosity (Pa s)
1	HMMM-1	391	0.12	5.07	1.99	65.30	4.49
2	HMMM-2	391	0.07	9.28	8.59	70.90	2.95
3	HMMM-3	391	0.18	5.52	8.53	63.90	3.97
4	HBMM-1	643	0.07	4.17	1.80	7.30	4.04
5	HBMM-2	643	0.19	2.65	26.96	51.00	2.40
6	HBMM-3	643	0.06	4.32	3.39	60.00	4.05
7	MMTC-1 (TMTBM)	471	0.15	3.50	3.42	93.30	3.34
8	MMTC-2	531	0.15	1.56	0.92	51.10	1.23
9	MMTC-3	530	0.14	25.37	0.12	76.30	25.47
10	MMTC-4	355	0.15	3.65	1.56	68.90	3.49
11	DBMB	390	0.18	1.22	0.25	50.20	0.52

Table 2.8-2: CHN elemental analysis results for the cross-linkers i.e. HMMM (hexamethoxymethyl melamine, HBMM (hexabutoxymethyl melamine, MMTC (methylol melamine type) and DBMB (dibutoxymethyl benzoguanamine)

Cross-linker	% C	% H	% N	% O
HMMM-1	45.60	7.60	23.15	23.65
HMMM-2	46.60	7.55	22.80	23.05
HMMM-3	45.55	7.55	23.00	23.90
HBMM-1	57.65	9.60	15.55	17.20
HBMM-2	60.25	9.95	15.00	14.80
HBMM-3	57.85	9.60	14.80	17.75
MMTC-1 (TMTBM)	57.55	10.45	14.60	17.40
MMTC-2	55.50	9.75	14.75	20.00
MMTC-3	54.35	9.40	15.80	20.45
MMTC-4	46.35	8.30	22.40	22.95
DBMB	61.85	9.00	14.35	14.80

Using ChemDraw™ software, (version, Std 11.0), the elemental composition of pure HMMM and pure HBMM compounds was established. Pure HMMM would have an elemental composition of C= 46.14% H= 7.74% N= 21.52% O= 24.59%. Pure HBMM would have an elemental composition of C= 61.65% H= 10.35% N= 13.07% O= 14.93%.

Comparing the results obtained for the HMMM type cross-linkers (1, 2 and 3) with the elemental data of the equivalent pure compound, a variation was observed of up to

~±1%C, ~±0.1%H, ~±1.5%N and ~±0.9%O. Similarly, the results obtained for the HBMM samples compared with those of the pure equivalent compound with approximate variations of ~±3%C, ~±0.7%H, ~±2%N and ~±2.5%O. These variations in the case of both the HMMM cross-linkers and the HBMM cross-linkers are to be expected because of the presence of small amounts of residual starting materials and the presence of possible oligomers or dimmers, (Fischer et al., 1996) which can be formed during the sample manufacturing process. With this interpretation, the HMMM and the HBMM cross-linker samples can be considered to be according to their description, as supplied.

2.8.4. Rheological behaviour of the amino cross-linkers

For the various cross-linkers, one would anticipate that information concerning the shear stress, the effect of temperature changes, the applied pressure and so on, would be relevant to optimising the processing of each cross-linker in a coating formulation. This is of significance if one wished to achieve a desired optimal performance property when one of these additives was to be used.

Figure 2.8-20 shows the results obtained from the rheological studies carried out on the hexamethoxymethyl melamine (HMMM) cross-linkers. The flow pattern that the cross-linkers exhibit as a function of temperature is shown in Figure 2.8-21.

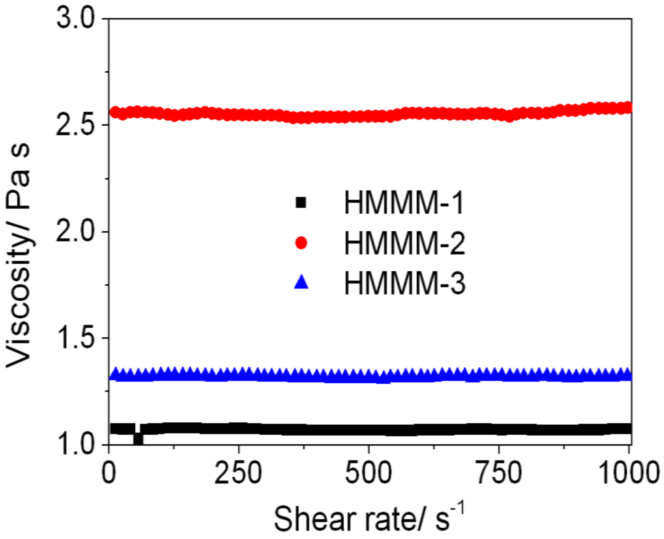


Figure 2.8-20: Viscosity/shear rate profile of the different grades of the hexamethoxymethyl melamine (HMMM) cross-linkers

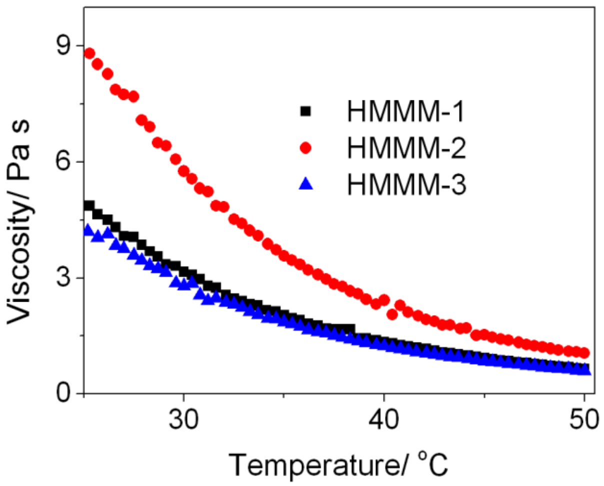


Figure 2.8-21: Viscosity/temperature profile of the different grades of the hexamethoxymethyl melamine (HMMM) cross-linkers

Figure 2.8-20 shows that the hexamethoxymethyl melamine cross-linkers exhibit different values of viscosity at each value of shear rate that was studied. These differences arise because of differences in extents of reaction and levels of oligomerisation during the synthesis of the cross-linkers, Section 2.4. The HMMM cross-linkers exhibited Newtonian flow behaviour over the shear rate region that was studied. As the shear rate was increased from 0.1 Pa s to 1000 Pa s, the viscosity values do not change considerably. Regarding viscosity-temperature relationships, Figure 2.8-21 indicates that the viscosity of the cross-linkers decreases as the temperature increases. This arises as a result of oligomer section chains gliding pass one another more easily as the thermal energy of the cross-linkers are increased, through an increase in temperature.

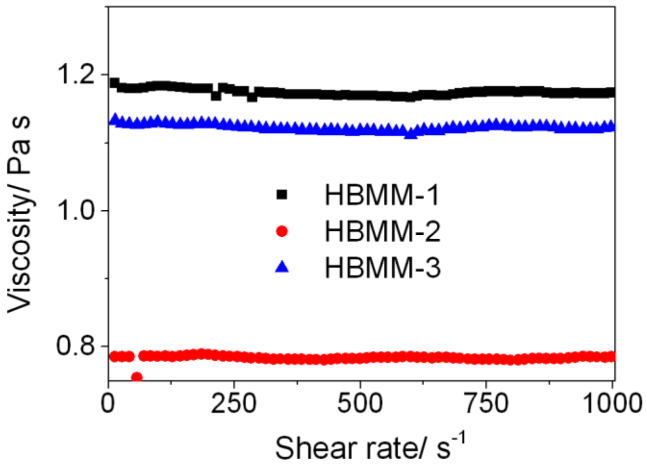


Figure 2.8-22: Viscosity/shear rate profile of the different grades of the hexabutoxymethyl melamine (HBMM) cross-linkers

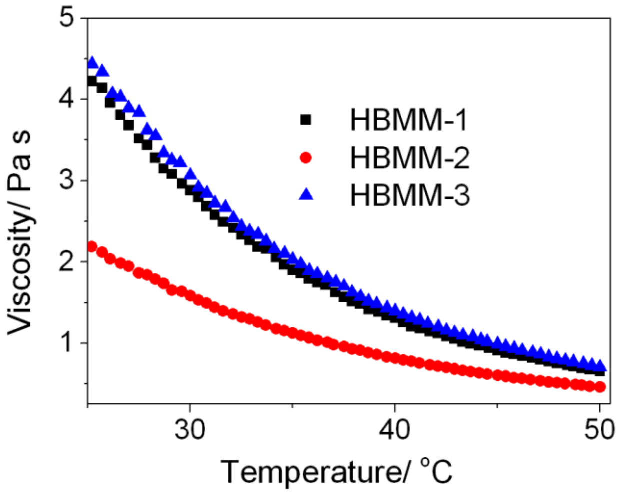


Figure 2.8-23: Viscosity/temperature profile of the different grades of the hexabutoxymethyl melamine (HBMM) cross-linkers

According to Figure 2.8-22, the hexabutoxymethyl melamine cross-linkers exhibited Newtonian flow behaviour over the shear rate region that was studied. As the shear rate was increased from 0.1 Pa s to 1000 Pa s, the viscosity values do not change considerably. Figure 2.8-23 indicates that the viscosity of the cross-linkers decreases as the temperature increases. As mentioned with the HMMMs, this decrease in viscosity arises as a result of oligomer section chains gliding pass one another more easily as the thermal energy of the cross-linkers are increased, through an increase in temperature.

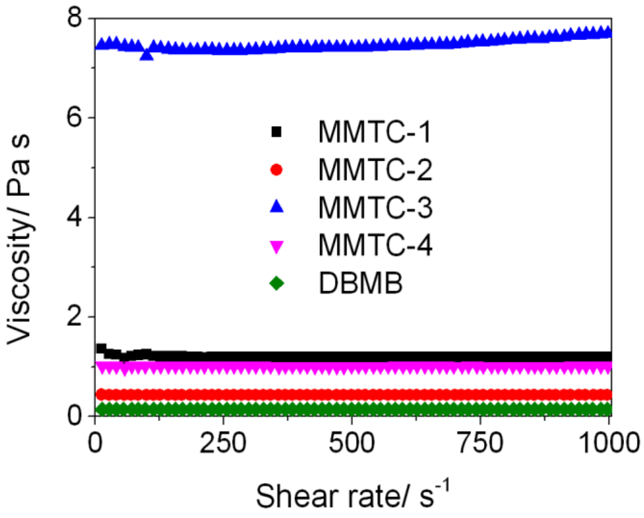


Figure 2.8-24: Viscosity/shear rate profile of the methylol melamine-type (MMTC) cross-linkers and the dibutoxymethyl benzoguanamine (DBMB) cross-linker

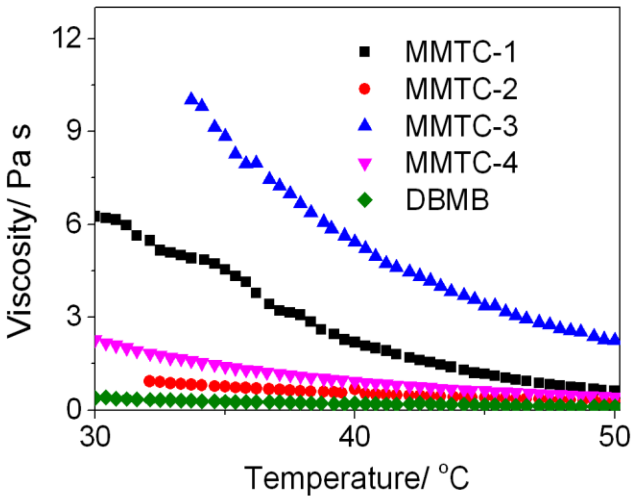


Figure 2.8-25: Viscosity/temperature plot of the methylol melamine-type (MMTC) cross-linkers and the dibutoxymethyl benzoguanamine (DBMB) cross-linker

Figure 2.8-24 shows that the methylol melamine-type (MMTC) of cross-linkers and the dibutoxymethyl benzoguanamine (DBMB) cross-linker exhibited Newtonian flow behaviour over the shear rate region that was studied. As the shear rate was increased, the viscosity values do not change considerably up to 1000 s^{-1}. As shown by Figure 2.8-25, the viscosity of the cross-linkers decreases as the temperature increases. Again, this can also be attributed to oligomer section chains gliding pass one another more easily as the thermal energy of the formulation is increased, through an increase in temperature.

A point that arises from temperature dependent studies relates to the influence of temperature on the flow/migration behaviour of the composite coating, as encountered after the application of the coating onto the metal substrate. This coating is then subjected to heating to >195 ^{o}C over 10 minutes, enabling flow dependent physical phenomena to exhibit their effect.

2.8.5. Flow kinetic behaviour of the amino cross-linkers

The results from the kinetic behaviour of the different amino cross-linkers are thought to provide information that could be used to achieve the desired optimal performance properties when one of these cross-linkers is used.

Arrhenius-type plots and the Casson-Asbeck plots, for the hexamethoxymethyl melamine (HMMM) cross-linkers are presented as Figure 2.8-26 and Figure 2.8-27, respectively. The values obtained for yield point, the infinite shear viscosity and the activation energy of flow for the cross-linkers are shown in Table 2.8-1.

The values of flow activation energy for the different HMMM cross-linkers are within a range of 65 – 71 kJ/mol. The values of infinite shear viscosity for the three cross-linkers fall within a range of 2.95 – 4.45 Pa s. The differences are attributed to their corresponding viscosity values and the extent of interaction in the oligomeric chains that are in each composition.

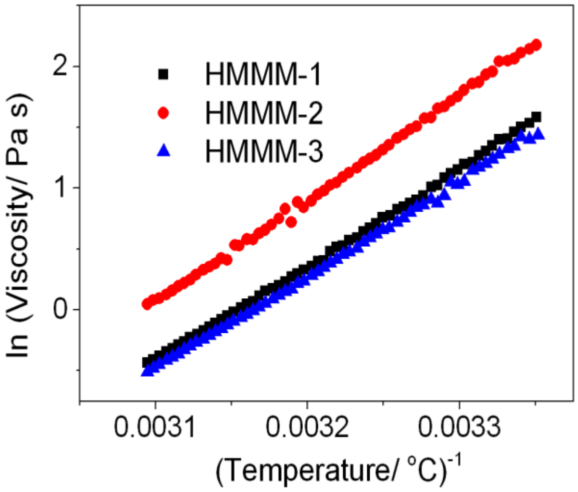


Figure 2.8-26: Arrhenius plot of the hexamethoxymethyl melamine (HMMM) cross-linkers

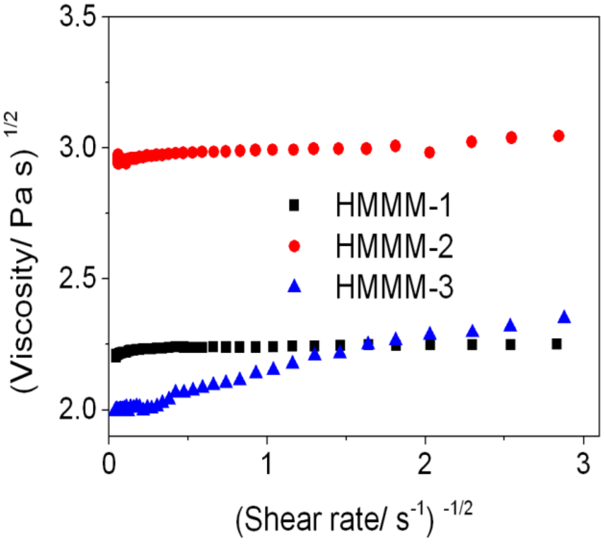


Figure 2.8-27: Casson-Asbeck plot of the hexamethoxymethyl melamine (HMMM) cross-linkers

The Arrhenius-type plots and the Casson-Asbeck plots of the hexabutoxymethyl melamine (HBMM) cross-linkers are presented as Figure 2.8-28 and Figure 2.8-29, respectively. The values obtained for yield point, the infinite shear viscosity and the activation energy of flow for the cross-linkers are shown in Table 2.8-1.

The values of infinite shear viscosity for the different HBMM cross-linkers are within a range of 2.4 – 4.0 Pa s. The values of flow activation energy for HBMM-2 (7.30 kJ/mol) was significantly lower than that obtained for HBMM-1 and HBMM-3, with values 51.0 and 61 kJ/mol, respectively. The elemental data of the HBMM-2 cross-linker (Table 2.8-2) varied in the %C value in comparison to the HBMM-1 and HBMM-3. Significant differences in the %C could imply the presence of greater amounts oligomer or greater extent of etherification in the cross-linker. This variation could result in the difference in the flow activation energy and could result in a non-linear pattern seen in the cross-linker's Arrhenius plot. Because the HMMM-2 gives a significantly lower flow activation energy, its flow behaviour would be the most sensitive to temperature.

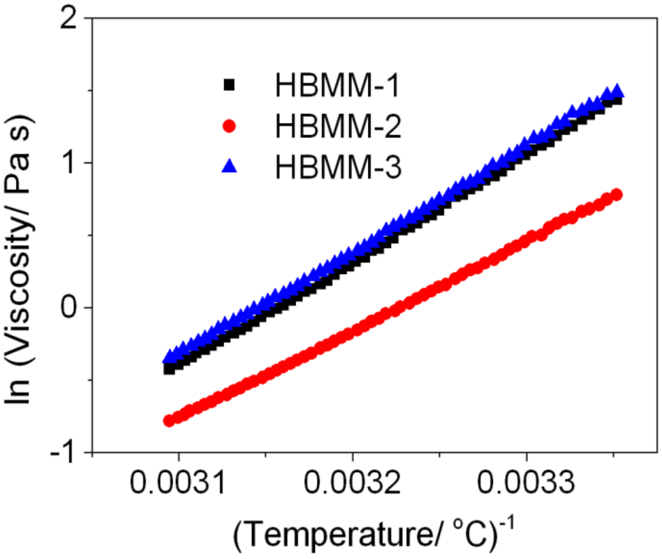


Figure 2.8-28: Arrhenius plot of the hexabutoxymethyl melamine (HBMM) cross-linkers

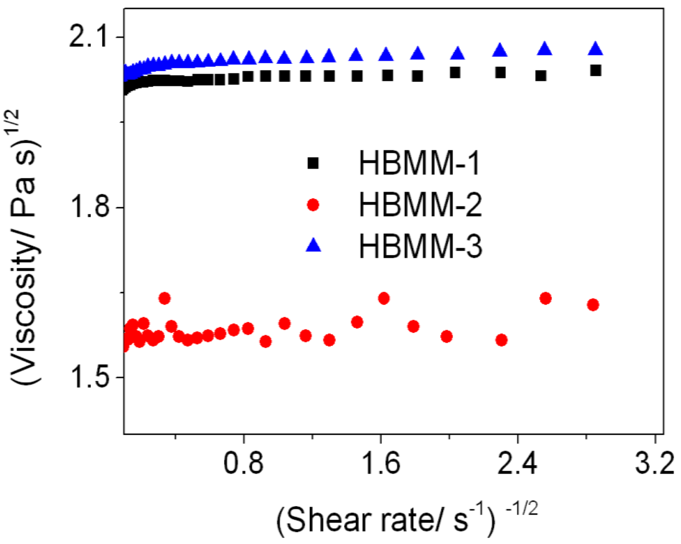


Figure 2.8-29: Casson-Asbeck plot of the hexabutoxymethyl melamine (HBMM) cross-linkers

The Arrhenius-type plots and the Casson-Asbeck plots of the methylol melamine-type (MMTC) cross-linkers and the dibutoxymethyl benzoguanamine (DBMB) cross-linker are presented as Figure 2.8-30 and Figure 2.8-31, respectively. The values obtained for yield point, the infinite shear viscosity and the activation energy of flow for the cross-linkers are shown in Table 2.8-1.

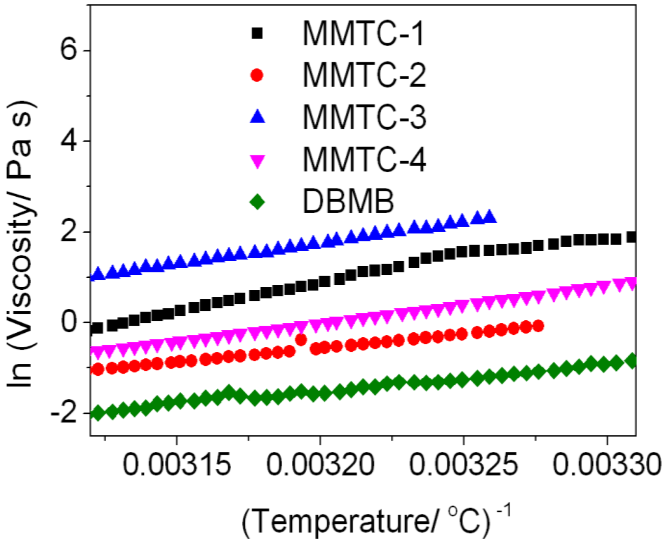


Figure 2.8-30: Arrhenius type plots of the methylol melamine-type (MMTC) cross-linkers and the dibutoxymethyl benzoguanamine (DBMB) cross-linker

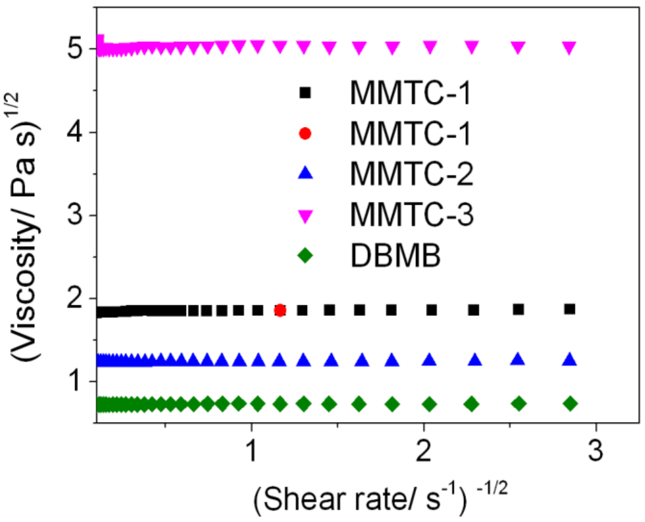


Figure 2.8-31: Casson-Asbeck plots of the methylol melamine-type (MMTC) cross-linkers and the dibutoxymethyl benzoguanamine (DBMB) cross-linker

Table 2.8-1 shows that, among the cross-linkers from the Casson-Asbeck plots and the Arrhenius type plots of the methylol melamine-type (MMTC) cross-linkers and the dibutoxymethyl benzoguanamine (DBMB) cross-linker, differences in the yield point, the infinite shear viscosity and the activation energy of flow are seen. MMTC-1 has the highest value of flow activation energy of 93.30 kJ/mol, indicating that this particular cross-linker will be least sensitive to temperature, during formulation, application and curing. These differences can be interpreted with respect to variations in the cross-linker chemistries. Also, the data could prove to be useful when trying to achieve desired performance properties when one of these additives was used. The lower the value of the flow activation energy, the more sensitive the flow of the cross-linker would be to temperature changes, (Solomon and Zhai, 2004).

2.8.6. Thermally induced reactions and decomposition patterns of the amino cross-linkers

The decomposition arising from the breakdown of the amino cross-linkers is represented by Figure 2.8-32. Differences in the thermal stability can be seen with those cross-linkers that are based on methylol melamine derivatives and those that are based on hexamethoxymethyl melamine (HMMM) and hexabutoxymethyl melamine (HBMM). Patterns emerge having relevance to the overall thermal stability of the cross-linkers.

Differences between members of each chemistry class are related to differences in the solids content, the degree of etherification and the degree of methylolation.

The order of the initial overall thermal stability is HBMMs> HMMMs> MMTCs> DBMB, indicating differences in the chemical events that occur during the thermal decomposition processes. Although some changes to these patterns are seen on heating, particularly for DBMB, the overall trends are maintained.

When each cross-linker is used in an epoxy coating formulation, the composite coatings are cured at 200 ^{o}C for 10 minutes (Section 3.5). The data in Figure 2.8-32 show that at the curing temperature of 200 ^{o}C, each cross-linker category has a distinct solids content contribution that it can make to the coatings. The HMMMs and the HBMMs will make similar solids contribution. This will be greater than the contribution that can be made by the MMTCs and the DBMB cross-linkers. This particular point becomes relevant when the cross-linkers are used in the coatings at loadings that are greater than those applied beyond "additive" amounts.

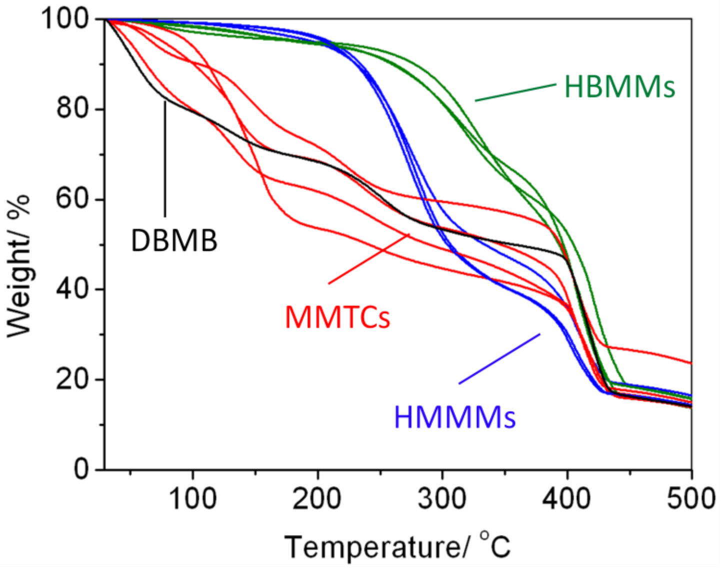


Figure 2.8-32: TGA decomposition profile (variation in weight/% with temperature) of the cross-linkers, hexamethoxymethyl melamine (HMMM); hexabutoxymethyl melamine (HBMM); methylol melamine-type cross-linkers (MMTC) and dibutoxymethyl benzoguanamine (DBMB)

These results are relevant to understanding the relationship between the thermal stability of the cross-linkers and the hydrolytic stability of the cross-linkers. Initial weight loss events, in each case, can be correlated to the loss of solvent(s). Later losses can be related to chemical reactions and to the occurrence of decomposition and the removal of by-products, as the heating continues up to 500 °C. Details of the physical-chemical changes that occur during the heating process are given in Figure 2.8-33, for the trimethylol tributoxymethyl melamine (TMTBM) cross-linker, with the associated functional group assignments, (Moore and Donnelly, 1963).

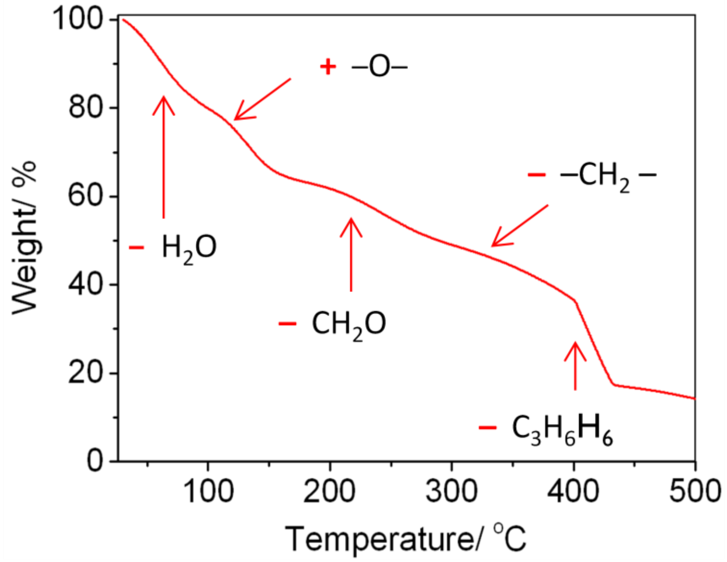


Figure 2.8-33: Thermal decomposition pattern of the trimethylol tributoxymethyl melamine cross-linker (TMTBM) showing the correlation between the thermal processes and the chemical processes that occur during decomposition

Figure 2.8-33 shows that when the trimethylol tributoxymethyl melamine cross-linker, (TMTBM) is heated from room temperature, water and other residual solvents are lost, corresponding to a weight loss of up to 20%. As the heating progresses, the methylol functional groups in the cross-linker react together leading to the formation of ether linkages. This continues up to around 140 °C where the cross-linker starts to lose formaldehyde as the etherified derivatives become unstable. This continues up to about 270 °C and is immediately followed by a breakdown of the methylene bridges, up to 400

^oC. Melamine is formed from about 400 ^oC, following the loss of methylene functionality, (Moore and Donnelly, 1963).

2.8.7. Behaviour of the different TiO_2 pigment grades

The different grades of the TiO_2 pigment are shown in Table 2.2-2. PW1 denotes one variation of the TiO_2 pigment, PW2 denotes a second variation of the TiO_2 pigment and PW3 denotes third variation of the TiO_2 pigment.

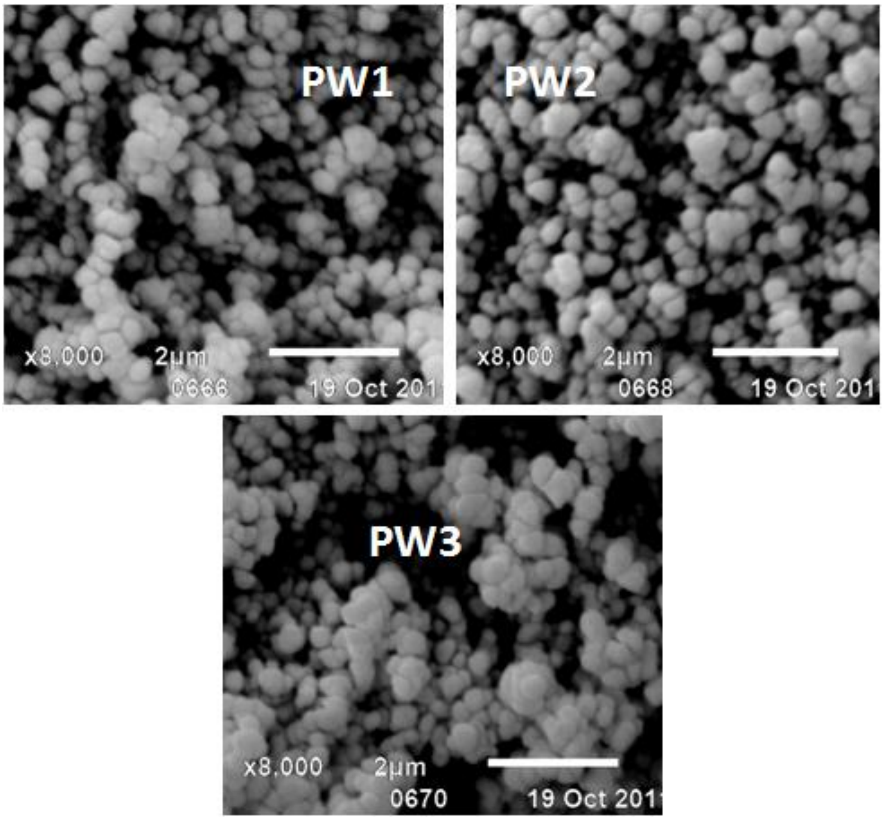


Figure 2.8-34: SEM micrographs from the three pigments grades. The PW denotes pigment white, referring to the grade of the TiO_2 pigment particles

The SEM images obtained for the three TiO_2 pigment types used in the overall study are shown in Figure 2.8-34. Although the shapes of the individual primary particles for each pigment grade appear to be roughly spherical, PW1 and PW3 show aggregated clusters of particles. The three variations of the pigment were sourced from Valspar, (Valspar France, 2010). Slight variations in terms of particle sizing and/or level of particle aggregation are to be expected. In Sections 5.14 and 5.15, the behaviour of the different pigment grades is represented in terms of their individual performance/behaviour towards melamine release and generation from pigmented epoxy-anhydride coatings.

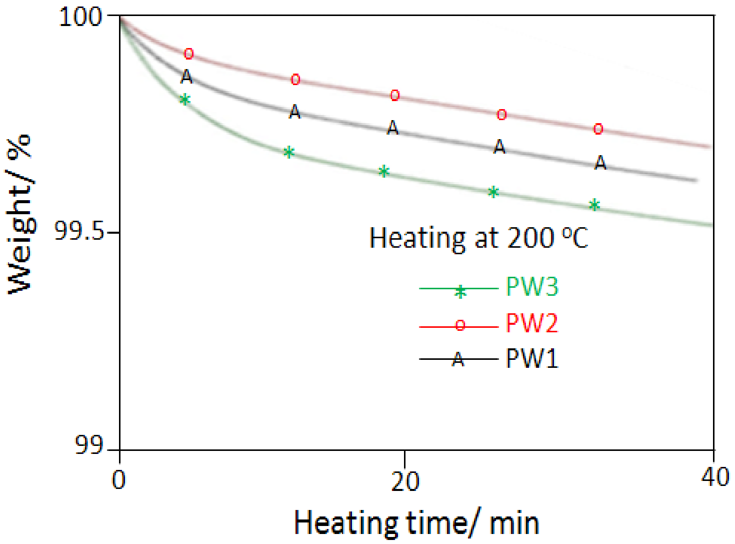


Figure 2.8-35: Variation in weight with time of heating, pastes of the TiO_2 pigment grades

The water retention behaviour, which can be used as a guide to the hydrophilicity of the three pigment grades, was compared, Figure 2.8-35. In the figure, the weight loss is shown as a function of the heating time, at 200 ^{o}C. Because the pigment types have shown moisture retention, even after drying their pastes at room temperature for 24 hours, they can be described as having a limited degree of hydrophilic behaviour. Such hydrophilicity can be of relevance to the interaction of the pigment particles when in compositions in either the liquid state or the solid state, through different types of intermolecular interaction that can arise, depending on the other components of a formulation.

Table 2.8-3: Titanium and aluminium content of the TiO_2 pigments

TiO_2 pigment	% Ti	% Al
PW1	50.10	1.58
PW2	47.46	1.40
PW3	52.13	2.18

In Table 2.8-3, the Ti (%) and the Al (%) elemental content of each of the three TiO_2 pigment grades is presented. The results can be considered to be quantitative. However, because of sensitivity issues, they should be treated in a semi-quantitative manner. It is clear from the results that the different grades of the pigment contain different amounts of aluminium. The differences arise as a consequence of the surface treatment of the pigment particles. The significance of these differences is further discussed in Section 5.15.

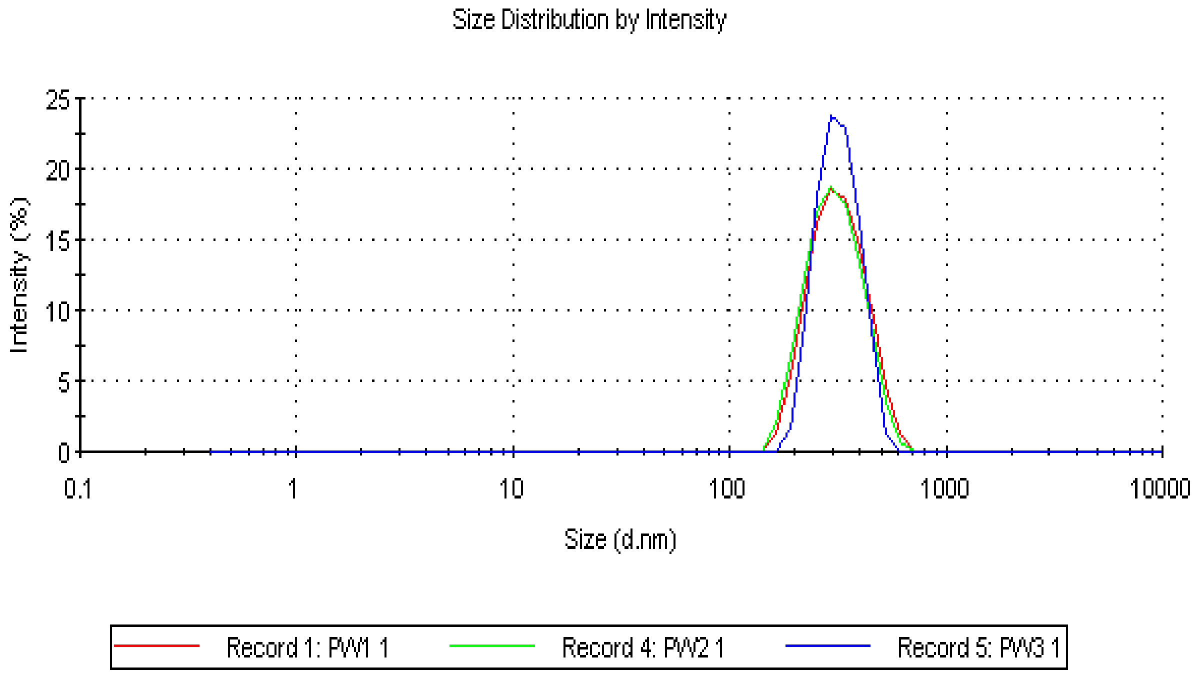


Figure 2.8-36: Size distribution plots for the three pigments

The particle size distribution and the zeta potential distribution of the three pigment grades (PW1, PW2 and PW3) are shown in Figure 2.8-36 and Figure 2.8-37, respectively. The average particle sizes obtained for PW1, PW2 and PW3 were 318 nm, 310 nm, and 355 nm, respectively. These results are in agreement with those derived from assessment of the SEM images of the pigments, in terms of the presence of aggregated clusters of particles. The traces show that PW3 has a slightly narrower size distribution followed by PW1 = PW2. The significance of these differences is further discussed in Section 5.15.

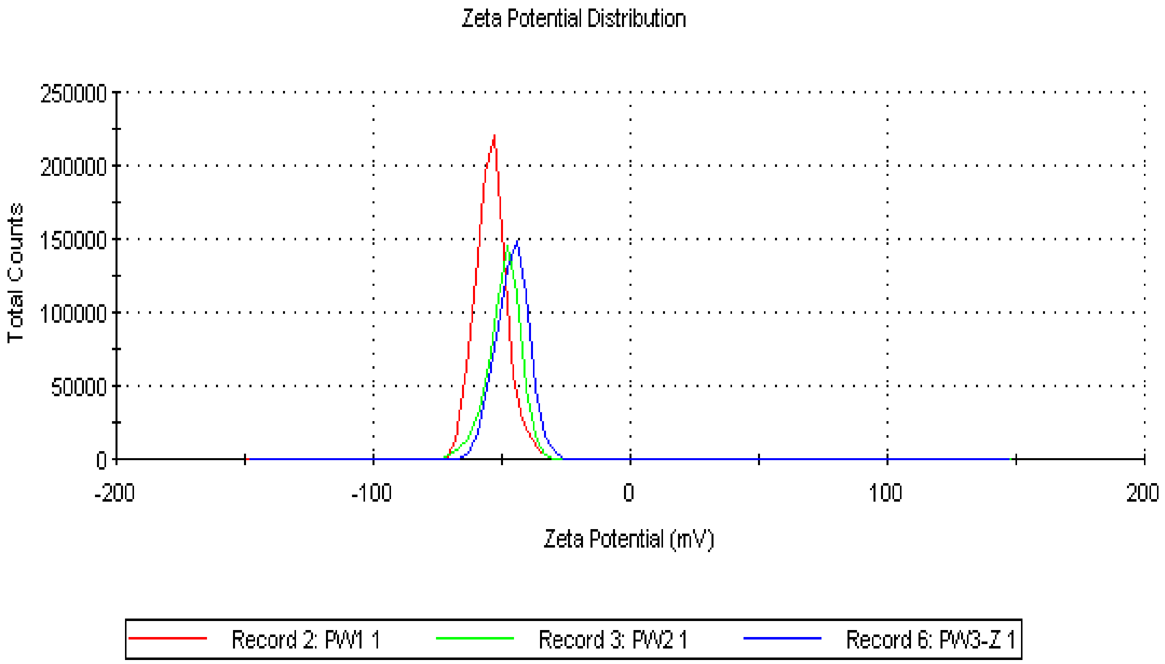


Figure 2.8-37: Zeta potential distribution for the three pigment grades

The zeta potential values obtained for the pigment samples were -54 mV, -49 mV and -46 mV for PW1, PW2 and PW3 samples, respectively. According to the literature, (Sheen et al., 2009), surface treated-TiO_2 particles can have zeta potential values in the range of -54 mV to -72.7 mV, depending on the depth/type of the treatment. The differences (significance etc) in zeta values that were obtained in this study are taken into consideration in Section 5.15, where the behaviour patterns of the different pigment grades in the coating formulations are considered.

2.8.8. Curing oven performance

2.8.8.1. Heating behaviour and cooling behaviour of the Werner Mathis curing oven

The results obtained from the temperature ramp calibration of the Werner Mathis oven are shown in Figure 2.8-38 and Figure 2.8-39, as plots of the temperature achieved as a function of the time allowed for heating, with respect to the locations of the samples in the oven unit.

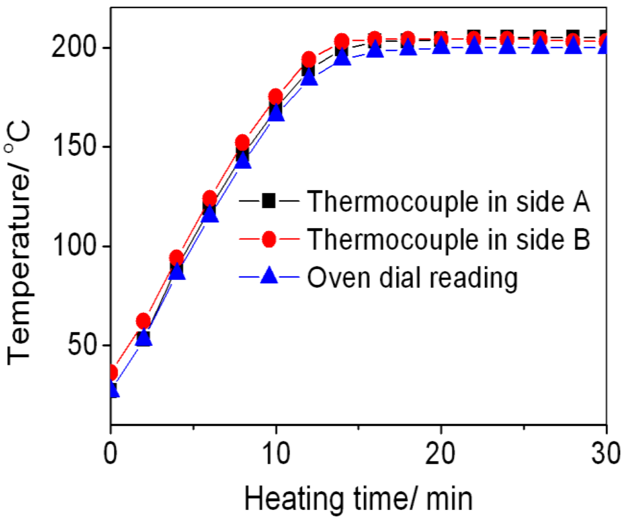


Figure 2.8-38: Behaviour of the two side compartments of the WM oven using Fan 1 setting

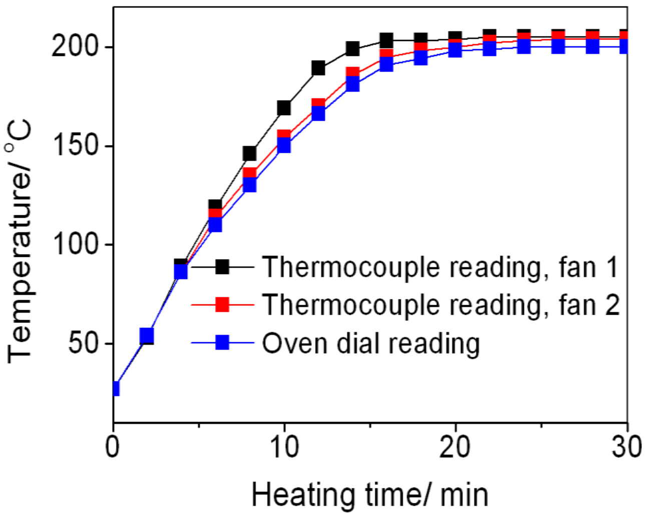


Figure 2.8-39: Heating up behaviour of the oven, showing the performance of the two fan settings of the WM oven

Both Figure 2.8-38 and Figure 2.8-39 indicate that, from room temperature (after turning the oven on), 15 minutes were required for the oven to reach 200 ^{o}C. The temperature of the oven then became stable at that temperature. Very similar heating behaviour was exhibited by Fan 1 and Fan 2 settings of the oven and similarly in the oven's side A and side B regions. The average thermostat correction value, (US Department of Interior, 1989) was 3 ^{o}C±1, at 200 ^{o}C.

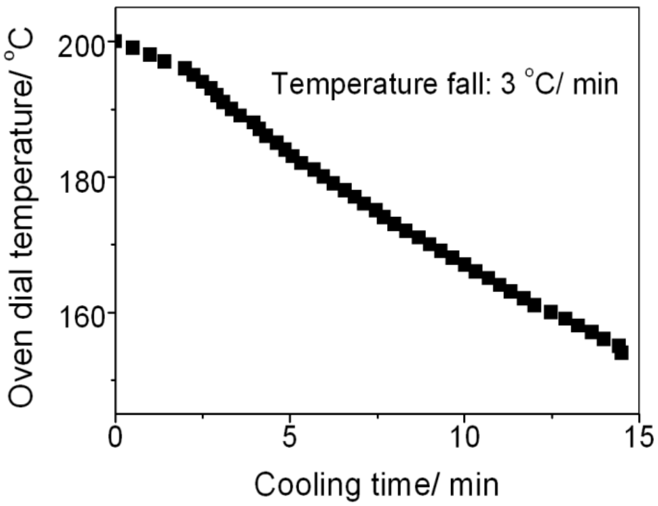


Figure 2.8-40: Cooling behaviour of the WM oven system

A study of the cooling behaviour of the oven, shown in Figure 2.8-40, indicates that on turning the heating in the oven off, while leaving the rotating fan(s) on, the temperature in the oven compartments fell at an average rate of 3 °C/ minute, in the temperature range from 200 °C to 150 °C.

2.8.8.2. Achieving 'peak metal temperature' in the oven

The results obtained from the isothermal calibration of the Werner Mathis oven are shown in Figure 2.8-41.

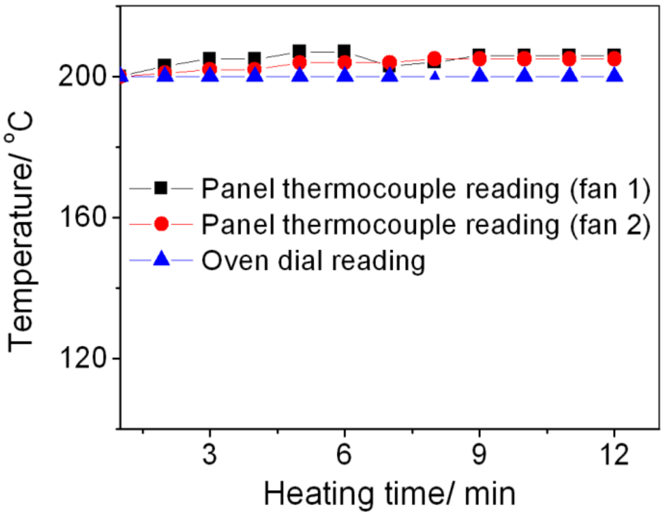


Figure 2.8-41: Variation in the temperature as the function of the times of heating- a temperature profile of a panel inside the WM oven

According to Figure 2.8-41, the average thermostat correction value was 4 ^{o}C±1, at 200 ^{o}C. The correction value is within industrially acceptable limits. In the can coating industry, the peak metal temperature (PMT) is considered to be a window range, for example 200 – 205 ^{o}C, because of temperature variations that can arise, in the oven, during curing processes. Provided that the temperature of the oven does not fall below or exceed the PMT, sufficient curing of the coatings can be expected, (Polaski et al., 2004).

2.9. Conclusions

For the analysis of amino cross-linker compounds, polymeric binders and TiO_2 pigment grades, accurate, effective analytical procedures were developed and authenticated. The procedures were repeatable and reliable with respect to the successful characterisation of the raw material samples.

The thermal, rheological, spectroscopic and chromatographic behaviour of the melamino cross-linkers have been investigated. The results from the characterisation of the cross-linkers have provided useful information about their viscosities, flow characteristics, molecular weight, functional groups as well as their residual melamine content. These cross-linkers exhibited different values of flow kinetics parameters. The differences were interpreted with respect to variations in the cross-linker chemistries, extents of etherification or methylolation. The data could prove to be useful when trying to achieve a desired optimal performance property if one of these cross-linkers was intended to be used beyond additive levels, in the coatings. The higher the value of the activation energy of flow, the more sensitive the flow of the cross-linker would be to temperature changes. The relevance of these data is discussed in more detail in the appropriate, later sections.

The CHN elemental analyses and NMR results have shown that the cross-linkers contain residual melamine-based products. There is also the indication that the cross-linkers contain relatively small amounts of derivative compounds. This latter point confirms supplier information and literature reports. The benzoguanamine cross-linker contains melamino components although it was supposed to be solely benzoguanamino. This contamination arises because of the incomplete synthesis of the cross-linker.

The three grades of the TiO_2 pigment gave similar characterisation data, namely similar particle size values, comparable zeta potential values and similar particle shapes. The three pigment grades exhibit moisture retention, even after drying their pastes at room temperature for 24 hours. Thus, the pigments exhibited a limited degree of hydrophilic behaviour, a confirmation that each TiO_2 core was surface treated. The behaviour of the three different TiO_2 pigment grades in relation to their contribution in melamine generation is discussed in Sections 5.15.

The overall results show the Werner Mathis oven to be consistent and to give a reproducible temperature profile. The oven was reliable, possessing good heating control and the required control of cooling. The results also indicate that the oven can provide controlled curing of the coated panels, achieving a required performance peak metal temperature.

Chapter 3: Formulation procedures, coating application and curing procedures

3.1. Introduction

In the industry, coatings are usually formulated using specific procedures, specific types of raw materials, specific amounts of each raw material and appropriate conditions of milling, mixing and stirring. After formulation, the coatings are usually tested in order to ensure that they possess the characteristics needed for them to be applied to the appropriate substrates. The application procedures require specified amounts of coatings to be deposited on the substrates. The application needs to be carried out using a process that gives good control and good repeatability. After application, the coatings are converted from the liquid state into the dried/cured states, through the controlled curing in an oven, for the required time periods, at specific temperatures.

This chapter concerns a detailed presentation of the procedures that were followed during coating formulation, coating application and during the curing of the coatings, on metal substrates, in the oven. As part of the migration studies, various conditions of coating formulation, several procedures of application and different conditions of curing were used. In each case, recommendations from the industry were followed.

3.2. Materials

The tin-plated sheets that were used as substrates in the studies were provided by Valspar, (Valspar UK, 2011). They were manufactured by Arcelor Mittal with specifications of 2.8/2.8 TH415 - 0.21mm, (Arcelormittal.com). The raw materials that were used in the development of all of the coating formulations that were used in the experiments were provided by Valspar, (Valspar France, 2010).

The different grades of the TiO_2 pigment are shown in Table 2.2-2. The three grades of the pigment differ from one another on the basis of average particle size and on the basis of the multilayer inorganic treatment over the TiO_2 core.

Table 2.2-2 provides a list of the three different grades of TiO_2 pigment particles that were used in the experiments, including the supplier, the quantity supplied and the average particle size distributions of the pigments. Characterisation data on the pigment grades are given in Section 2.8.7. The PW2 grade of the TiO_2 pigment was chosen and used in further experiments, except where studies of the behaviour the three grades of the pigment were carried out. The choice was based on the results obtained and discussed in Section 5.15.

Table 2.2-3 provides a list of the cross-linking compounds that were used in the experiments, including relevant chemical descriptions of the cross-linker molecules and of their suppliers. The cross-linkers were used in the same manner in the coatings. Based on the results, discussed in Section 5.4 and Section 6.3, specific cross-linkers were chosen to represent their respective chemical classes. Thus, in Chapters 5 and 6, in the results, any mention of hexamethoxymethyl melamine (HMMM) refers to HMMM-2, any mention of hexabutoxymethyl melamine (HBMM) refers to HBMM-3 and any mention of trimethylol tributoxymethyl melamine (TMTBM) refers to MMTC-2.

Table 3.2-1 provides a list of all of the polymeric binders that were characterised and used in the formulation of various epoxy-based coatings. In the table, information concerning the composition of each binder system is provided and the reasons given (by Valspar, France) for their incorporation into the respective coating formulation.

Table 3.2-2 provides a list of all the polymeric binders that were characterised and used in the formulation of various poly(ester)-based coatings. In the table, information is provided on the composition of each binder system and the reasons for their incorporation into the respective coating formulation.

Table 3.2-1: Polymeric binders used in the epoxy-based coatings

Acronym	Polymer description
Epoxy binder (EP1)	This is a binder composition that is produced from Bis-phenol A type compounds. It is incorporated into epoxy anhydride coatings in order to provide cross-linking with melamino compounds.
Anhydride binder (AN1)	This is a carboxylic acid-based binder component. It is used in epoxy-anhydride coating formulations to enhance cross-linking, during curing.
Epoxy binder (EP2)	This binder composition is produced from Bis-phenol A type compounds. It is incorporated into epoxy phenolic coatings in order to enhance molecular weight development.
Phenolic binder (PH1)	This is a phenolic binder that is produced from the polymerisation of phenolic monomers. It is used in epoxy coatings for reactivity/flexibility purposes.
Phenolic binder (PH2)	This is a phenolic binder that is produced from t-butyl phenol. It is used to promote a “gold” shade in the cured epoxy phenolic coating, when required.

Table 3.2-2: Polymeric binders used in the poly(ester)-based coatings

Acronym	Polymer description
Poly(ester) binder (PE1)	This is a linear poly(ester) polymer that is used to provide flexibility/hardness, porosity resistance and water sterilisation resistance to the coatings.
Urea binder (U1)	This is a urea-formaldehyde binder that has been etherified with butanol, dissolved in a butanol/xylene blend (3:1). It is used to promote cross-linking in the coating.
Phenolic binder (PH3)	This is a phenolic binder composition that is produced from etherified phenolic compounds. It is used for reactivity provision purposes in the coating.
Phenolic binder (PH4)	This is a phenolic binder composition that is produced from t-butyl phenol. It is used in poly(ester) coatings for flexibility purposes.
Phenolic binder (PH5)	This is a binder system that is produced from phenol and other phenolic derivatives. It is used to prevent the development of staining in poly(ester) coatings that arises from exposure to sulphur-based compounds.
Poly(ester) binder (PE2)	This binder operates on the basis of a linear poly(ester) chemistry. It is used to impact flexibility/hardness, adhesion and barrier film properties to the coatings.
Acrylic binder (AC1)	This is an acrylic additive binder. It is produced from specific acrylic acid monomers and used to enhance adhesion and other performance properties.
Phenolic binder (PH6)	This is a cross-linkable phenolic binder, derived from phenol-based monomers. It is used to improve the adhesion of poly(ester) coatings to substrates.

3.3. Formulation of coatings

3.3.1. Formulation of epoxy-anhydride based polymer solutions

Each epoxy-anhydride based polymer solution was prepared according to the procedures provided by Valspar, (Valspar France, 2010). The components were as follows: epoxy resin precursor, EP1, an anhydride-based polymer, AN1, propylene glycol monomethyl ether acetate (solvent), 2-n-butoxyethyl acetate (solvent), ethylene glycol monomethyl ether acetate (solvent) and cyclohexanone (solvent).

A glass container was prepared and marked. The epoxy resin precursor, EP1 (40.0 g) and the anhydride-based polymer, AN1 (4.4 g) were mixed with propylene glycol monomethyl ether acetate (3.1 g), using a Heidolph mixer, Type RZRI, (Opticsplanet.com), for 5 minutes. 30.0 g of 2-n-butoxyethyl acetate, 20.5 g of ethylene glycol monomethyl ether acetate and 2.0 g of cyclohexanone were added into the container. The contents of the container were mixed thoroughly until a “solution” was formed.

3.3.2. Formulation of pigmented epoxy-anhydride coatings

A glass container was prepared and marked. The epoxy polymer solution, prepared as described in Section 3.3.1 (14.5 g), the dispersing agent (0.25 g) and the PW2-TiO_2 pigment (23.5 g, Table 2.2-2), were mixed in the glass container using a Heidolph mixer, Type RZRI, (Jeolusa.com), for 10 minutes, at a speed of 2000 rpm. 0.5 g of 2-butoxyethanol was added to the mix and stirring was continued for further 1 hour. The mixing was stopped. A Hegman gauge, (Caltechindia.com) was used to check the dispersion quality, (by ensuring that there were no particles above 9 microns). The Hegman gauge was used according to established procedures, (ISO 1524, DIN 53-203 and ASTM D1210). 4.0 g of 2-butoxyethyl acetate, 1.5 g of 2-butoxyethanol, 51.0 g of the epoxy polymer solution, 0.5 g of one option of the melamino cross-linkers, (Table 2.2-3), 0.2 g of propylene glycol monomethyl ether acetate, 0.2 g of flow additive, 1.5 g of naphtha-light aromatic™ and 2.35 g of 2-butoxyethanol were added to the mixture, under agitation. The mixing was continued for 10 minutes. 100 g of the pigmented epoxy-anhydride coating were, thus, prepared and ready to be studied and applied.

A series of pigmented (using PW2-TiO_2) epoxy-anhydride coatings was then formulated, each using one option of the eleven melamino cross-linker compounds, according to the procedure described above.

Three pigmented epoxy-anhydride coatings were also formulated according the standard procedure described above. Each of these coatings contained one option of the three TiO_2 pigment grades that were described in Table 2.2-2.

3.3.3. Formulation of un-pigmented epoxy anhydride coatings

All of the un-pigmented epoxy anhydride coatings were formulated according to the procedure described in Section 3.3.1, by the mixing and agitation of the specified components. No pigment was included in these formulations.

3.3.4. Formulation of epoxy phenolic coatings

A glass container was prepared and marked. 64.5 g of the epoxy polymer solution, prepared as described in Section 3.3.1, 17.0 g of phenolic binder PH1 (Table 3.2-1), 5.2 g of phenolic binder PH2 (Table 3.2-1), 0.25 of one option of the melamino cross-linkers (Table 2.2-3) 0.25 g of flow additive and 4.0 g of propylene glycol monomethyl ether acetate were added into the container. The contents of the container were mixed using a Heidolph mixer, Type RZRI (Opticsplanet.com), for 10 minutes, at a speed of 2000 rpm. 0.3 g of ethylene glycol monomethyl ether acetate, 1.0 g of phosphoric acid and 7.5 g of propylene glycol monomethyl ether acetate were added into the mixture, under agitation. The mixing was continued for 10 minutes. 100 g of the epoxy-phenolic coating were thus prepared and made ready to be studied.

3.3.5. Formulation of poly(ester)-urea coatings

A glass container was prepared and marked. 60.05 g of the poly(ester) polymer PE1 (Table 3.2-2), 2.5 g each of one option of melamino cross-linker (Table 2.2-3) 19.7 g of solvent mixture, 0.76 g of urea polymeric binder U1 (Table 3.2-2), 9.16 g of phenolic polymer PH3 (Table 3.2-2), 3.26 g of phenolic polymer PH4 (Table 3.2-2) and 3.56 g of phenolic polymer PH5 (Table 3.2-2) were added into the glass container, under agitation and mixing. The mixing was continued for 15 minutes. 100 g of poly(ester)-urea coating were thus prepared and made ready to be studied and applied.

A series of poly(ester)-urea coatings was then formulated, each using one option of the melamino cross-linker compounds, according to the procedures described above. A separate coating was also prepared according the procedure described above, but containing no melamino cross-linking compound. This particular coating was labelled PP01.

3.3.6. Formulation of poly(ester)-acrylic coatings

A glass container was prepared and marked. 53.07 g of the poly(ester) polymer PE2 (Table 3.2-2), 5 g each of one option of melamino cross-linker (Table 2.2-3) 1.25 g of the phenolic polymer PH6 (Table 3.2-2), 4.18 g of the acrylic polymer AC1 (Table 3.2-2) and 36.5 g of the solvent blend were added into the glass container, under agitation and mixing using the Heidolph mixer, Type RZRI, (Opticsplanet.com). The mixing was continued for further 15 minutes until a “solution” was formed. 100 g of poly(ester)-acrylic coating were thus prepared and ready to be studied and applied.

A series of poly(ester)-acrylic coatings was then formulated, each using one option of the eleven melamino cross-linker compounds, according to the procedures described above.

3.4. Coating applications methods

3.4.1. Application of coatings using K-bar coaters

Typically, the tin-coated steel-plate substrates used were A4 in size (Arcelormittal.com). The formulations were thoroughly mixed prior to application. Two tinplate-coated steel sheets were coded and then coated using the appropriate coating formulation, identified as pigmented epoxy-anhydride coating, unpigmented epoxy-anhydride coating, epoxy-phenolic coating, poly(ester)-urea coating and poly(ester) acrylic coating. The TiO_2-pigmented epoxy-anhydride coatings were applied on to the tinplated substrates at a deposition weight/area value of 12 gm^{-2}, using a K-bar coater, (Number 3), (Rkprint.co.uk). The un-pigmented epoxy-anhydrides coatings and the epoxy-phenolic coatings were each applied on to tinplated substrates at weight/area value of 6 gm^{-2}, using a K-bar, (Number 3).

The poly(ester)-urea coatings were applied onto the tinplated substrates at a deposition weight/area value of 8 gm^{-2}, using a K-bar coater, Number 4 (Rkprint.co.uk). Using the same procedure, the poly(ester)-acrylic coatings were applied onto the tinplated substrates at a deposition weight/area value of 12 gm^{-2}, using a K-bar coater, Number 6, (Rkprint.co.uk). The different amounts of coating deposited were designed take into account the different solid contents of the different coatings.

3.4.2. Application of coatings using the controlled screen printing technique

An alternative procedure for applying coatings onto the metal substrate was assessed, this being a screen printing technique. A semi-automatic screen printer, Roku Print (SD05), was used, (Rokuprint.com). The pressure and the speed controls that were built in the instrument were used. The coating was forced on to the tinplated substrate through the open areas of the stainless stencil mesh surface, using a squeegee. The mesh dimension of the woven screen was 32µm in thread diameter and 56µm in aperture size. The delivered thickness of the applied stencil emulsion was approximately 20µm. Through this method, the coating was successfully applied onto the substrate. The film weight thickness of the coating layer that was applied was evaluated according to the procedure described in Section 4.3.1.

3.5. Curing of formulated liquid coatings

The coated metal tinplates were loaded on to the carrier drive of the Werner Mathis oven, (Mathisag.com) and driven into the oven at a speed of 2m/minute. After the appropriate exposure time was reached, depending on the coating type, (for example, 10 minutes at 200 ^{o}C, for the epoxy coatings or 12 minutes at 195 ^{o}C, for the poly(ester) coatings), the panels were removed, allowed to cool and made ready for evaluation.

3.5.1. The one-step curing procedure

In the one-step curing procedure, coated panels were driven into the oven and then remained in the oven for the entire curing duration, (for example 12 minutes at 195 ^{o}C, for the poly(ester) coatings). The panels were then removed from the oven and allowed to cool to room temperature.

3.5.2. The two-step curing procedures

3.5.2.1. Two-step curing with “resting” of coatings in between steps

This procedure was used in certain specified experiments when the coatings were cured in two different steps, with a “resting” stage between the two steps. Coated tinplated panels were driven into the oven and held in the oven for a particular time duration, (for example 8 minutes at 195 ^{o}C). The panels were then removed from the oven heating compartment for them to “rest”, (for a period of 5 minutes, as an example). After the “resting” period, the panels were then driven back into the oven for a second curing session, for a specified duration, (for example 4 minutes at 195 ^{o}C). After the second exposure time was completed, the panels were then removed from the oven and cooled to room temperature.

Table 3.5-1 provides details of the curing conditions that were used to cure the epoxy-based coatings and the poly(ester)-based coatings.

3.5.2.2. Two-step curing based on a “wet-on-dry” procedure

This procedure was also adopted for certain specified experiments where one coating layer was applied and cured in the oven for the required time, (10 minutes, at 200 ^{o}C, for the epoxy coatings and 12 minutes, at 195 ^{o}C, for the poly(ester) coatings). The panels were then removed from the oven heating compartment and cooled to room temperature. A second coating layer was then applied on top of the first, cured layer. The panels were then returned into the oven in order to cure the second layer that was applied, for the required time, (10 minutes, at 200 ^{o}C, for the epoxy coatings and 12 minutes, at 195 ^{o}C, for the poly(ester) coatings). The panels were then finally removed, cooled and prepared for evaluation.

Table 3.5-1: Conditions for curing coatings, targeting two-step curing with "resting" of coatings in between steps

Epoxy-based coating systems, cured at 200 °C		
First curing/ min	Resting period/ min	Second curing/ min
10	0	0
8	2	2
4	2	6
4	5	6
4	10	6
Poly(ester)-based coating systems, cured at 195 °C		
First curing/ min	Resting period/ min	Second curing/ min
12	0	0
8	2	4
6	2	6
6	5	6
6	10	6

3.5.3. Curing time variation studies

For experiments involving the curing of the epoxy coatings, in which the effects of the curing temperature on any melamine release were monitored, the range of curing temperatures of the curing oven, was 160, 180, 200, 220 and 240 °C, for 10 minutes.

The poly(ester) coatings were investigated for the effects of the curing temperature on any melamine release. Thus a series of coatings was cured, in each case, at 155, 175, 195, 215 and 235 °C, for 12 minutes.

3.6. Discussion of results

3.6.1. Coating application procedures

The reproducibility of the coating application procedures depends on the flow characteristics of the coatings. Each time a certain coating film thickness was intended to be applied onto the substrate, a range of K-bar coaters was assessed to establish the most appropriate coater that was needed for the appropriate circumstances. This was necessary because viscosity of the coatings could change significantly over time.

3.6.2. Observation of panels after curing of coatings

In the Werner Mathis oven, all of the curing procedures were reproducible. Observations of several panels did not show any signs of under-cure (hue paleness in the case of unpigmented epoxy anhydride coatings) or over-cure (yellowness in the case of TiO_2-pigmented epoxy anhydride coatings). Similarly, surface reflectance studies that were carried out on random coatings did not show significant variations between the different zones across the coating's surface.

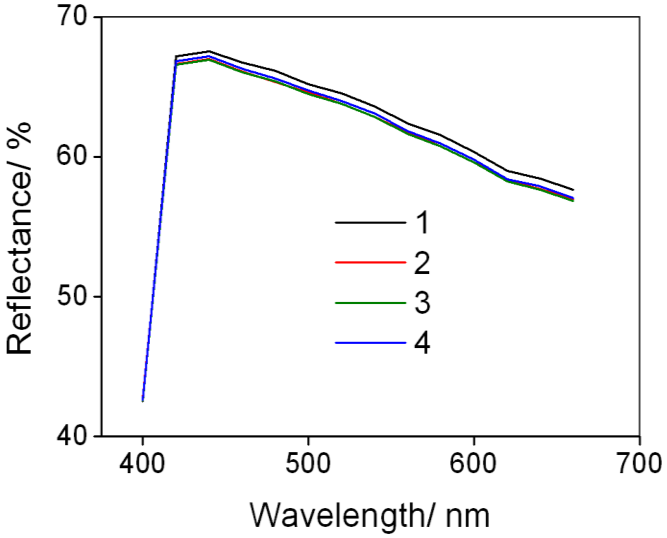


Figure 3.6-1: Surface reflectance properties of four different locations on a panel coated with a PW2 pigmented epoxy anhydride coating

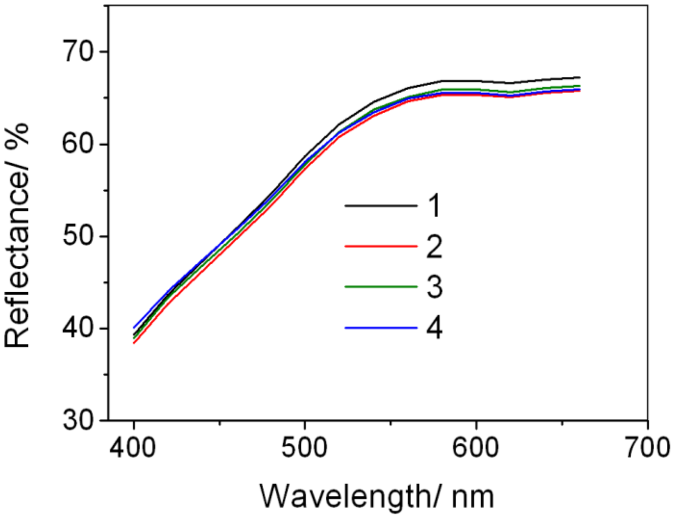


Figure 3.6-2: Surface reflectance properties of four different locations on a panel coated with an unpigmented epoxy phenolic coating

From the spectrophotometric measurements that were carried out on the panels, (Figure 3.6-1 and Figure 3.6-2), it can be inferred that uniform panel coating and curing occurred since very similar spectral properties of the different locations on the panels, in each case were observed. Therefore, in this regard, the Warner Mathis curing oven provided a consistent and a reproducible means of controlling the curing of the coating on the panels.

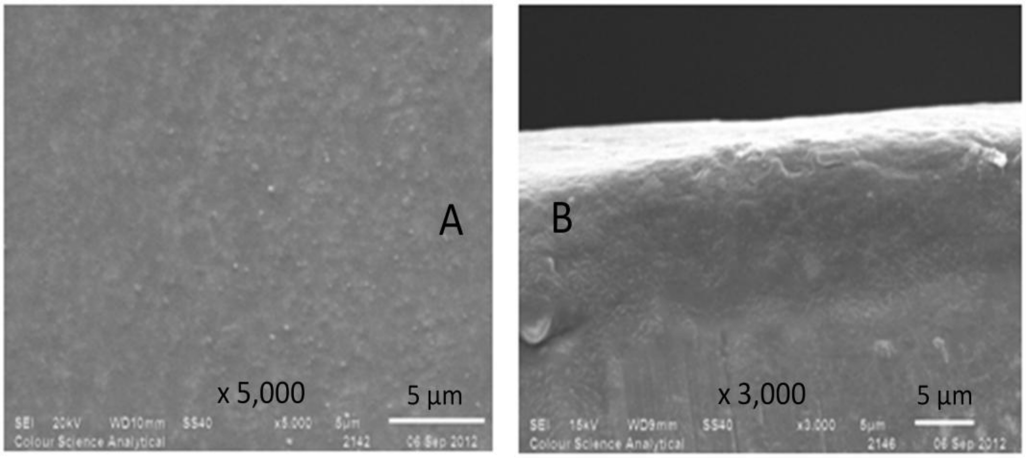


Figure 3.6-3: SEM micrographs, A: the surface of a cured, hexamethoxymethyl melamine (HMMM) cross-linked, PW2-pigmented epoxy anhydride coating and B: the cross-section of the same pigmented epoxy anhydride coating

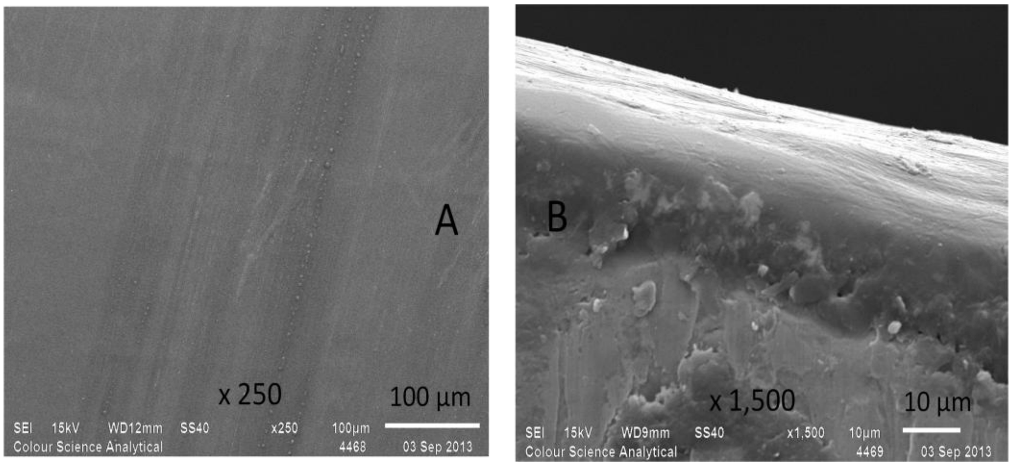


Figure 3.6-4: SEM micrographs, A: the surface of a cured, hexamethoxymethyl melamine (HMMM) cross-linked, unpigmented epoxy anhydride coating and B: the cross-section of the same unpigmented epoxy anhydride coating

In Figure 3.6-3, the SEM micrographs show the surface and the cross-section of a TiO_2 pigmented, hexamethoxymethyl melamine HMMM cross-linked, epoxy anhydride coating. Figure 3.6-4 shows the SEM micrographs of the surface and the cross-section of an unpigmented, hexamethoxymethyl melamine (HMMM) cross-linked, epoxy anhydride coating. Both figures shows that the coatings have been applied and cured uniformly, suggesting that the procedures used were appropriate. In both figures, there was no evidence of voids, surface irregularities, surface porosity or any major surface defects.

3.7. Conclusions

The results from various, relevant formulation and application procedures are discussed in detail in Section 5 and Section 6. From the work covered in this section, the following points are relevant.

1. The coatings were successfully applied to the tinplated substrates using K-bar coaters. The coating application and the testing procedures were effective and reliable.

2. The coating application procedures were reproducible. It was observed that a change in the viscosity of the coatings over time could affect the mass of coating that deposited per unit area of the substrate.

3. Observations and instrumental measurements of the cured coatings have shown that the coatings were successfully applied. There was no evidence of voids, micro-cracks, surface irregularities, surface porosity or any major surface defects in the coatings that were studied.

Chapter 4: Analyses of liquid coatings, of cured coatings and related migration studies

4.1. Introduction

The performance characteristics of coatings are highly dependent on their physical and chemical properties and on how these properties vary with the cure temperature. Many physical and chemical procedures can be used to define coatings and to help monitor their performance. For example, if a cured coating is too hard and not flexible enough, it might develop micro-cracks on drying/curing/storage/use or be subject to significant failure when the metal substrate is bent. Also if a liquid coating does not possess the correct rheological properties, there will be difficulties in applying it to the substrate, in flow out, in the development of adherence and coherence and in achieving desired appearance attributes.

In the analyses and characterisation of liquid coatings, rheological methods of analysis can help give an understanding of the flow characteristics of the coatings. Also through these methods, the viscoelastic and response properties of the coatings can be evaluated. From the procedures, the viscosity, yield point, moduli features and kinetic parameters, [related to chemical change (curing) and physical change (drying)] can be obtained. Other desirable tests that can be applied to liquid coatings include the solids content estimation and spectrophotometric analyses

In the characterisation of cured coatings, mechanical testing, spectrophotometric analyses and thermal analytical tests are important. Typical mechanical tests such as indentation tests, hardness tests and flexibility tests can provide significant information that can be used in providing understanding of the performance of the coatings, under controlled conditions or otherwise (in service). Surface reflectance studies are examples of techniques that can be used to monitor variations in terms of the appearance coatings after curing. Thermal analytical tests such as TGA and DSC can be used to yield information relating to the decomposition characteristics of coatings and can also be used to mimic changes occurring during curing processes.

In addition to providing a detailed account of the methods and procedures that were followed to test/analyse the liquid coatings and the cured coatings, this section also covers the migration tests that were carried out to monitor any release of melamine, benzoguanamine and formaldehyde or related low molar mass analogues from coatings into food simulants. Such migration is similar to that which might occur as a consequence of retorting foods in contact with the coatings. The retort procedures were carefully operated, using standard procedures, in order to mimic the pasteurisation, the sterilisation and/or the pressure cooking that canned food items undergo.

The migration procedures and the data manipulations were targeted to answer questions such as:

1. How much melamine, benzoguanamine or formaldehyde was released into food simulants per unit area of the coating used?
2. During the release process, how much of the cross-linker that was used in the coating was hydrolysed into the starting compounds?
3. What was the amount of each migrant species in the retorted food simulant, after the retorting procedure?
4. Does the amount of melamine, benzoguanamine or formaldehyde that was released into the food simulants exceed or stay within the limits allowed by regulations related to the performance of coatings that are intended to come into contact with food?

4.2. Procedures in the analyses of the liquid coatings

4.2.1. Rheological characterisation

Rheological evaluations were carried on out on selected coatings using a TA−Instruments ARES-G2 unit, (Tainstruments.com). The evaluations were run under a continuous shear ramp mode at, 30 ^{o}C. A steel parallel plate with a 40mm diameter, together with a truncation gap of 50 µm, was used.

For the analysis of each coating, sufficient of the appropriate sample was poured on to the rheometer-based-plate to cover the parallel plate. Excess sample was then removed after the plate had made contact with the sample. While the shear rate was increased from 1 Pa s to 1000 Pa s, 50 viscosity value points were collected, during a total run time of 5 minutes.

4.2.2. Solid content estimations

In each case, 1 g of the wet coating was applied onto a metal dish and cured in an oven at 200 ^{o}C, for 30 minutes. Equation 1.8-1, Section 2.5.2, represents the relationship associated with determining the % of the total solids in the formulations.

4.2.3. Flow time estimations

For each of the liquid coating formulations, filtration was carried out using 100-micron filters, (Coleparmer.co.uk). Flow measurements were then carried out according to established standard procedures. ISO cup 6 was used for epoxy coatings according to ISO 2431, at 25 ^{o}C. DIN cup 4 was used for poly(ester) coatings according to D4212-10, at 20 ^{o}C. The specifications for the flow criteria that were used are shown in Table 4.2-1.

Table 4.2-1: Criteria for measuring the flow time of liquid coating formulations

Coating type	Flow cup	Flow time range
Unpigmented epoxy anhydride	ISO 6	47 – 53 seconds
Pigmented epoxy anhydride	ISO 6	65 – 75 seconds
Epoxy phenolic	ISO 6	47 – 53 seconds
Poly(ester) urea	DIN 4	85 – 105 seconds
Poly(ester) acrylic	DIN 4	28 – 35 seconds

For each measurement, a known volume of coating was introduced into the appropriate flow cup. The coating was allowed to flow under the influence of gravity, through an orifice that was located at the bottom of the cup, until the coating had drained. The flow time was then recorded in seconds. A second, repeat measurement was then carried out. The coating was thinned with solvent or concentrated up, if the flow time fell outside the criterion in Table 4.2-1.

4.2.4. Thermogravimetric analyses

4.2.4.1. Isothermal analysis

A TA Universal Instrument V4.1D, (Tainstruments.com) was used for this aspect of the study, to investigate any specific mass loss processes that might represent the cure conditions of the coatings concerned. The experiments were carried out under a nitrogen atmosphere, with a N_2 gas flow rate of 20 mL per minute. For each epoxy coating, approximately 10 mg was heated isothermally at 200 ^{o}C, for 10 minutes. Through an analogous procedure, 10 mg of each poly(ester) coating were heated isothermally at 195 ^{o}C, holding for 12 minutes.

4.2.4.2. Temperature ramp analysis

Thermal decomposition profile studies were carried out on selected coating formulations to establish the thermal behaviour/properties of each, (relevant to the amount of melamine that each contains). This study was undertaken to establish whether or not the thermal stability of the coatings changed as the cross-linker contents was varied. The thermograms were recorded using a TA Universal Instrument V4.1D, (Tainstruments.com), over a temperature range of 0 – 500 ^{o}C, using a temperature increase rate of 10 ^{o}C/min and a N_2 gas flow rate of 20 mL/min. Known quantities (approximately 10 mg) of the samples were used for each evaluation.

4.2.5. Ageing studies, under laboratory conditions

Selected representative coating samples were studied to establish the effects (if any) of wet ageing on the amount of melamine that might be generated/released from the panels that had been coated with formulations that had been aged for known periods.

The ageing studies were carried out by sealing the wet coatings in appropriate vessels allowing them to stand under laboratory conditions, for specified periods. After the specified period, the wet coatings were applied on to tinplated substrates and cured under the conditions described in Section 3.5.1. Standard retort tests were then carried out at 131 ^{o}C for 1 hour. In each case, the results obtained from the melamine release/generation experiments were compared with those obtained from similar experiments that were applied to coatings that had not been aged.

4.3. Procedures used in the analyses of the cured coatings

4.3.1. Film weight thickness evaluations

The mass per unit area of the solid "cured" coatings was determined gravimetrically, according to the procedures and equations that were described in Section 1.8.2.1.

In the assessment, any relevant soluble components of the "cured" coatings were removed from a 10 cm x 5 cm panel, by rubbing or by dissolution in acetone. After the detachment (removal) of the coating, the panel was then re-weighed.

4.3.2. Surface wetting studies

The surface tension of doubly-distilled de-ionised water, of 3% (v/v) aqueous acetic acid and of 10% (v/v) aqueous ethanol was evaluated using a manual torsion balance that was equipped with a Du Nouy ring, (Thomassci.com). This analysis was carried out on the basis of ASTM D 179 and ASTM D 1331 established methods. Measurements were carried out by gently dipping the ring into the liquids, separately, to establish contact. While the ring was slowly pulled, an elongated film was formed in the ring. Surface tension readings were taken at the point of the ring break-up from the liquid surface. Each surface tension measurement was repeated three times and an average value was adopted, as long as the values were within an acceptable level of consistency.

The three solutions whose surface tension values were investigated were then used in the measurement of the contact angle of the test samples. This provided a basis for the study of interactions at the liquid-to-cured coating solid interface. Small drops (sessile drops) of the solutions were applied to the cured coating panels and the contact angle that the fluid made on the panel surface was recorded using a Livereel-ϴ-Meter, (Jiang, 2008). Each measurement was repeated three times and an average value was adopted in each case, on the basis that the range was within acceptable limits.

4.3.3. Surface reflectance studies

Reflectance spectrophotometric measurements were carried out on the surface of the dry coating panels, in duplicates, using an X-Rite 504 (interface 86) spectrophotometer, (Xrite.com). The specular included (SPIN) mode of analysis was used, excluding Lch data parameters from the measurement.

Prior to measurements, the instrument was calibrated by measuring the reflectance (%) values of a standard "white panel" and a standard "black hole". After these measurements, the instrument was made ready for panel analysis. These calibration steps ensured that the instrument provided spectral reflectance measurements to a 0.1% standard deviation.

4.3.4. Hardness testing

The "practical" hardness (resistance to penetration) of the cured coating surfaces was measured using a Sheen Instrument's pendulum hardness rocker, type 7262, (Sheeninstruments.com). Measurements were carried out in triplicate, according to the established standard methods of DIN 53 157 and ISO 1522.

Typically, a coated panel of 100 cm^2 area was used. The panel was mounted on the base that was attached to the cross bar. The counter was set to zero and the rocker was released. The hardness of the surface or the degree of dampening was measured in terms of the number of times the light beam was broken by a projecting plate that was allowed to swing to and fro through an angle of 6^o. With each complete rock, a value of 1 was recorded. During this procedure, the shield "door" was closed in order to protect the measurement system from interference, from air currents. Each time, the final reading was taken when the counter finally stopped. The hardness value of each sample was measured in triplicate and an average value determined on the basis that the repeat values all fell within acceptable consistency limits.

4.4. Migrant extraction and migration studies

4.4.1. Surface rubbing-based extractions

The blooming of components, from the bulk of the coating to the surface can take place during curing/storage, under certain conditions. In order to establish whether or not blooming might have occurred in any of the coated panels, surface rubbing of the cured coated panels was carried out to determine whether or not any substances of interest could be extracted from the surface into a solvent. In a typical procedure, a coated and cured surface was wiped with a piece of test material wetted with solvent. The method used was in accordance with DIN 13523-11 and ASTM D740-05 established methods.

The materials that were considered for this rubbing aspect of the studies were 100% cotton fabric (0.3 g, 4 cm^2), 100% poly(ester) fabric (0.2 g, 4 cm^2) and cotton wool (0.2 g). One sample of each cloth, soaked in 10% (v/v) aqueous ethanol, was used to rub across the cured coating surface, (25 cm^2 in area). 50 and 100 rubbing cycles were separately carried out. Each cloth was then placed into its individual glass vial containing 10 mL of 10% (v/v) aqueous ethanol. The vial was then retorted according to the procedure detailed in Section 4.4.3.

4.4.2. Room temperature solvent extractions

For the room temperature migrant extraction studies, a 0.25 dm^2 (5cm x 5cm area) of each representative coated, cured tinplated steel sample and 10 mL solvent were used. The solvents were chosen to cover a broad range of solubility parameter values. The solvents/solutions used were acetonitrile, distilled water, toluene, dichloromethane, diethyl ether, xylene, a 3% (v/v) aqueous acetic acid solution and a 10% (v/v) aqueous ethanol solution. The basis of the extraction tests was to identify and to quantify any melamino compound that might have been released from the coatings to the various solvents.

4.4.3. Retorting of cured coatings

This analytical procedure was a modified version of that reported in the literature, (Bradley et al., 2011). Here, in a typical procedure, 0.25 dm^2 (5cm x 5cm area) of coated, cured tinplate was immersed in 10 mL of 3% (v/v) aqueous acetic acid, (as a food simulant), in a glass vial. The container was then sealed using a crimper, (Labhut.com) and introduced into a Prestige, 6L High Dome pressure cooker, (Prestige.co.uk). The pressure cooker was heated to 131 ^oC and maintained at this temperature for 1 hour. After this time, the pressure vessel was cooled to room temperature. Then, an aliquot of the simulant was taken for analysis of melamine, benzoguanamine and formaldehyde.

The procedure was repeated using an aqueous solution containing 10% (v/v) of aqueous ethanol instead of the 3% (v/v) aqueous acetic acid.

4.4.3.1. Retort time variation studies

Here, selected coating panels were studied, in a kinetic manner, to establish the effects of the retorting time, at the standard 131 ^oC, on melamine release, on benzoguanamine release and on formaldehyde release. According to the procedure described in Section 4.4.3, series of epoxy coating panels, and a series of poly(ester) coating panels were retorted for 30, 60, 120, and 180 minutes, at 131 ^oC.

4.4.4. Melamine analyses

4.4.4.1. Analysis of melamine standard solutions

UV absorption spectra of the melamine standard solutions were recorded using a Varian 50-Probe, (Chem.agilient.com). The measurements were carried out at 25 ^oC. The concentrations of the standard solutions were 1.25, 2.5, 5, 10, 20, 40 and 80 µg/mL.

4.4.4.2. Evaluation of the amount of melamine migrants in retorted samples

All of the samples that were obtained from the retort procedure, (Section 4.4.3), were tested for their melamine content, arising from migration, according to the HPLC procedure described in Section 4.4.4.1. After data collection, a linear regression plot of the peak height provided by the standard solutions, against their concentration, was developed.

4.4.4.3. Determination of the melamine concentration, after extraction

The concentration (C) (µg/mL) of melamine that was detected in the medium isolated from each retorted coating sample was obtained from the straight line regression graph, (Equation 9). Each concentration was converted into a migrant concentration value (µg/6dm^2). In these calculations, the exposed area (A) of coatings (dm^2) and the volume (V) of aqueous food simulant (mL) are taken into account. The relationship is given in Equation 4.4-1.

$$C_{(\mu g/6dm^2)} = C_{(\mu g/mL)} \times \frac{V_{(mL)}}{A_{(dm^2)}} \times 6$$

Equation 4.4-1: Melamine migration concentration equation

In the equation, the conventional surface area to mass ratio of 6 dm^2 per kg (or litre) was applied.

4.4.4.4. Determination of the % hydrolysis of cross-linker to melamine

The extent of cross-linker hydrolysis to melamine was calculated according to Equation 4.4-2.

$$\%\ \mathbf{Hydrolysis} = \frac{\mathbf{Experimental\ yield}\ (\mu g/\mathbf{6dm^2})}{\mathbf{Theoretical\ yield}\ (\mu g/\mathbf{6dm^2})} \times \mathbf{100}\%$$

Equation 4.4-2: % Hydrolysis to melamine equation

The experimental yield of melamine was the value that was determined through chromatographic evaluations and acquired on the basis of straight line regression calculations, as shown in Equation 4.4-3.

$$\mathbf{Y = MX + C}$$

Equation 4.4-3: Linear regression equation

Here, Y = Peak height of melamine standards, from HPLC

M = Slope of the straight line regression graph.

X = Concentration of melamine standard solutions (µg/mL).

C = Intercept from the straight line regression graph.

The theoretical yield of melamine was obtained from Equation 4.4-4. This represents the amount of melamine that would be yielded from the complete hydrolysis of a certain amount of melamino cross-linker, used in any particular coating formulation.

$$\textbf{Theoretical Yield} = \textbf{MDV} \times \textbf{SMR} \times \textbf{FWT} \times \%\textbf{CRL}$$

Equation 4.4-4: Melamine yield equation

SMR= the conventional surface area to mass ratio of 6 dm^2.

FWT= film weight thickness (g/m^2).

The *%CRL* is the weight percent of the cross-linker in the total wet coating formulation.

In Equation 4.4-5, MDV = melamine degradation value. This represents the conversion of the cross-linker into melamine. Thus, as an example, one mole of hexamethoxymethyl melamine (HMMM: 390 g/mol) will give rise to one mole of melamine (126 g/mol). Thus, for HMMM,

$$\textbf{MDV} = \frac{\textbf{126 g/mol}}{\textbf{390 g/mol}}$$

Equation 4.4-5: Melamine degradation equation

4.4.4.5. Determination of the molar concentration of melamine migrants

The molar concentration of melamine migrant was calculated according to Equation 4.4-6. This equation represents the number of moles of melamine that migrated into each litre of retorted food simulant.

$$\textbf{Molar Conc.}_{\textbf{(mol/L)}} = \frac{\%\ \textbf{Hydrolysis} \times \textbf{Density of retorted solution}_{\textbf{(g/L)}}}{\textbf{100}\ \% \times \textbf{Molar mass}_{\textbf{(g/mol)}}}$$

Equation 4.4-6: Melamine molar concentration equation

In the equation, the density of the food simulant was taken into account (~1 g/cm^3). The molecular mass of melamine was also considered.

4.4.5. Benzoguanamine analyses

All analyses for benzoguanamine, in the standard solutions and in retorted coating samples, were carried out according to the HPLC procedure that was described in Section 2.4.6.

After the analysis of the calibration solutions and subsequent data collection, a linear regression plot of the peak height of each of the standard solutions against their concentration was developed. This plot was used in determination of the benzoguanamine content of various compositions.

4.4.5.1. Determination of benzoguanamine concentration, after extraction

The concentration (µg/mL) of benzoguanamine that was detected from each extraction solution was obtained using the data related to the linear regression graph, in a similar manner to that described in Section 4.4.4.4. These concentrations were converted into migration values (µg/6dm^2), taking into consideration the exposed area (A) of coatings (dm^2) and the volume (V) of aqueous food simulant (mL). The relationship that was shown in Equation 4.4-1 was used for the calculations.

4.4.5.2. Determination of the % hydrolysis of cross-linker to benzoguanamine

The % hydrolysis of cross-linker that resulted in the release of benzoguanamine was calculated using Equation 4.4-7 and Equation 4.4-8. The experimental yield of benzoguanamine was the value that was obtained through HPLC evaluations and straight line regression calculations. In Equation 4.4-7, the benzoguanamine degradation value (BDV) was used in place of the stated MDV value that was used in Equation 4.4-5, for the HMMM cross-linker determination. The general case is shown in Equation 4.4-8.

$$\mathbf{BDV} = \frac{\mathbf{187\ g/mol}}{\mathbf{390\ g/mol}}$$

Equation 4.4-7: Benzoguanamine degradation equation

$$\mathbf{BDV} = \frac{\mathbf{Molar\ mass\ of\ benzoguanamine}}{\mathbf{Molar\ mass\ of\ the\ cross - linker}}$$

Equation 4.4-8: Generalised benzoguanamine degradation equation

4.4.6. Formaldehyde analyses

4.4.6.1. Analysis of formaldehyde standard solutions

1 mL of each of the standard solutions was transferred into a 12 mL glass vial. To each vial, 1 mL of chromotropic acid salt solution and 8 mL of a 75% (v/v) sulphuric acid were added. The vials were placed in a water bath at 60 ^{o}C for 20 minutes and were then left to cool to room temperature for 1 hour, (Stratton and Bradley, 2011).

Each of the samples was then transferred into a 10 mm cuvette cell. The absorbance was measured at 574 nm, using a double beam Varian Cary-50 UV-Visible spectrophotometer, (Chem.agilient.com). After data collection, a linear regression plot of the absorbance against the concentration of each standard solution was developed.

4.4.6.2. Determination of formaldehyde migrant, in retorted samples

Samples obtained from the retort procedure, (Section 4.4.3) were tested for their formaldehyde content, (as a migrant), according to the spectrophotometric procedure described in Section 4.4.6.2.

4.4.6.3. Formaldehyde concentration evaluations, after extraction

The concentration (µg/mL) of formaldehyde migrant that was detected from each extraction solution was determined using a straight line regression procedure in a manner that was described in Section 4.4.4.4. The concentrations were converted into migration values (µg/6dm^2), taking into consideration the exposed area (A) of coatings (dm^2) and the volume (V) of aqueous food simulant (mL). The relationship that was shown in Equation 4.4-1 was used for the calculations.

4.4.6.4. Determination of the % hydrolysis of cross-linker to formaldehyde

The % hydrolysis of cross-linker leading to the release of formaldehyde was calculated on the basis of Equation 4.4-9 and Equation 4.4-10. The experimental yield of formaldehyde was the value that was obtained through spectrophotometric evaluations and the use of straight line regression calculations. In Equation 4.4-9, the formaldehyde degradation value (FDV) was used in place of the stated MDV value that was used for the HMMM cross-linker in Equation 4.4-5. The general case is shown in Equation 4.4-10.

$$\mathbf{FDV} = \frac{\mathbf{6(30)\ g/mol}}{\mathbf{390\ g/mol}}$$

Equation 4.4-9: Formaldehyde degradation equation

$$\text{FDV} = \frac{\text{Molecular mass of formaldehyde}}{\text{Molecular mass of cross} - \text{linker}}$$

Equation 4.4-10: Generalised formaldehyde degradation equation

In the FDV estimation, an assumption was made that, in theory, for each mole of HMMM that becomes completely hydrolysed, 6 moles of formaldehyde are released.

4.4.6.5. Determination of the formaldehyde release during the curing of coatings

Experiments were carried out with the aim of investigating the amount of formaldehyde that would be released during the curing of epoxy coating formulations and poly(ester) coating formulations. Two separate procedures were followed.

In the first procedure, a distillation set up was developed. 10 g each of poly(ester)-urea coating and each of poly(ester)-acrylic coating were placed into separate 50 mL round bottom flasks. The flasks fitted with condensers were heated in an oil bath at 195 ^{o}C, for 90 minutes. The heating was then stopped and portions of the distillates were taken for analysis of their melamine, benzoguanamine and formaldehyde content.

In the second procedure, a Shimadzu GC-MS (QP2010) unit, equipped with an AOC-500 auto-injector was used, (Shimadzu.com). 0.1 g each of poly(ester)-urea coating and of each poly(ester)-acrylic coating were placed into separate 20 mL GC-type-vials. The vials were sealed using a crimper and were then incubated in the GC-oven for 12 minutes, at 195 ^{o}C. After the set exposure time, aliquots of the headspace gas were injected into the GC instrument for analysis. The conditions used for the analysis are given below:

Column: *BTX-5, 0.25 µm, (30 m x 0.25 mm)* (Sge.com)

Column temperature: *200 ^{o}C*

Injection volume: *1 µL*

Detection: *Mass spectrometry*

Flow rate: *0.5 mL of argon per minute*

Run time: *25 min*

4.4.7. Stability of the migrants when in the extraction solutions

In separate experiments, the stability of melamine, of benzoguanamine and of formaldehyde respectively, contained in the retorted 10% (v/v) aqueous ethanol food simulants was investigated.

After the retorting of various, selected coatings, according to the procedure described in Section 4.4.3, the simulants were isolated from the metal plates, sealed and stored under laboratory conditions. After 1, 7, 14 and 30 days of storage, portions were taken from each of the solutions and the amount of melamine, of benzoguanamine and of formaldehyde in each was determined.

4.4.8. Stability of melamine-precursor compounds when in the retorted solution

This study was designed to establish whether or not, through further retorting of the extracted solutions, the melamine-precursor compounds that were contained in the retorted solutions could yield more melamine through hydrolytic routes.

Selected coating panels were used to represent the various epoxy coatings and poly(ester) coatings. After the coatings were retorted in 10% (v/v) aqueous ethanol solutions and after the metal panels were removed, according the procedure described in Section 4.4.3, 10 mL of each solution were sealed in a vial, using a crimper. The vials were then retorted in the pressure cooker for 1 hour, at 131 ^{o}C. The vials were removed from the pressure cooker after the heating was complete and were allowed to cool to room temperature. Aliquots of the solutions were then taken for analysis of their melamine content using HPLC. The amounts of melamine in these solutions were compared to those that were obtained using the first retort procedures (Section 4.4.3).

4.4.9. Study of the further release of migrants following additional retorting of the isolated panels

This aspect of analysis was designed to establish whether or not further melamine would be released, through hydrolysis, as a result of further retorting of isolated retorted panels, in fresh aqueous food simulants.

Selected coating panels were used to represent the various epoxy coatings and poly(ester) coatings. After the coatings were retorted in 10% (v/v) aqueous ethanol solutions, according the procedure described in Section 4.4.8, the metal panels were removed from the vials and then thoroughly rinsed with a 10% (v/v) aqueous ethanol solution. The coating panels were then each placed into a separate 20 mL crimp vial containing 10 mL of 10% (v/v) ethanol food simulant. The vials were then sealed and retorted in a pressure cooker for 1 hour, at 131 ^{o}C. The vials were removed from the cooker after the required exposure time and were allowed to cool to room temperature. Aliquots of the solutions were then taken for the analysis of their melamine contents, their benzoguanamine contents and formaldehyde contents, as appropriate, respectively. The amounts of these migrants, as detected, were evaluated and the data were shown to be consistent with further migrant release via hydrolysis.

4.5. Discussion of results

4.5.1. Rheological characteristics of coatings

Figure 4.5-1 to Figure 4.5-4 present the flow properties of hexamethoxymethyl melamine (HMMM) containing representative epoxy anhydride coating formulations. On visual assessment of the epoxy coatings, differences were apparent in the viscosity of the formulations as a function of their solids content and whether or not a pigment was used in formulation.

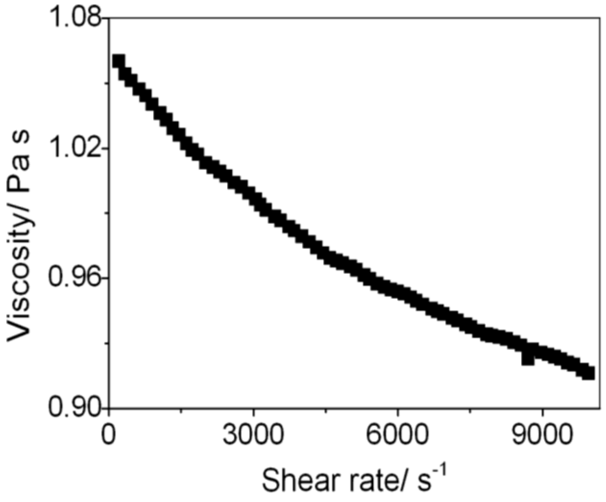


Figure 4.5-1: Viscosity profile of hexamethoxymethyl melamine (HMMM) containing, unpigmented epoxy anhydride coating formulation

The viscosity profile shown in Figure 4.5-1 can conveniently represent all of the unpigmented epoxy anhydride coatings that were formulated, each containing a different cross-linker, Section 3.3.3. This is because the coatings only vary in the type of cross-linker that was used in formulation. In each case, the cross-linker was only 0.5% of total formulation. Section 2.8.4 shows that the each cross-linker in isolation exhibits Newtonian flow behaviour. Since the coating in Figure 4.5-1 exhibits shear thinning behaviour, then, the contribution of the cross-linker to the overall coating's rheology is minimal.

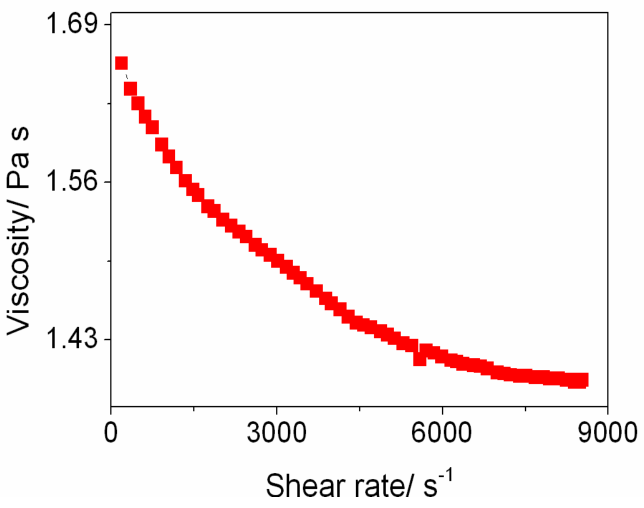


Figure 4.5-2: Viscosity profile of hexamethoxymethyl melamine (HMMM) containing, PW2-pigmented epoxy anhydride coating formulation

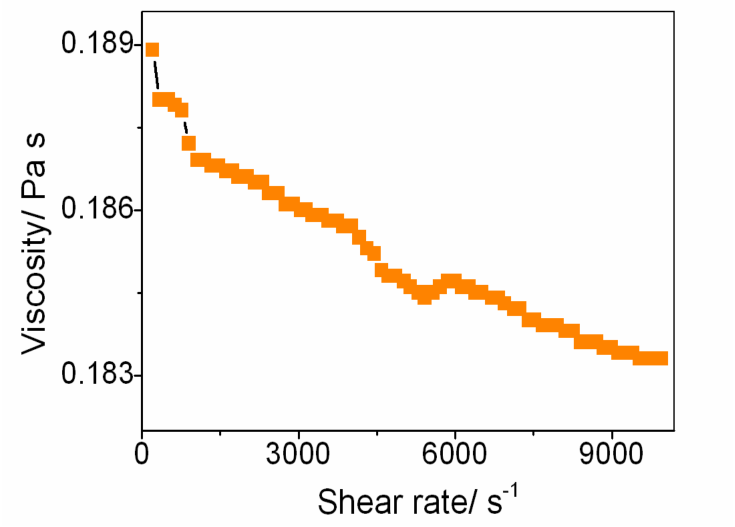


Figure 4.5-3: Viscosity profile of hexamethoxymethyl melamine (HMMM) containing, epoxy phenolic coating formulation

Figure 4.5-2 and Figure 4.5-3 demonstrate that shear thinning flow behaviour is exhibited by both the PW2-pigmented epoxy anhydride coating and the epoxy phenolic coating. Over the shear rate range that was used, the viscosities decrease with an increase in the shear rate. Again the overall contributions of the cross-linkers to the rheology of the coatings were minimal. With respect to viscosity values, at any given shear rate value, [PW2-pigmented epoxy anhydride coatings] >> [Un-pigmented epoxy anhydride coatings] >> [epoxy anhydride coatings]. All three coatings have demonstrated a decrease in viscosity as the shear rate was increased. This particular shear thinning behaviour is important and desirable during the application of the coatings onto the metal substrates.

Figure 4.5-4 and Figure 4.5-5 present the flow properties of hexamethoxymethyl melamine (HMMM)-containing representative poly(ester) coating formulations. On visual assessment of the coatings, differences were apparent in the viscosity of the formulations as a function of their solids contents and volatile organic contents.

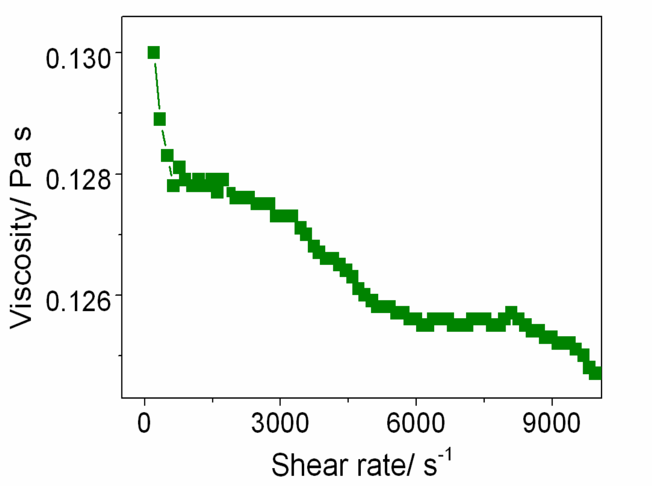


Figure 4.5-4: Viscosity profile of hexamethoxymethyl melamine (HMMM) containing coatings, poly(ester)-urea coating formulation

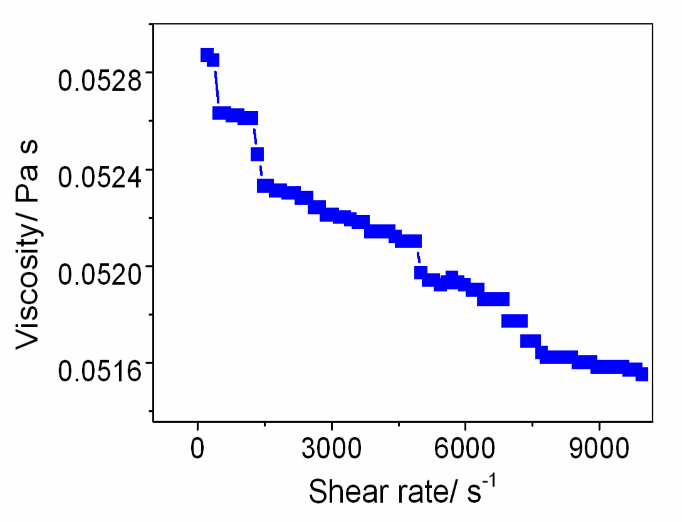


Figure 4.5-5: Viscosity profile (viscosity versus shear rate) of hexamethoxymethyl melamine (HMMM) containing coatings, poly(ester)-acrylic coating formulation

Figure 4.5-4 and Figure 4.5-5 show the flow characteristics of the two representative poly(ester) coatings. Both coatings exhibit shear thinning flow behaviour, where, over the shear rate range that was used, the viscosities decrease with an increase in the shear rate. In this case also, the overall contributions of the cross-linkers to the rheology of the coatings were minimal, the cross-linkers alone exhibiting Newtonian flow behaviour, Section 2.8.4. Therefore, the rheology of the coatings, in each case, was dominated by the poly(ester) polymeric binders that were used in large amounts during formulation

(Table 3.2-2). With respect to viscosity values, at any given shear rate value, [poly(ester)urea coatings] >> [poly(ester)-acrylic coatings] >> [epoxy anhydride coatings]. This significant difference in viscosity arises because of the significant difference between the solids content of the two poly(ester)-based coatings. The poly(ester)-urea coating contains 44% solids while the poly(ester)-acrylic coating contains 32% solids. Both coatings have demonstrated a decrease in viscosity as the shear rate was increased. This particular shear thinning behaviour was important and desirable during the application of the coatings onto the metal substrates.

4.5.2. Thermal behaviour of coatings

Each component in a coating formulation can play a role in affecting the thermal performance and decomposition behaviour of the coatings through the contribution made on the basis of the solids contents of the coatings. In this regard, TGA was carried out to monitor the thermal behaviour of the epoxy coatings and of the poly(ester) coatings. The TGA results arising from the thermal analytical studies of the hexamethoxymethyl melamine (HMMM)-containing, epoxy-based coating formulations are presented in Figure 4.5-6. The TGA analyses were carried out using a 10 ^{o}C/min heating rate.

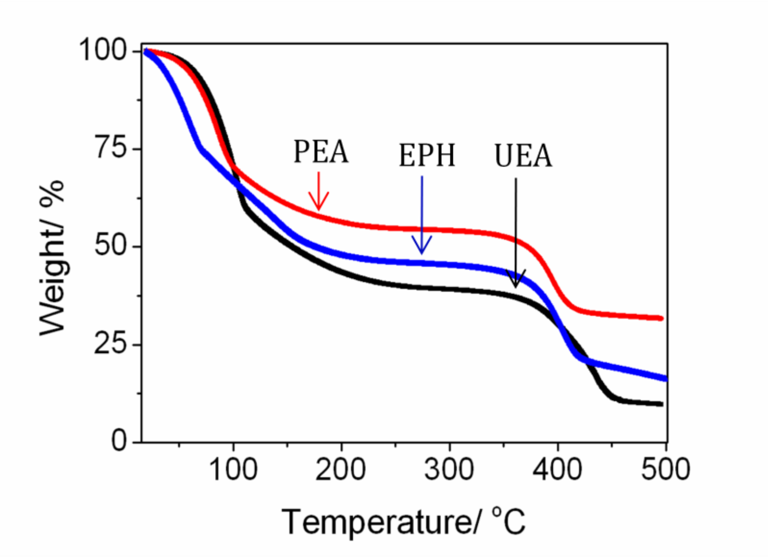


Figure 4.5-6: TGA profile of hexamethoxymethyl melamine (HMMM)-containing coatings, UEA: unpigmented epoxy anhydride coating, PEA: pigmented epoxy anhydride coating and EPH: epoxy phenolic coating

The TGA results, shown in Figure 4.5-6 indicate that there is a considerable difference in the decomposition behaviour and in the solid contents amongst the three epoxy-based coating formulations. The thermograms show a consistent but different weight loss in each case. These weight loss differences can be correlated to the loss of solvent and to the occurrence of different types of decomposition as the heating continues, to around 420 °C. In each case, the TGA profile can be divided into three stages. Stage 1 involves loss of solvent components through a drying process as the temperature was increased from 25 °C to about 120 °C. The first phase of stage 1 involves removal of "free" solvent from 25 °C to about 90 °C while the second phase of stage 1 involves removal of "bound" solvent from 90 °C to about 120 °C. In the figure, the behaviour of both the pigmented epoxy anhydride coating and the unpigmented epoxy anhydride was similar, being different from the behaviour of the epoxy phenolic coating. This difference arises because of the different solvent composition of the coatings, as indicated in Section 3.3.

Stage 2 of the TGA curves, as shown in Figure 4.5-6, in each case, represents film development, curing and network formation. This follows stage 1 and occurs from about 120 °C to about 370 °C. This also depends on the chemistry of each formulation and the non-volatile matters that each formulation contains. Stage 3 constitutes the decomposition phase and occurs from about 370 °C to 500 °C. The level of residue that remains after 500 °C depends on the non-volatile matter content of each coating. The pigmented epoxy anhydride coating gives the highest residue because of the PW2 TiO_2 pigments particles that were incorporated in the formulation.

Table 4.5-1: Values of solids content of HMMM cross-linked coatings

Coating type	Solids content (at 200 °C)
Unpigmented epoxy anhydride	41 % ±1
PW2-pigmented epoxy anhydride	56 % ±1
Epoxy phenolic	45 % ±1
Poly(ester) urea	44 % ±2
Poly(ester) acrylic	32 % ±1

The results obtained from the solids content analyses carried out of different coatings are shown in Table 4.5-1. The variation in the values of solids contents amongst the various coatings arises because of the differences in levels of non-volatile matter that was used in the formulation of each coating, Section 3.3. The results shown in Table 4.5-1 according to procedures in Section 4.2.2 were found to be consistent with the TGA based solids estimations which can be obtained from Figure 4.5-6 and Figure 4.5-7.

The TGA-based thermal decomposition behaviour of the hexamethoxymethyl melamine (HMMM) containing, poly(ester) coating formulations are presented in Figure 4.5-7. The TGA analysis was carried out using a 10 ^{o}C/min heating rate.

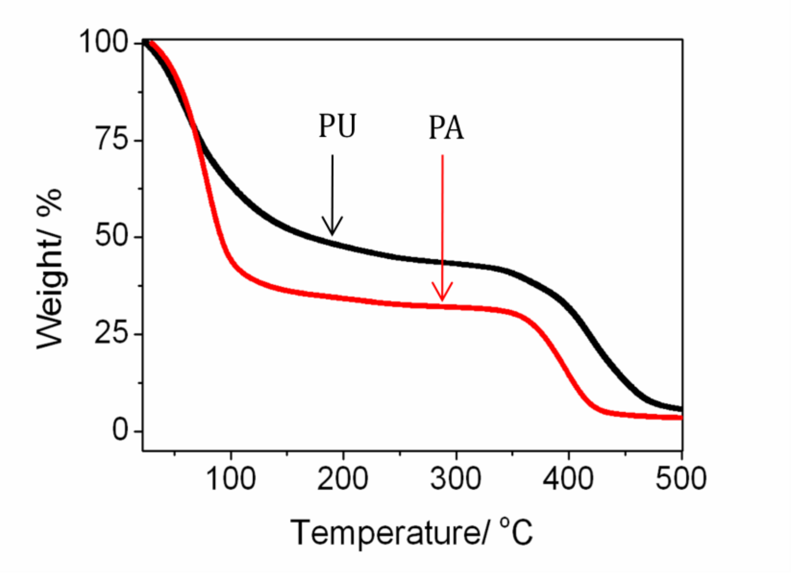


Figure 4.5-7: TGA profile of hexamethoxymethyl melamine (HMMM) containing coatings, PU: poly(ester)-urea coating and PA: poly(ester)-acrylic coating

In Figure 4.5-7, the thermograms can also be divided into three stages. Stage 1 involving loss of solvent components, stage 2 involving film development, curing and network formation and stage 3 involving the decomposition of the coatings. Stage 1 involves, in steps, the removal of both “free” solvent and bound solvent from 25 ^{o}C to about 110 ^{o}C for the poly(ester)-acrylic coating and up to about 140 ^{o}C for the poly(ester)-urea coating. This difference arises because of differences in the boiling points and evaporation rates of solvents that were used in the formulation of the coatings, Section 3.3. Stage 2 of the TGA decomposition as shown in Figure 4.5-7, represents film development, curing and network formation. This follows stage 1 and occurs from about 110 ^{o}C to about 370 ^{o}C. Depending on the chemistry of each formulation and the non-volatile material that each formulation contains, the weight loss and the solids achieved at each phase of stage 2 differs. Stage 3 constitutes the decomposition phase and occurs from about 370 ^{o}C to 500 ^{o}C. The level of residue that remains after 500 ^{o}C was comparable because both formulations are dominated by essentially similar poly(ester) polymeric binders.

4.6. Conclusions

Accurate, effective analytical procedures were developed and authenticated for the analysis of the liquid coatings and the cured coatings and for the study of the migration behaviour of melamine, of benzoguanamine and of formaldehyde from coatings into food simulants, during retorting procedures.

All of the liquid coatings that were characterised rheologically showed shear thinning behaviour which was dominated by the polymeric binders that were used in formulation. The viscosity of each coating decreased when the shear rate was increased. This behaviour is important and desirable in the application of the coatings onto the metal substrates.

The TGA data from the liquid coatings provided useful information concerning the solvent evaporation process and the solids contents of each coating. The values are important in the consideration of the levels of organic and inorganic matter that are contained in the coatings, after heating/curing at specific temperatures.

Chapter 5: Epoxy coatings— study of the migration of melamine, the migration of benzoguanamine and the migration of formaldehyde

5.1. Introduction

The aims of this section of the total study were to investigate and to gain an understanding into the release/migration of amino related substances from the amino cross-linked, epoxy-based coatings that are widely used in can making applications. Thus, the amino cross-linker amount, cross-linker chemistry and the effects of curing time and of curing temperature on melamine release, benzoguanamine release and formaldehyde release from selected epoxy-based coatings were evaluated.

This chapter concerns the results obtained from studies of food contact epoxy coatings. The options chosen were: (1) unpigmented epoxy anhydride coatings, (2) TiO_2-pigmented epoxy anhydride coatings and (3) epoxy phenolic coatings.

Various experiments were carried out using selected representative cross-linkers to investigate the tendency of the cured coatings to release melamine, benzoguanamine and formaldehyde, as appropriate, after the coatings were retorted in food simulants, at elevated temperatures. Retorting of the coatings at 131 ^{o}C, for 1 hour, in selected food simulants, was used to represent the food sterilisation process. The potential for the epoxy coatings to release low molecular weight compounds was also investigated through room temperature studies.

In the studies of pigmented epoxy anhydride coatings, changes that took place over two weeks, three months and six months storage periods, respectively were monitored to establish the potential for coatings to age, with respect to melamine release and migration. This is important because, in the can coatings industry, it may be up to two weeks after formulation before the coatings are delivered to a user. It may take up to three months, in some instances, before the coatings are used in the can making processes, (Valspar France, 2010).

The results obtained from all the migration studies are expressed in µg/6dm^2, (where 1ppb = 1µg/6dm^2), as this is a standard way of expressing the migration of low molecular weight compounds into foods or into food simulants. To obtain a trend by which the performance of the various cross-linking compounds could be compared, the results were then converted into values of % hydrolysis of cross-linker to melamine or to the other analytes. This was achieved by taking into account the molecular weight of each cross-linker, the thickness of each coating and the area of the coating that was used, in each case.

Unless specified, any mention of HMMM refers to HMMM-2. Any mention of HBMM refers to HBMM-3. Any mention of TMTBM refers to MMTC-1. Details regarding the cross-linkers are provided in Table 2.2-3 and in Section 2.8.2 to Section 2.8.6.

5.2. The effect of food simulant composition on melamine release from cured, retorted epoxy coatings

Food simulants are considered to be appropriate, simplified models of foodstuff that can be used to mimic foods for migration testing. European Commission Directive 82/11/EEC allows the use of 3% (v/v) aqueous acetic acid and 10% (v/v) aqueous ethanol solutions in such migration studies, (European Commission, 1982). Information relating to the type of food that each simulant mimics is given is Section 1.10.

The food simulants 3% (v/v) aqueous acetic acid and 10% (v/v) aqueous ethanol were used in controlled studies, under the same conditions to monitor the release of melamine and the hydrolysis of cross-linkers in pigmented epoxy anhydride coatings and unpigmented epoxy anhydride coatings. The results that were obtained are shown in Table 5.2-1 and Table 5.2-2.

In cross-linker identification, HMMM denotes hexamethoxymethyl melamine. MMTC denotes methylol melamine-type cross-linker. HBMM denotes hexabutoxymethyl melamine and DBMB denotes dibutoxymethyl benzoguanamine.

The results from the study of the effect of the food simulant composition on the release of melamine and on cross-linker hydrolysis, from unpigmented epoxy anhydride coatings, are shown in Table 5.2-1. These results provide a basis to the understanding of the migration behaviour of the specific coating in the two different food simulants, a point that is of relevance when the coatings come into contact with different food compositions.

Table 5.2-1: Amount of melamine released and extent of cross-linker hydrolysis, from unpigmented epoxy anhydride coatings, cross-linked with different amino cross-linkers, cured for 10 minutes at 200 ^{o}C and retorted in food simulants at 131 ^{o}C, for 1 hour

Melamine release in µg/6dm^2 and Cross-linker hydrolysis				
Cross-linker	Using 3% aqueous acetic acid		Using 10% aqueous ethanol	
HMMM-1	754 ±2	99 % ±2	564 ±8	74 % ±2
HMMM-2	650 ±4	85 % ±2	525 ±11	69 % ±3
HMMM-3	692 ±2	91% ±2	567 ±6	75 % ±1
HBMM-1	390 ±3	82% ±2	321 ±7	71 % ±2
HBMM-2	590 ±1	98% ±2	562 ±2	97 % ±3
HBMM-3	403 ±1	86% ±3	374 ±3	82 % ±2
MMTC-1 (TMTBM)	432 ±3	68% ±3	497 ±3	79 % ±1
MMTC-2	270 ±2	47% ±2	294 ±4	53 % ±1
MMTC-3	300 ±5	54% ±1	224 ±5	40 % ±2
MMTC-4	330 ±2	30% ±1	371 ±6	34 % ±2
DBMB	91 ±2	9% ±1	78 ±2	7% ±1

Table 5.2-1 and Table 5.2-2 respectively show that the release of melamine from both the unpigmented epoxy anhydride coatings and the PW2-pigmented coatings occurred when either of the food simulants was used. There was more release of melamine when the 3% (v/v) aqueous acetic acid food simulant was used, but the difference was not large and it was not the case for every coating. The higher is likely because of the greater acidity of the acetic acid solution. Both food simulants can be considered to be hydrolytic solvents, (Brown, 2013).

The 3% (v/v) aqueous acetic acid, pH 3.5, showed more surface interaction with the coatings than did the 10% (v/v) aqueous ethanol, pH 6.5, when contact angle studies were carried out, perhaps also contributing to greater hydrolysis of the cross-linkers in the coatings, thus, releasing more melamine. In literature reports, where migration studies were carried out for other purposes, it was shown that there was greater release into the 3% (v/v) aqueous acetic acid in comparison to the 10% (v/v) aqueous ethanol, (Sidwell and Forrest, 2000).

The results for the effect of the food simulant composition on the release of melamine and cross-linker hydrolysis from PW2-pigmented epoxy anhydride coatings are presented in Table 5.2-2.

The results shown in Table 5.2-1 compare with those shown in Table 5.2-2. Both sets of results show that generally, the 3% (v/v) aqueous acetic acid, leads to greater hydrolysis of the cross-linkers in the coatings, thus, releasing more melamine than when the 10% (v/v) aqueous ethanol food simulant was used. Again, the 3% (v/v) aqueous acetic acid gave lower values of contact angle on the surface of the coatings than those values obtained using 10% (v/v) aqueous ethanol. Thus, the greater the interaction of the food simulant with the surfaces prior to and during the retorting of the coatings, the greater was the melamine release from the coatings. Another factor to be borne in mind is that the two simulants differ with regards to solution/solubility properties and chemical reactivity.

Table 5.2-2: Amount of melamine released and extent of cross-linker hydrolysis, from PW2-pigmented epoxy anhydride coatings, cross-linked with different amino cross-linkers, cured for 10 minutes at 200 °C and retorted in food simulants at 131 °C, for 1 hour

Melamine release in µg/6dm^2 and Cross-linker hydrolysis				
Cross-linker	Using 3% aqueous acetic acid		Using 10% aqueous ethanol	
HMMM-1	573 ±4	56% ±2	404 ±2	35 % ±2
HMMM-2	425 ±1	37% ±1	391 ±2	34 % ±1
HMMM-3	585 ±3	50% ±4	418 ±4	36 % ±2
HBMM-1	240 ±2	34% ±1	217 ±5	31 % ±2
HBMM-2	295 ±2	41% ±3	423 ±3	59 % ±3
HBMM-3	260 ±3	37% ±2	250 ±4	36 % ±2
MMTC-1 (TMTBM)	285 ±3	30% ±3	226 ±3	23 % ±1
MMTC-2	145 ±4	24% ±3	242 ±2	28 % ±3
MMTC-3	300 ±5	35% ±3	317 ±1	37 % ±3
MMTC-4	250 ±6	17% ±3	193 ±3	15 % ±2
DBMB	85 ±2	8% ±1	71 ±2	6 % ±2

The overall results show that all of the coatings are susceptible to the release of melamine through cross-linker hydrolysis. In each case, melamine release and subsequent migration was well below the current 2.5 mg/6dm^2, limit set by European regulatory agencies, (European Union, 2011b). The 10% (v/v) aqueous ethanol simulant was used more often in subsequent work reported here, because its gives greater instrument compatibility, caused less corrosion of the metal substrate, and since the results can generally be related to those obtained using a 3% (v/v) aqueous acetic acid as a food simulant.

The results given in Table 5.2-1 and Table 5.2-2 show the effect of the chemical behaviour of the cross-linkers on melamine release and on cross-linker hydrolysis in the epoxy coatings. Such effects were studied in further detail and the results are presented in Section 5.4.

A comparison of the results given in Table 5.2-1 with those in Table 5.2-2 shows that there was an effect of the presence of the TiO_2 particles on melamine release and on cross-linker hydrolysis. Such effects were studied in further detail and the results are presented in Section 5.14 to Section 5.16.

5.3. Release behaviour of epoxy coatings to yield melamine, benzoguanamine and formaldehyde into various solvents, at room temperature

The results that were obtained with regards to the release, following the non-thermal immersion/exposure of cured coated panels in various extraction “solvents” are shown in Table 5.3-1.

For this aspect of the study, HMMM cross-linked pigmented and unpigmented epoxy anhydride coatings were used, according to the procedure given in Section 4.4.1. The “solvents” chosen to cover a range of total solubility parameter (TSP) values, consisted of polar and non-polar solvents, with aqueous and non-aqueous representatives. TSP represents a contribution from polar forces, dispersion forces, Van der Waals forces and H-bonding, as a property of the solvent. The solubility parameter equation is shown in Equation 5.3-1, (Barton, 1991).

$$\partial_T = \partial_d + \partial_p + \partial_h$$

Equation 5.3-1: Hansen solubility parameter equation

In Equation 5.3-1, ∂_T denotes the total solubility parameter, ∂_d denotes contribution of the dispersion component, ∂_p denotes contribution of the polar component and ∂_h denotes contribution of the hydrogen bonding component.

Table 5.3-1: Release from cured panels coated with pigmented epoxy anhydride coatings, treated with different solvents at room temperature, for 24 hours

"Solvent"	TSP of "solvent"	Melamine release	Benzoguanamine release	Formaldehyde release
D.I Water	47.9	<LOD	<LOD	<LOD
Acetonitrile	24.6	<LOD	<LOD	<LOD
Dichloromethane	19.8	<LOD	<LOD	<LOD
Chloroform	19.0	<LOD	<LOD	<LOD
Toluene	18.2	<LOD	<LOD	<LOD
Xylene	18.0	<LOD	<LOD	<LOD
3% Acetic acid	–	<LOD	<LOD	<LOD
10% Ethanol	–	<LOD	<LOD	<LOD

TSP: total solubility parameter, $(MPa)^{1/2}$ and LOD: limit of detection

The results in Table 5.3-1 show that, at room temperature (25 ^{o}C), either the migrants melamine, benzoguanamine and formaldehyde were not released after 24 hour immersion in the various solvents or that any release during the procedure was below the limit of detection (LOD) for each of the migrants. Using the procedures described in Section 4.4.1, the migrant compounds were not extracted from the surface of the coatings when the surface rubbing-based extraction studies were carried out. The LOD values were 17 µg/6dm^2 for melamine, 15 µg/6dm^2 for benzoguanamine and 1 µg/6dm^2 for formaldehyde.

Contrary to the room temperature treatments and the surface rubbing procedures, retorting the coatings, at a temperature of 131 ^{o}C in an aqueous acetic acid simulant or in an aqueous ethanol simulant, (Sections 5.4 to 5.9) resulted in melamine release. Therefore, the extent of melamine generation from epoxy-based coatings, through hydrolysis, is strongly affected by the temperature. These points are further discussed in Section 5.4 through to Section 5.16.

5.4. The effect of cross-linker chemistry on melamine release from cured, retorted epoxy coatings

The results that relate to the contribution of cross-linker chemistry to the amount of melamine that the cured, retorted coatings released into 10% (v/v) aqueous ethanolic food simulant are shown in Table 5.4-1 and Table 5.4-2. All of the coatings were cured at 200 ^{o}C for 10 minutes and were then retorted in 10% (v/v) aqueous ethanol, at 131 ^{o}C, for 1 hour.

In Table 5.4-1, the amounts of melamine released from all coatings are expressed in µg/6dm^2. In Table 5.4-2, the results are expressed in term of the percentage of each cross-linker hydrolysed during the retorting of the coatings. Based on such results, the performance of the coatings and the cross-linkers that they contain, can be compared.

Table 5.4-1: Amount of melamine released from epoxy coatings, cross-linked with different amino cross-linkers and cured for 10 minutes, at 200 °C

	Melamine release/ (µg/6dm^2)		
Cross-linker	Unpigmented epoxy anhydride coating	Pigmented epoxy anhydride coating	Epoxy phenolic coating
HMMM-1	564 ±8	404 ±9	187 ±4
HMMM-2	525 ±11	391 ±5	151 ±5
HMMM-3	567 ±6	418 ±4	173 ±4
HBMM-1	321 ±7	217 ±11	110 ±6
HBMM-2	582 ±2	423 ±5	124 ±4
HBMM-3	374 ±3	250 ±6	98 ±8
MMTC-1 (TMTBM)	497 ±3	226 ±4	95 ±3
MMTC-2	294 ±4	242 ±3	83 ±3
MMTC-3	224 ±5	317 ±4	85 ±4
MMTC-4	371 ±6	193 ±4	78 ±6
DBMB	79 ±4	71 ±3	24 ±4

The results show that all of the coatings, each containing a different grade/chemistry of cross-linker are susceptible to the release of melamine through cross-linker hydrolysis. In each case, any melamine release and subsequent migration was within the current, approved limits set by European regulatory agencies, (European Union, 2011b).

Table 5.4-2: % hydrolysis of the cross-linker as a consequence of autoclaving epoxy coatings cross-linked with different amino cross-linkers and cured for 10 minutes, at 200 ^{o}C

	Hydrolysis of cross-linker to yield melamine)		
Cross-linker	Unpigmented epoxy anhydride coating	Pigmented epoxy anhydride coating	Epoxy phenolic coating
HMMM-1	74 % ±2	35 % ±2	64 % ±1
HMMM-2	69 % ±3	34 % ±2	52 % ±2
HMMM-3	75 % ±1	36 % ±2	60 % ±3
HBMM-1	71 % ±2	31 % ±1	62 % ±2
HBMM-2	97 % ±3	59 % ±3	70 % ±3
HBMM-3	82 % ±2	36 % ±1	55 % ±2
MMTC-1 (TMTBM)	79 % ±1	23 % ±2	40 % ±1
MMTC-2	53 % ±1	28 % ±1	39 % ±2
MMTC-3	40 % ±2	37 % ±2	40 % ±1
MMTC-4	34 % ±2	15 % ±2	20 % ±3
DBMB	10 ±1	6 % ±2	7 % ±2

The melamine release behaviour of the two alkylated cross-linkers (HMMM and HBMM) was similar, being different from that exhibited by the methylol-type of cross-linker. The former released more melamine under aqueous ethanolic retorting conditions than did the latter. There are reactivity differences between the alkylated cross-linkers and the methylol-type cross-linkers. The methylol-type cross-linkers would be expected to have greater cross-linking tendencies, during curing, as a result of the availability of the highly reactive $–CH_2OH$ functional groups. Ether functional groups (C–O–C) are less reactive than hydroxyl functional groups (–OH), (Jacobs, 1997). There is also a tendency, during the curing of the coatings, for the alkylated cross-linkers to lose their etherifying alcohol, allowing for them to cross-link with the bulk binder through $–CH_2OH$. Methylol-type cross-linkers can directly enter into cross-linking reactions since they do not need to lose any alcoholic group. This point is further discussed in Section 7.7.

The dibutoxymethyl benzoguanamine (DBMB)-cross-linked coatings released the least melamine. This is not surprising since this cross-linker contains the least amount of the active melamino component that could potentially be hydrolysed. The fact that the benzoguanamine cross-linked coating yielded melamine can be explained by appreciating the history of this cross-linker's manufacture process. As explained in Section 2.8.3, after production, the benzoguanamine product can contain up to 2% melamine, either as an impurity or as an additive. The melamine impurities have the potential to compete with the benzoguanamine, in reactions, during the preparation of the cross-linker. Thus, a benzoguanamino cross-linker, containing a melamino component would be produced.

5.5. Kinetic aspects of the release of melamine from cured, retorted epoxy coatings

The experimental results from the kinetic studies relating to melamine release are shown in Figure 5.5-1 to Figure 5.5-6. In each case, the amount of melamine released from the coatings into the food simulants and the % of cross-linker that was hydrolysed in the process are shown. The amounts released by the coatings into the food simulants are well below the 2.5 $mg/6dm^2$ approved current limit. The "% hydrolysis results" allow a comparison to be made between all of the different cross-linkers that were used in the coatings.

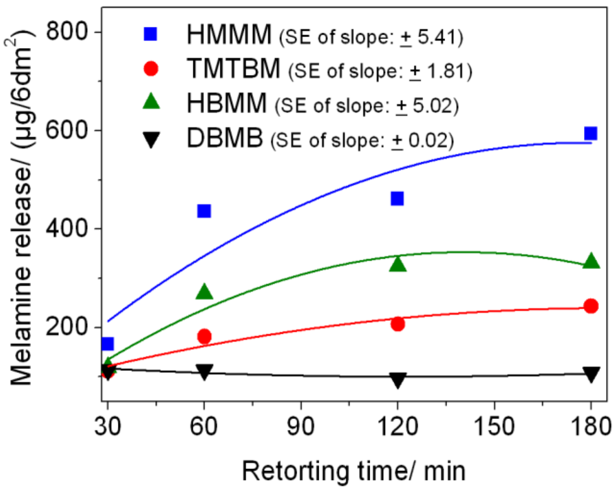


Figure 5.5-1: Unpigmented epoxy anhydride coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

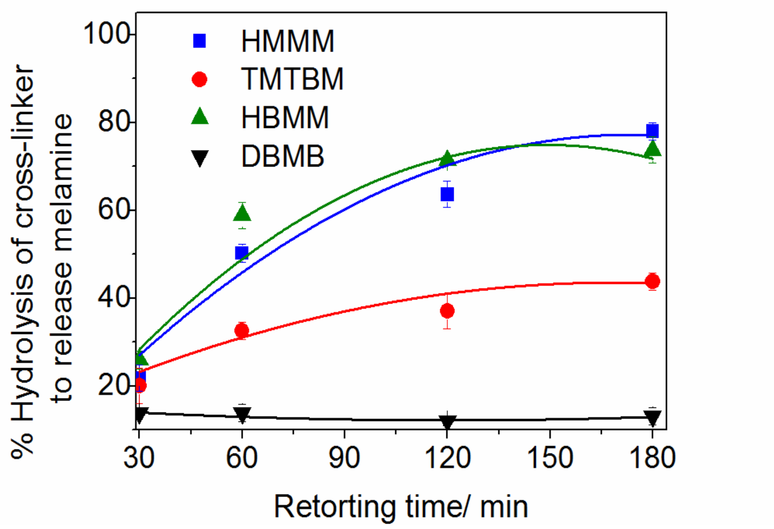


Figure 5.5-2: Unpigmented epoxy anhydride coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

According to Figure 5.5-1, under all of the conditions under which the coatings were retorted, melamine release into 10% (v/v) aqueous ethanol food stimulant was within current European regulations, (European Union, 2011b). Figure 5.5-1 was translated into Figure 5.5-2 in order to allow for comparison of cross-linker contribution to coating hydrolysis to be made. The hexamethoxymethyl melamine (HMMM) and the hexabutoxymethyl melamine (HBMM) gave a similar hydrolysis pattern that was different from that exhibited by the trimethylol tributoxymethyl melamine (TMTBM) cross-linker. Consideration of the TGA results shown in Section 2.8.6, shows that HMMMs and HBMMs have similar thermal decomposition patterns which are different from that of TMTBM and dibutoxymethyl benzoguanamine (DBMB). This is largely because the TMTBM and the DBMB cross-linkers possess methylol functional groups. Although the melamine release process is dominated by chemical events and by thermal events, the methylol functionality has the greater tendency to react during curing, leading to a greater cross-link density than can be achieved by HMMM or HBMM, (Jacobs, 1997). The TMTBM cross-linked coating was less susceptible to cross-linker hydrolysis during the retorting of the coatings.

The dibutoxymethyl benzoguanamine (DBMB) cross-linker gave the lowest value of hydrolysis to melamine compared with the other cross-linkers. This is because compositionally, the DBMB has a limited tendency to hydrolyse to melamine since the melamine produced arises from melamino impurities in the cross-linker. However, the bulk of the cross-linker composition is predominantly based on benzoguanamino components, (Inchem.org, 2001). The results suggest that during the retorting process, the contaminant melamine was released during the first 30 minutes.

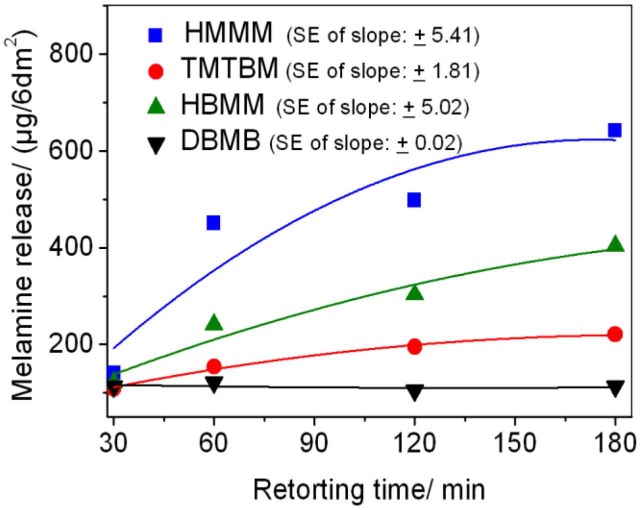


Figure 5.5-3: PW2-pigmented epoxy anhydride coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

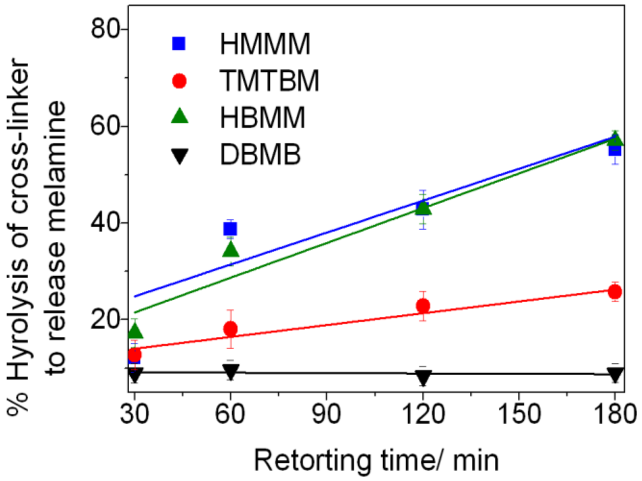


Figure 5.5-4: PW2-pigmented epoxy anhydride coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

Figure 5.5-3 shows that the order of release of melamine was [HMMM cross-linked coatings] > [HBMM cross-linked coatings] > [TMTBM cross-linked coatings] > [DBMB cross-linked coatings]. This sequence arises because of differences in reactivity and differences in available melamine per cross-linker unit. The amount of melamine that can potentially be released agrees with the release order described above. According to Figure 5.5-4, the HMMM and the HBMM cross-linked coatings gave a similar overall hydrolysis pattern because they have comparable chemical functionality, since both fall into the class of etherified amino cross-linkers. The TMTBM cross-linked coatings gave lesser hydrolysis of the cross-linker because during curing, a greater extent of cross-linking reaction was achieved compared to that which occurred when HMMM and HBMM cross-linkers are/were used, (Jacobs, 1997).

As shown in Figure 5.5-4, as a consequence of coating retorting, cross-linker hydrolysis increases linearly with an increase in retorting time, except for DBMB cross-linked coatings. The DBMB cross-linker has a limit to the amount of melamine that it can release. The melamine release arises from melamino impurities in this cross-linker. With regards to the DBMB cross-liked coatings, the results shown in Figure 5.5-4 are consistent with those in Figure 5.5-2 and Figure 5.5-6, suggesting that all of the available melamine impurity components must have been released during the early stages of retorting processes.

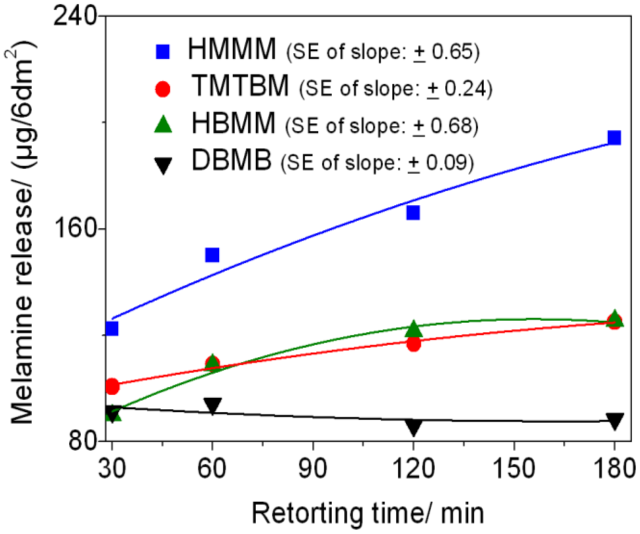


Figure 5.5-5: Epoxy phenolic coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

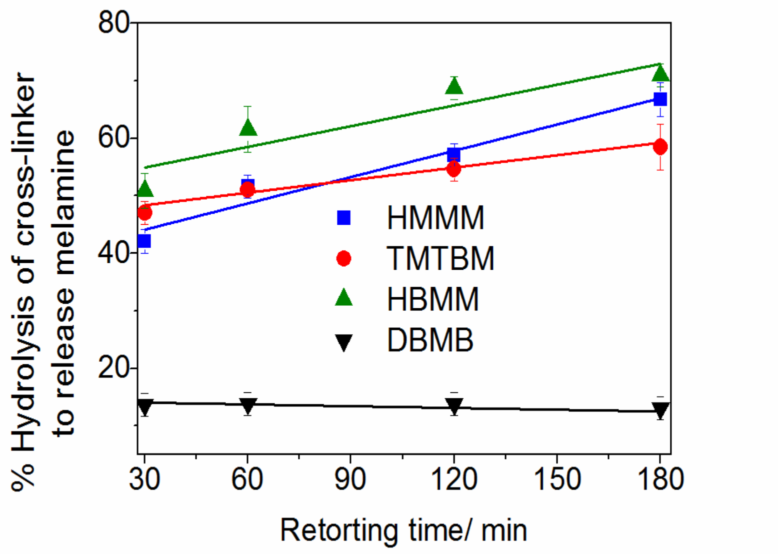


Figure 5.5-6: Epoxy phenolic coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

With the epoxy phenolic coatings, the melamine release into the 10% (v/v) aqueous ethanol food simulant increased with an increase in the retorting time. Again, the DBMB cross-linker contains a restricted amount of melamine that can be generated from the coating.

When the data shown in Figure 5.5-1 to Figure 5.5-6 are extrapolated to the zero retorting time, the results indicate that in each case, melamine was available for release even before retorting of the coatings commenced. This point agrees with the findings in Section 6.15 where it is shown that the generation of melamine commenced during the curing of the coatings. Any melamine that might have been released during the curing process must have been locked in the coating as a result of film formation. This available melamine then becomes extracted when the coatings are subjected to elevated temperature retorting, under aqueous conditions. It has already been shown that the room temperature treatment of the coatings in “solvents” does not lead to any release of melamine, (Section 5.2).

These results mean that there is potential for melamine release to occur from amino coatings into the food when the canned packaging undergoes autoclaving, sterilisation and pasteurisation during processing. The longer the period under which the high temperature treatments were applied, the greater was the tendency of the coatings to release melamine, until all of the melamine was released. The rate of release was proportional to the amount available for release. The permitted levels of such contaminants are likely to be reduced, in line with WHO advice. Thus, these data give a bench mark for the intended technologies.

5.6. Kinetic aspects of the release of benzoguanamine from cured, retorted coatings

The experimental results from the kinetic studies carried out to assess the release of benzoguanamine from dibutoxymethyl benzoguanamine (DBMB) cross-linked coatings are shown in Figure 5.6-1 and Figure 5.6-2. These results need to be considered in the context of the current 5 mg/6dm^2 or 5 ppm EU allowed specific migration limit (SML) of benzoguanamine in food contact materials, (European Union, 2011a).

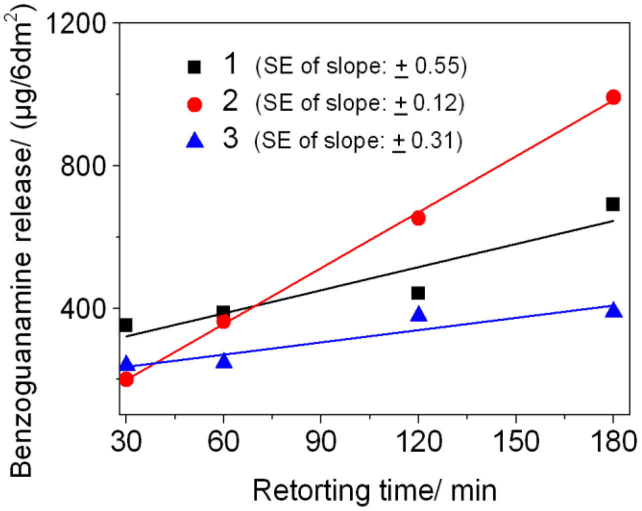


Figure 5.6-1: Dibutoxymethyl benzoguanamine (DBMB) cross-linked coatings, 1: unpigmented epoxy anhydride, 2: PW2-pigmented epoxy anhydride and 3: epoxy phenolic

The results in Figure 5.6-1 show that the amount of benzoguanamine that is released from the coatings during retorting increases with an increase in retorting time. In each case, under the conditions for which the coatings were studied, the amounts released were within the current approved legislations, (European Union, 2011a). When the results shown in Figure 5.6-1 are extrapolated to zero retorting time, the results indicate that in each case, benzoguanamine was already available for release even before retorting of the coatings commenced. This point agrees with the discussion provided in Section 5.5 where it is stated that there was a tendency of partial cross-linker breakdown to release either melamine and formaldehyde or benzoguanamine and formaldehyde as a result of thermal effects during the curing process. In Section 2.8.6, during discussion of the TGA-based behaviour of the trimethylol tributoxymethyl melamine (TMTBM) cross-linker, it was stated that the thermal process can lead to the formation of the cross-linker starting materials. The findings in Section 6.15 show that during the curing of the coatings, there is a considerable possibility that partial cross-linker breakdown would occur. Any migrant compound that was released during the curing process would be expected to be locked into the coating as a result of film/network formation. This migrant would then become extracted when the coatings are subjected to elevated temperature retorting, under aqueous conditions.

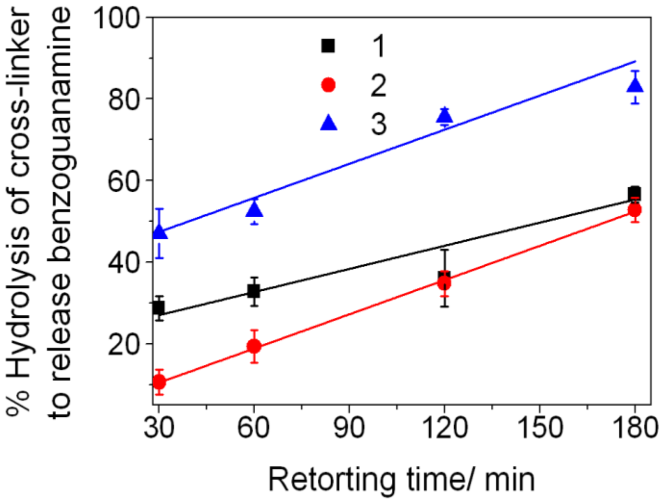


Figure 5.6-2: Dibutoxymethyl benzoguanamine (DBMB) cross-linked coatings, 1: unpigmented epoxy anhydride, 2: PW2-pigmented epoxy anhydride and 3: epoxy phenolic

Both Figure 5.6-1 and Figure 5.6-2 show that the hydrolysis of a dibutoxymethyl benzoguanamine (DBMB) cross-linked coating, as a result of retorting in the 10% (v/v) aqueous ethanol simulant, is dependent on the chemistry of the coatings. According to Figure 5.6-2, [Hydrolysis in the epoxy phenolic coating] > [Hydrolysis in the unpigmented epoxy anhydride coating] > [Hydrolysis in the PW2-pigmented epoxy anhydride coating]. When surface wetting studies were carried out, using the 10% (v/v) aqueous ethanol simulant, the DBMB cross-linked epoxy phenolic coating gave a lower contact angle of 67^o compared with the values obtained when the DBMB cross-linker was used in the unpigmented epoxy anhydride coating ($72\,^o$) or in the PW2-pigmented epoxy anhydride coating ($71\,^o$). This means that the 10% (v/v) aqueous ethanol simulant gave greater surface interaction with the epoxy phenolic coating, leading to greater hydrolysis of the cross-linker to form benzoguanamine, during retorting. The PW2-pigmented epoxy anhydride coating gave less cross-linker hydrolysis than its unpigmented counterpart because of the contribution of the TiO_2 pigment in promoting greater cross-linking in the coating, Section, 5.14. It is suspected that the hydrophilic pigment particles possess catalytic activity and that this can have an effect on the curing process.

The results overall show that there is a potential for benzoguanamine release to occur from the amino-based coatings into the food when the canned product undergoes autoclaving or sterilisation. The longer the period over which the high temperature treatments were applied, the greater was the tendency of the coatings to release benzoguanamine in the process. Thus, both the rate of the release and the rate of the hydrolysis are proportional to the amount of cross-linking agent that is available for release.

5.7. Kinetic aspects of the release of formaldehyde from cured, retorted coatings

The results for the release kinetics of formaldehyde, from the selected epoxy coatings into the 10% (v/v) aqueous ethanol food simulants, are shown in Figure 5.7-1 to Figure 5.7-6. All of the coatings were retorted at the standard temperature of 131 °C, following curing in the oven at 200 °C for 10 minutes. The results can be compared with the 15 mg/6dm^2 or 15 ppm EU allowed migration limit of formaldehyde from food contact materials, (European Commission, 2005b).

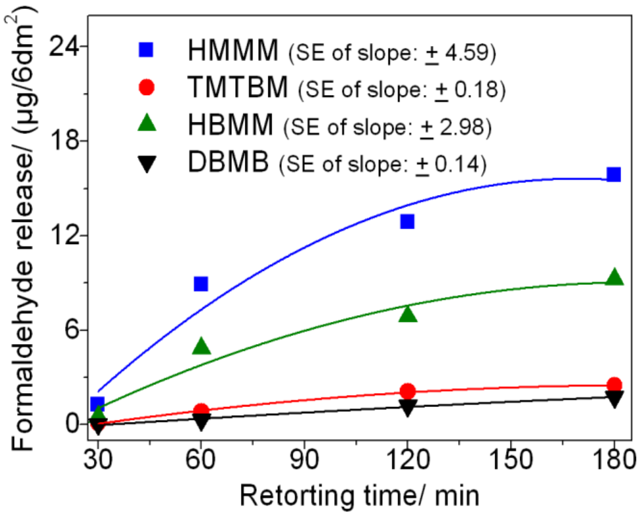


Figure 5.7-1: Unpigmented epoxy anhydride coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine. Retort tests were carried out at 131 °C

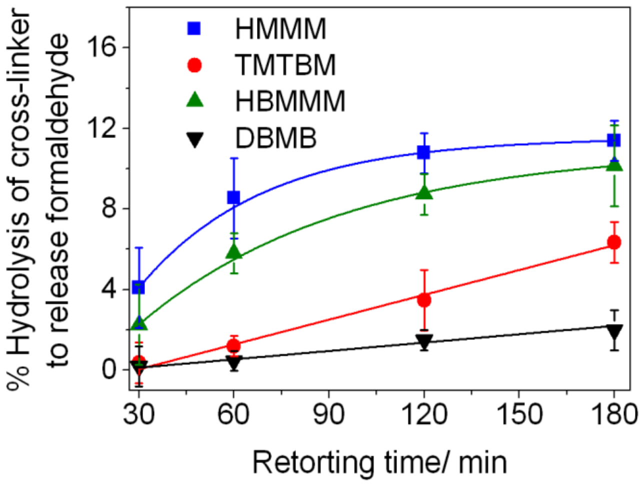


Figure 5.7-2: Unpigmented epoxy anhydride coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

Figure 5.7-1 and Figure 5.7-2 show clearly that retorting the various unpigmented epoxy anhydride coatings at 131 ^{o}C leads to the release of formaldehyde. The longer the period of time over which the coatings are retorted the greater is the amount of formaldehyde that is released through hydrolysis. Formaldehyde continues to be released with continued retorting of the coatings until the cross-linker is fully hydrolysed. The amounts of formaldehyde released from the unpigmented epoxy anhydride coatings are significantly below the current specific migration limit (SML) of 15 mg/6dm^{2} or 15 ppm, (Bradley et al., 2010, Danielles, 2008).

According to Figure 5.7-1, the order of release of formaldehyde was [HMMM cross-linked coatings] > [HBMM cross-linked coatings] > [TMTBM cross-linked coatings] = [DBMB cross-linked coatings]. The amount of formaldehyde that can potentially be hydrolysed per cross-linker molecule agrees with the release order described above. In Figure 5.7-2, the HMMM and the HBMM cross-linked coatings gave a similar overall hydrolysis pattern because they have comparable chemical functionality. Both are considered to fall into the class of etherified amino cross-linkers. The difference in the extent of hydrolysis between the two coatings depends largely on the hydrolysis pathway. The TMTBM and the DBMB cross-linked coatings gave lesser hydrolysis of cross-linker because during curing, a greater extent of cross-linking reaction was achieved compared to when HMMM and HBMM cross-linkers were used. This is because both the TMTBM and the DBMB contain methylol groups in comparison to the HMMM and HBMM both of which contain a less reactive ether functionality, (Jacobs, 1997).

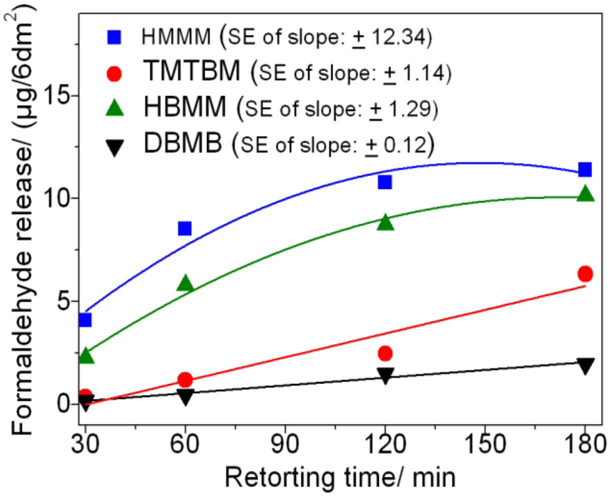


Figure 5.7-3: PW2-pigmented epoxy anhydride coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

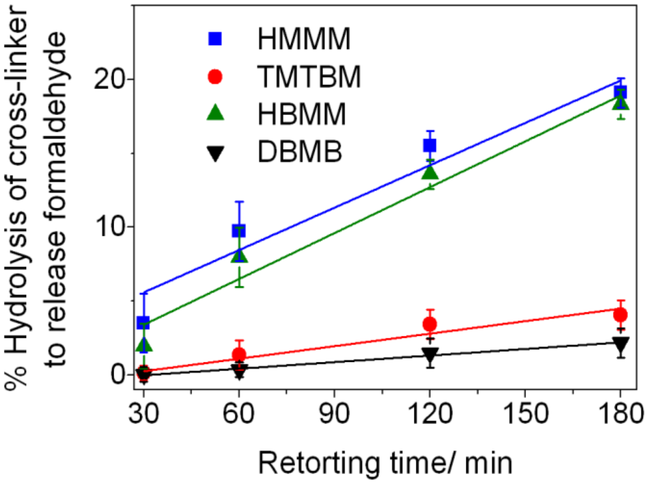


Figure 5.7-4: PW2-pigmented epoxy anhydride coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

The formaldehyde release behaviour of the PW2-pigmented epoxy coatings, shown in Figure 5.7-3, was similar to that exhibited by their unpigmented counterparts, shown in Figure 5.7-1. When both figures are compared, one can conclude that the release of formaldehyde from the coatings through hydrolysis was dominated by the presence of the epoxy binder system and that the behaviour of each cross-linker was the similar whether the TiO_2 pigment was used or not. As the coatings are retorted, the concentration of cross-linker decreases whereas the amount of formaldehyde released into the 10% (v/v) aqueous ethanol food simulant increases.

For the PW2-pigmented epoxy anhydride coatings, the order of release of formaldehyde was [HMMM cross-linked coatings] = [HBMM cross-linked coatings] > [TMTBM cross-linked coatings] = [DBMB cross-linked coatings]. As explained elsewhere, this pattern agrees with the reactivity and functionality of the cross-linkers. HMMM and the HBMM contain etherified functional groups and are therefore thought to be less reactive during curing than are the more reactive TMTBM and DBMB, both of which contain methylol functional groups.

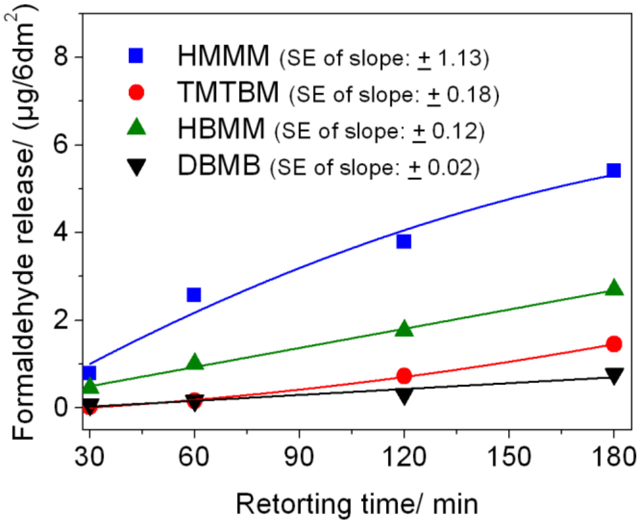


Figure 5.7-5: Epoxy phenolic coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

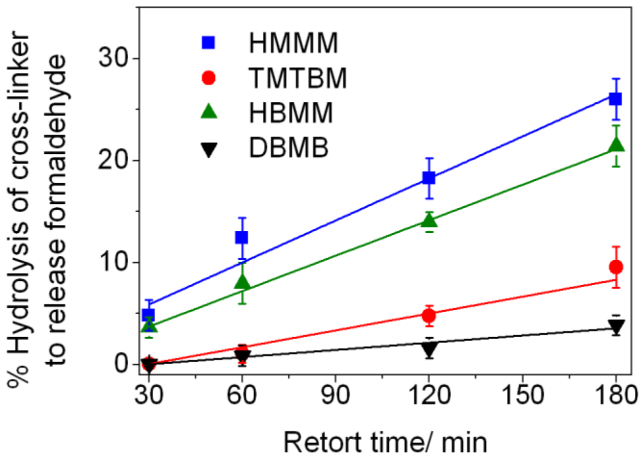


Figure 5.7-6: Epoxy phenolic coatings, each containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

The formaldehyde release behaviour of the epoxy phenolic coatings was not different from that exhited by both the PW2-pigmented and the unpigmented epoxy anhydride coatings. Figure 5.7-5 and Figure 5.7-6 show clearly that retorting the coatings at 131 ^{o}C leads to the release of formaldehyde. The longer the coatings are retorted, the greater is the amount of formaldehyde released through hydrolysis.

As the epoxy phenolic coatings were retorted, the amount of cross-linker decreased where as the concentration of formaldehyde released into the 10% (v/v) aqueous ethanol food simulant increased. Again, the extent of the release depends on the composition, reactivity and functionality of the cross-linkers. HMMM and the HBMM contain etherified functional groups and are therefore thought to be less reactive during curing than are the more reactive TMTBM and DBMB, both of which contain methylol functional groups, (Jacobs, 1997).

The cross-linker molecules were melamino-formaldehyde or benzoguanamino-formaldehyde-based products. A comparison of these results with those presented in Sections 5.5 to 5.6 shows that, there was much less generation of formaldehyde than there was generation of either melamine or benzoguanamine. When this disparity was investigated, it was observed that some of the formaldehyde in the cross-linker was lost during the curing of the coatings. This point was confirmed by other studies, discussed in Section 6.15.

5.8. The effect of the amount of amino cross-linker used in formulation on the performance of epoxy coatings

The results from the investigation of the effect of the cross-linker content of several epoxy anhydride coatings, on the performance of the coatings are shown in Figure 5.8-1 to Figure 5.8-10. All of the coatings were cured at 200 °C for 10 minutes. As a consequence of varying the cross-linker amount, the results are expressed in terms of how much melamine was released from the coatings, the percentage of the cross-linker that was hydrolysed, the effect on the thermal decomposition pattern and the effect on the hardness of the coating films.

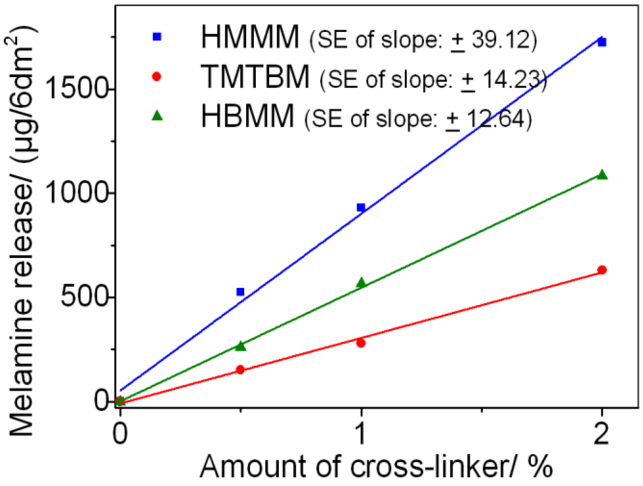


Figure 5.8-1: Unpigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

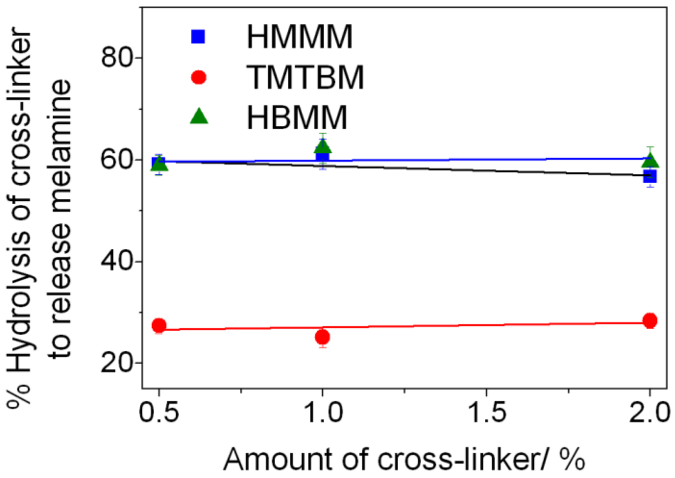


Figure 5.8-2: Unpigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Based on the results in Figure 5.8-1 and Figure 5.8-2, for the unpigmented epoxy anhydride coatings, melamine release from the coatings increased with an increase in the amount of cross-linker in the coating, even though the extent of hydrolysis did not change significantly, with variations in the cross-linker content. This behaviour held true for each class of the cross-linkers. The slope of each graph and the extent of the release depended on the composition, the reactivity and the functionality of the cross-linkers. To explain the contribution of the cross-linker chemistry on the release process, Figure 5.8-2 could be considered as the normalised version of Figure 5.8-1. This is because in Figure 5.8-2, the differences in film thickness and solids content have been taken into account.

As shown in Figure 5.8-2, hydrolysis of the cross-linker component of the unpigmented epoxy anhydride coatings was dependent on the choice of the cross-linker. Accordingly, [Hydrolysis of HMMM cross-linked coating] = [Hydrolysis of HBMM cross-linked coating] > [Hydrolysis of TMTBM cross-linked coating]. HMMM and the HBMM contain etherified functional groups and are therefore thought to be less reactive during curing compared with the more reactive TMTBM and DBMB, both of which contain methylol functional groups, (Jacobs, 1997). As a result, the TMTBM cross-linked coating becomes less susceptible to cross-linker hydrolysis because of greater cross-linking and interlocking of the coating.

Figure 5.8-3 shows that an increase in the cross-linker content of the coatings up to 2% does not significantly change the thermal decomposition of the coatings. Similarly, such a change did not affect the hardness of the coatings. The above findings were found to be true because the cross-linkers were used in small proportions and therefore, the amounts used would probably have little or no effect on the thermal behaviour of the coatings or the extent of the hydrolysis. When the cross-linker contents of the coatings were increased, the hardness values of the coatings remained at 117 ±1 HU.

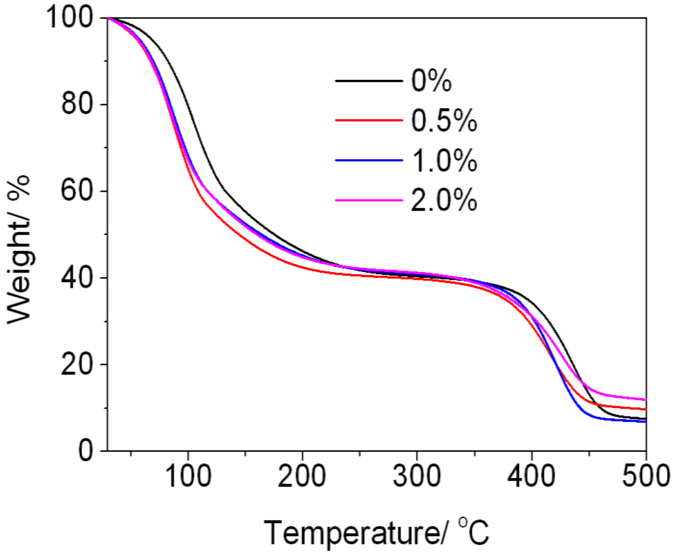


Figure 5.8-3: Unpigmented epoxy anhydride coatings containing different amounts of cross-linker (hexamethoxymethyl melamine, HMMM)

The results for the PW2-pigmented epoxy anhydride coatings are shown in Figure 5.8-4 to Figure 5.8-6. The melamine release from the coatings increased with an increase in the amount of cross-linker in the coating, even though the extent of hydrolysis did not change significantly with variations in the cross-linker content. For the same reasons, the release patterns and the conclusions drawn for the unpigmented epoxy coatings apply to the PW2-epoxy coatings except for the fact that there was lesser hydrolysis of cross-linker to melamine in the PW2-pigmented epoxy anhydride coatings.

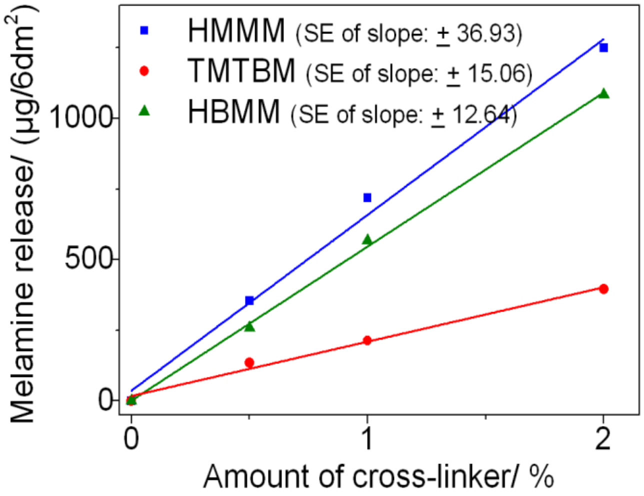


Figure 5.8-4: PW2-pigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

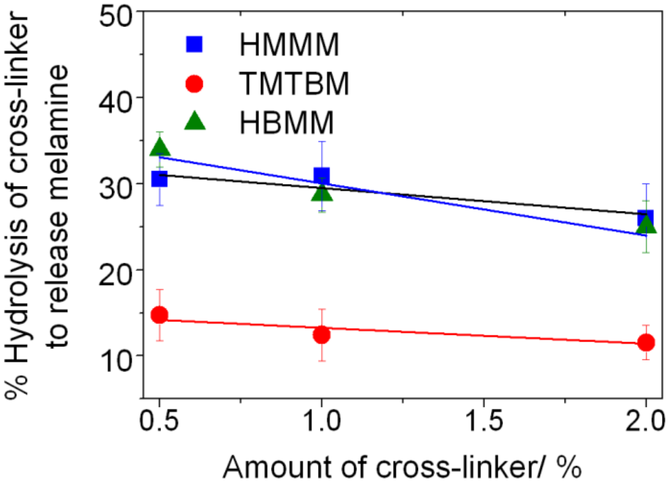


Figure 5.8-5: PW2-pigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Lesser hydrolysis of the cross-linker to melamine in the PW2-pigmented coatings than with the unpigmented epoxy anhydride coatings arises because of the catalytic activity of TiO_2 pigment particles used in formulation. This point is considered in detail in Section 5.14. Figure 5.8-5 shows that the hydrolysis of the cross-linker component of the PW2-

pigmented epoxy anhydride coatings was dependent on the choice of the cross-linker. Accordingly, [Hydrolysis of HMMM cross-linked coating] = [Hydrolysis of HBMM cross-linked coating] > [Hydrolysis of TMTBM cross-linked coating]. HMMM and the HBMM contain etherified functional groups and therefore would be expected to be less reactive during curing than the TMTBM and DBMB, both of which contain methylol functional groups, (Jacobs, 1997). As a result, the TMTBM cross-linked coating is less susceptible to cross-linker hydrolysis because of greater cross-linking and interlocking of the coating.

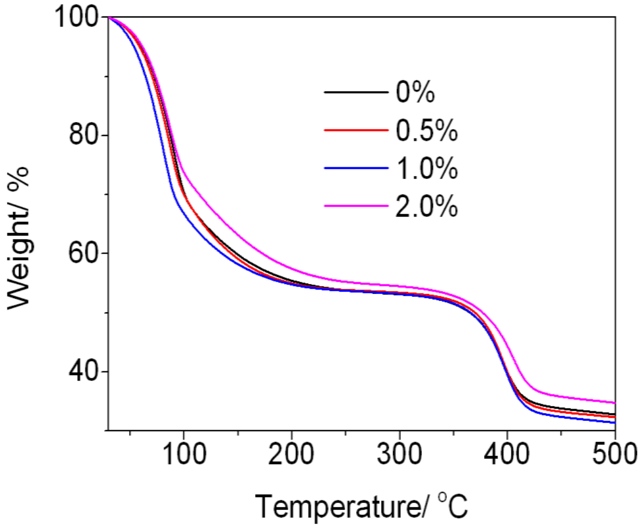


Figure 5.8-6: PW2-pigmented epoxy anhydride coatings containing different amounts of cross-linker (hexamethoxymethyl melamine, HMMM)

Figure 5.8-6 shows that an increase in the cross-linker content of the coatings up to 2% does not significantly change the thermal decomposition behaviour of the coatings. In addition, such action did not affect the hardness of the coatings. When the cross-linker content of the coatings was increased, the hardness values of the coatings remained at 72 ±1 HU. This average value was less than that obtained for un-pigmented epoxy anhydride coatings (117 HU). Without the TiO_2 pigment particles, a more cohesive coating film would be achieved when the coatings were cured at the appropriate curing temperature.

The results shown in Figure 5.8-6 indicate that the decomposition patterns and the effect of the cross-linker amount are consistent with the results that were obtained from the unpigmented epoxy anhydride coatings shown in Figure 5.8-3. Again, it is logical to state that the cross-linkers were used in small proportions and therefore the amounts used would probably have little or no effect on the thermal behaviour of the coatings or on the extent of the hydrolysis. The consistent behaviour of the unpigmented epoxy anhydride coatings and the TiO_2-pigmented epoxy anhydride coatings in their melamine release arose because both coatings consist of the same binder chemistry.

The results from the study of the effect of cross-linker amount on the behaviour of the epoxy phenolic coatings are shown in Figure 5.8-7 to Figure 5.8-9.

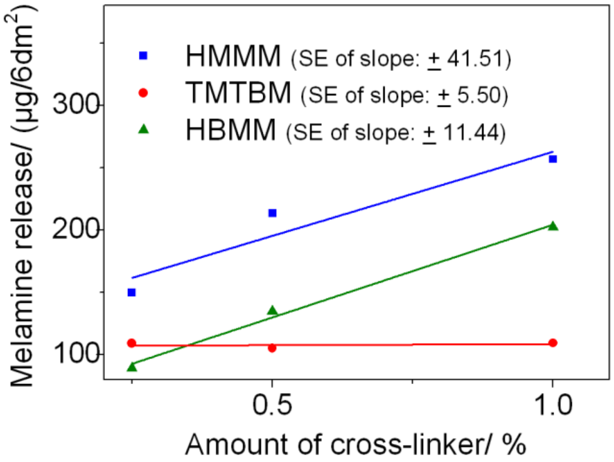


Figure 5.8-7: Epoxy phenolic coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

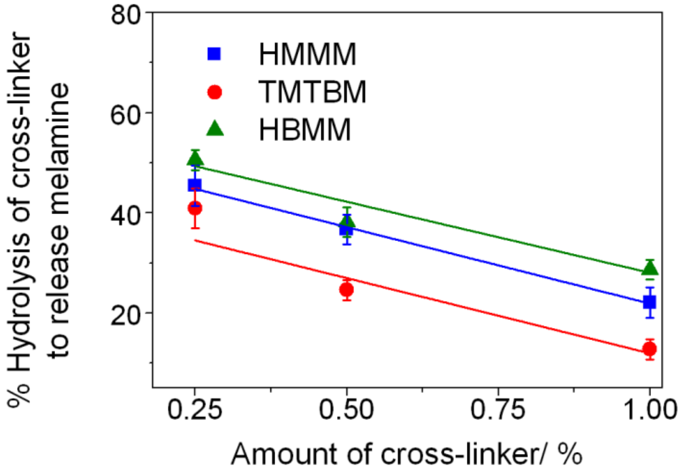


Figure 5.8-8: Epoxy phenolic coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

The results given in Figure 5.8-7 for the epoxy phenolic coatings show that, except for the use of trimethylol tributoxymethyl melamine (TMTBM), there was an increase in the melamine release as the cross-linker content of the coatings was increased. However, the hydrolysis of the TMTBM cross-linker to melamine follows the usual pattern. Relative to the epoxy anhydride coatings and the epoxy phenolic coatings, the significant difference in terms of cross-linker hydrolysis probably arises from the different chemical/reaction behaviour of the phenolic binders and the epoxy binders during curing and in the pathways that the hydrolyses follow.

In Figure 5.8-8, the hydrolysis of the HMMM cross-linked coating is compared with the hydrolysis of the HBMM cross-linked coating. Both cross-linkers are of similar reactivity and both contain etherified functional groups. In Section 2.8.6, Figure 2.8-32, HMMM and the HBMM were shown to have comparable thermal behaviour. The hydrolysis of the TMTBM cross-linked coating was less than that achieved by the HMMM and the HBMM cross-linked coatings. As explained in previous sections, the difference arises because of difference in reactivity amongst the two sets of cross-linkers. TMTBMs contain a more reactive methylol functional groups, in comparison to the less reactive etherified functionality of both the HMMM and the HBMM, (Jacobs, 1997). As a result, the TMTBM cross-linked coating is less susceptible to cross-linker hydrolysis because of the greater cross-linking and interlocking of the coating.

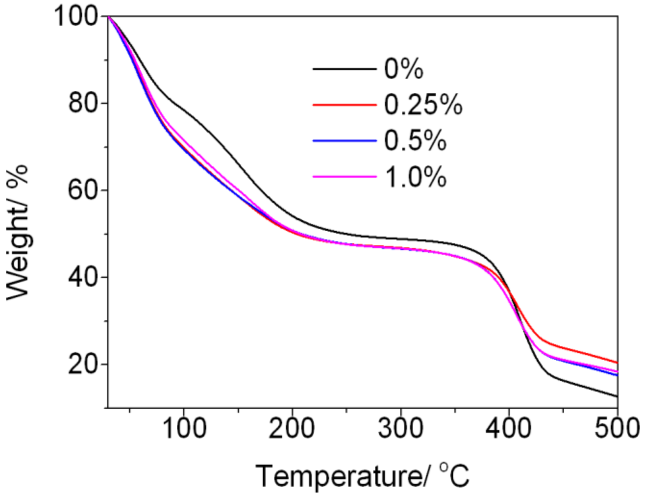


Figure 5.8-9: Epoxy phenolic coatings containing different amounts of cross-linker (hexamethoxymethyl melamine, HMMM)

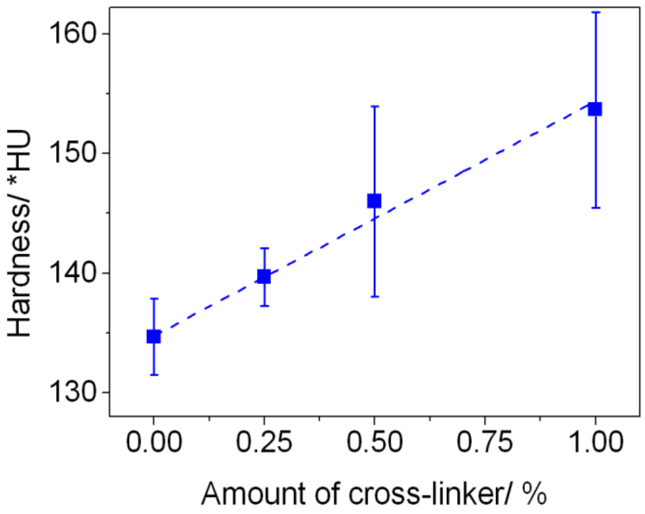


Figure 5.8-10: Hardness values from HMMM cross-linked epoxy phenolic coatings that contain different amount of the cross-linker

Contrary to observations made with the epoxy anhydride coatings, the amount of the cross-linker in the phenolic coatings has an effect on the overall residual solids of the coatings and on the hardness of the coatings, as shown in Figure 5.8-9 and Figure 5.8-10, respectively. It is likely that the cross-linkers are more compatible with the phenolic binder composition then they were with the epoxy binder composition. It is therefore likely that, in the epoxy phenolic coatings, an environment is created where the cross-linkers are better able to blend into the coatings, to participate better in the network/film formation and have effects on/control over the thermal behaviour and the hardness of the coatings.

5.9. The effects of curing time and of curing temperature on the release of melamine

The results obtained from the studies carried out to ascertain the effects of the curing time on the amount of melamine that was released from the epoxy coatings are shown in Figure 5.9-1 to Figure 5.9-6. The curing temperature was 200^{o}C.

The overall results show that, for the coatings that were studied, melamine release into the 10% (v/v) aqueous ethanol food simulant, in all cases, decreased with increase in the curing time. Curing the coatings for a longer time, at the appropriate temperature (200^{o}C), would induce more cross-linking/interlocking in the system, causing melamine release to be reduced. Therefore, to reduce melamine migration from epoxy coatings, curing of the coatings in the oven for a longer duration is recommended. The benefits of increasing the curing time are further discussed in Section 5.10.

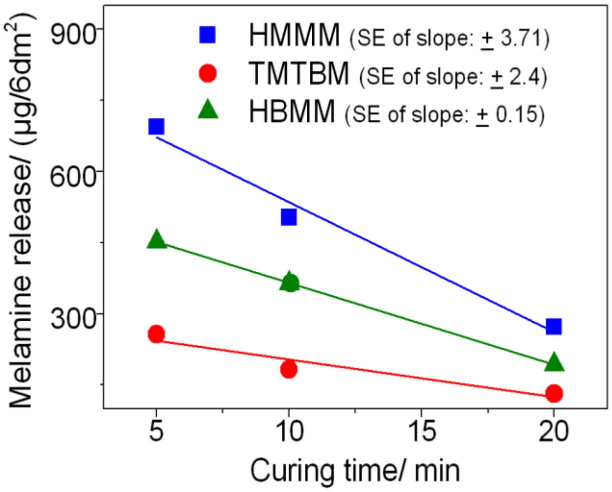


Figure 5.9-1: Unpigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

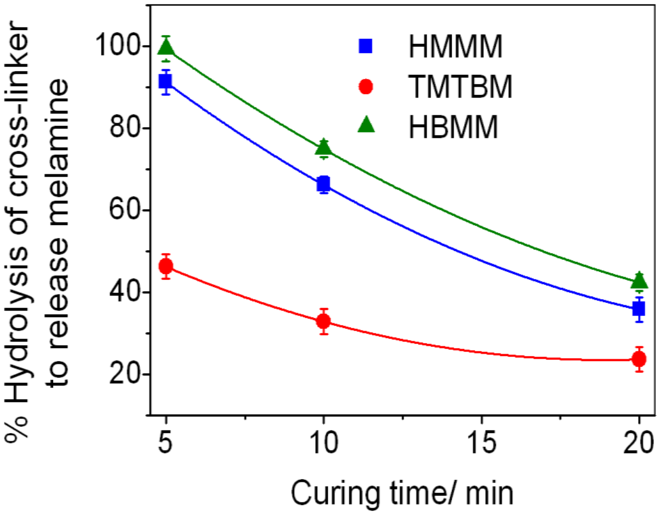


Figure 5.9-2: Unpigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Figure 5.9-1 and Figure 5.9-2 show that when the unpigmented epoxy anhydride coatings were cured for a longer time, at the standard 200°C, both the melamine release and the extent of cross-linker hydrolysis decrease accordingly. The following points were observed.

- At each curing time, the sequence of the release of melamine and of the cross-linker hydrolysis was [HMMM cross-linked coatings] > [HBMM cross-linked coatings] > [TMTBM cross-linked coatings]. The HMMM cross-linked coatings and the HBMM cross-linked coatings gave a similar hydrolysis decrease pattern. Thus, they cross-link and hydrolyse through a similar pathway because both are etherified amino cross-linkers.

- The TMTBM cross-linked coatings gave less hydrolysis of cross-linker because, during curing, a greater extent of cross-linking was achieved compared to when HMMM and HBMM cross-linkers were used. The TMTBM contains methylol groups while the HMMM and HBMM both of which contain a less reactive ether functionality, (Jacobs, 1997).

The effects of the curing temperature on the amount of melamine released from the PW2-pigmented epoxy anhydride coatings are shown in Figure 5.9-3 and Figure 5.9-4. All of the coatings were cured at the standard 200°C curing temperature.

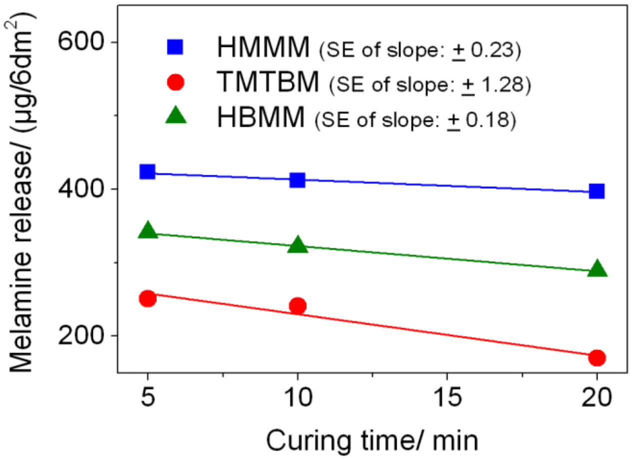


Figure 5.9-3: PW2-pigmented epoxy coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

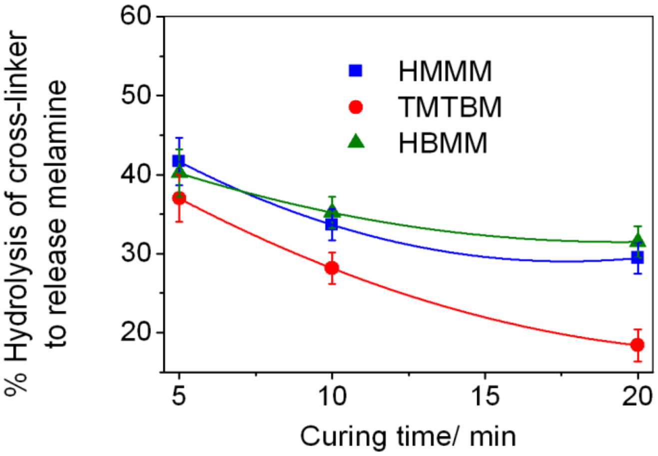


Figure 5.9-4: PW2-pigmented epoxy coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

The overall release and hydrolysis behaviour of the PW2-pigmented epoxy anhydride coatings, (Figure 5.9-3 and Figure 5.9-4.) can be compared with the behaviour of their un-pigmented counterparts, (Figure 5.9-1 and Figure 5.9-2). Accordingly, the following points can be clearly identified:

- There was overall lower release of melamine and reduced hydrolysis of the cross-linkers in the PW2-pigmented epoxy anhydride coatings compared to the behaviour of each cross-linker when each coating was formulated without the TiO_2 pigment particles. Clearly, this points to the benefit of using the TiO_2 pigment in formulations. In Section 5.14, the consequences arising from the presence of and the benefit from the pigment particles are further investigated and discussed.

- Curing the coatings at the stated temperature for a longer period allows more cross-linking. Thus, the longer the period for which the coatings are cured, a more inter-locked structure was achieved, making it more difficult for melamine to be released during the retorting of the coatings in the 10% (v/v) aqueous ethanol food simulant.

- The TMTBM-cross-linked coatings gave less hydrolysis of the cross-linker to melamine than did either the HMMM cross-linked coatings or the HBMM cross-linked coatings. During curing, a greater extent of cross-linking reaction should be achieved compared to when HMMM and HBMM cross-linkers are used. The TMTBM contains methylol groups, whereas HMMM and HBMM both contain a less reactive ether functionality, (Jacobs, 1997).

Figure 5.9-5 shows the effect of an increase in curing time on the melamine release behaviour of the selected epoxy phenolic coatings. Figure 5.9-6 shows a normalised version of Figure 5.9-5, allowing comparisons to be made between the hydrolysis tendencies of each epoxy phenolic cross-linked coating system, to form melamine, during retorting at 131°C for 1 hour.

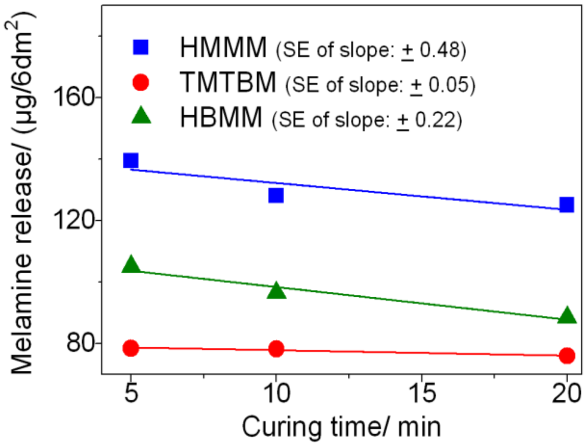


Figure 5.9-5: Epoxy phenolic coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

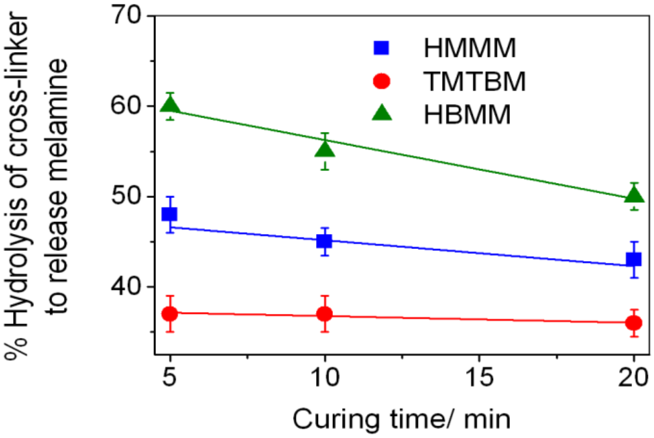


Figure 5.9-6: Epoxy phenolic coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Figure 5.9-5 and Figure 5.9-6 indicate that an increase in the curing time of epoxy phenolic coatings, at the standard 200°C curing temperature, has a minimal effect on the amount of melamine that is released and on the extent of cross-linker hydrolysis in the coatings.

In Figure 5.9-6, the hydrolysis pattern of the epoxy phenolic coatings was [Hydrolysis by HBMM cross-linked coatings] > [Hydrolysis by HMMM cross-linked coatings] > [Hydrolysis by TMTBM cross-linked coatings]. This order occurred because of the differences in their reactivity during curing.

For the epoxy phenolic coatings that were studied, an increase in the curing time at the standard curing temperature had a limited effect on melamine release and on the hydrolysis of the cross-linkers, Figure 5.9-5 and Figure 5.9-6. The data indicate that five minutes curing might have been a sufficient time for the coatings to achieve sufficient cross-link density.

The effects of the curing temperature on the amount of melamine that was released from epoxy coatings are shown in Figure 5.9-7 to Figure 5.9-12. All of the coatings were cured for 10 minutes.

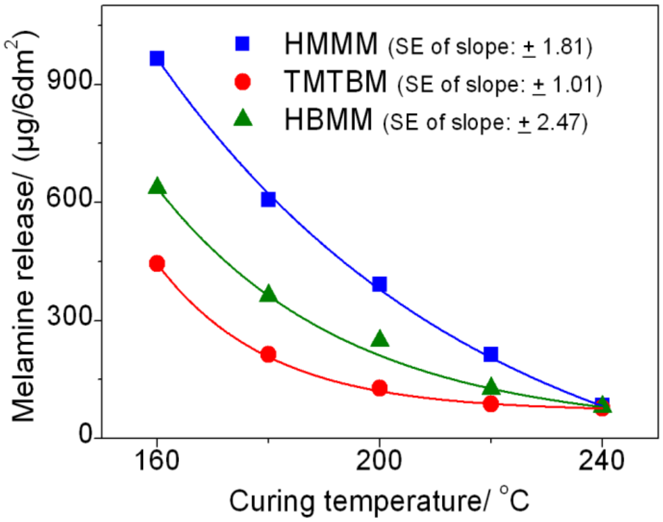


Figure 5.9-7: Unpigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

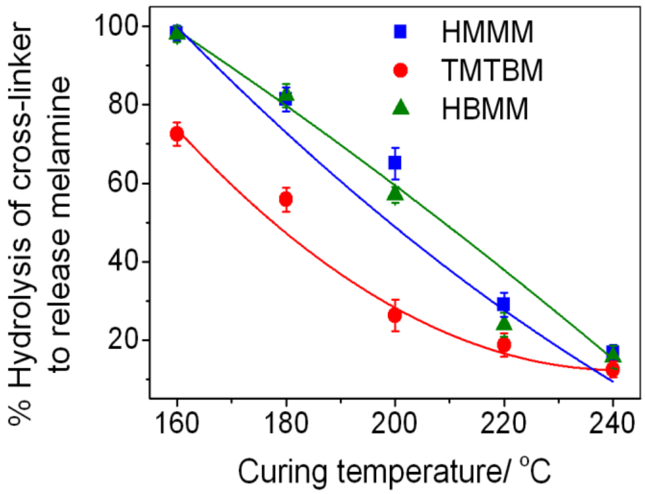


Figure 5.9-8: Unpigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

For the unpigmented epoxy anhydride coatings, Figure 5.9-7 and Figure 5.9-8 show that the curing temperature is a factor in affecting the amount of melamine that was released from the coatings and the extent of cross-linker hydrolysis in the coatings. The higher the curing temperature, the better the results were with respect to lowering the release of melamine from the coatings, after retorting in the 10% (v/v) aqueous ethanol food simulant.

Figure 5.9-7 is the normalised version of Figure 5.9-8. This shows that the hydrolysis pattern of the unpigmented epoxy anhydride coatings was found to be [Hydrolysis by HBMM cross-linked coatings] $\geq$ [Hydrolysis by HMMM cross-linked coatings] > [Hydrolysis by TMTBM cross-linked coatings]. This hydrolysis pattern and sequence of hydrolysis by the HMMM cross-linked coatings and the HBMM cross-linked coatings arises because of their similar chemistry, their similar curing mechanism and their similar reactivity. The TMTBM cross-linked coating was the most resistant to cross-linker hydrolysis.

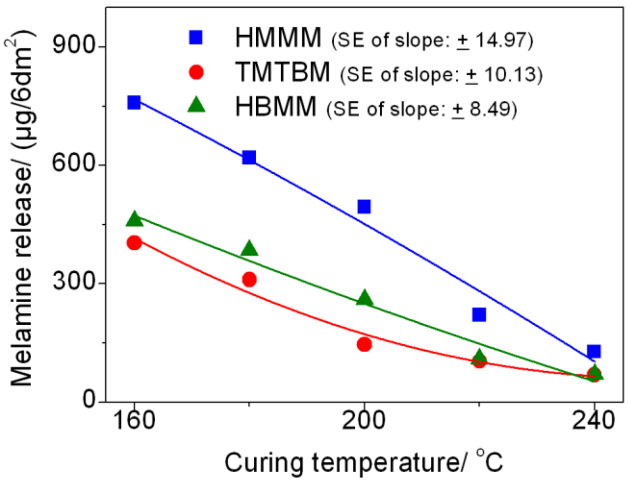


Figure 5.9-9: PW2-pigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

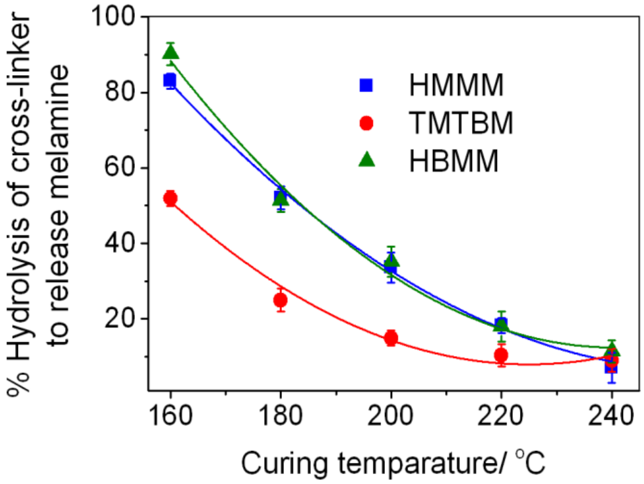


Figure 5.9-10: PW2-pigmented epoxy anhydride coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Figure 5.9-9 and Figure 5.9-10 show that for the PW2-pigmented epoxy anhydride coatings, the release of melamine and the extent of cross-linker hydrolysis were reduced when the curing temperature was increased in stages from 160°C to 240°C, for the standard 10 minutes curing time. Overall, the results show that:

- The PW2-pigmented epoxy anhydride coatings gave lower release of melamine than is released by un-pigmented epoxy anhydride coatings. The fact that the coatings were formulated and applied in the same manner to allow comparisons to be made, shows that the TiO_2 pigment helped to reduce the amount of melamine that the coatings released. In Section 5.14, the role played by the pigment particles is further discussed.

- Figure 5.9-10 shows that the TMTBM cross-linked coatings gave less hydrolysis of cross-linker to melamine than did the HMMM cross-linked coatings or the HBMM cross-linked coatings. During curing, a greater extent of cross-linking was achieved than when HMMM and HBMM cross-linkers were used.

The effects of the curing temperature on the amount of melamine that was released from epoxy phenolic coatings are presented in Figure 5.9-11. The effects of the curing temperature on the hydrolysis of the cross-linker components of the same coatings are given in Figure 5.9-12. Figure 5.9-12 is a normalised form of Figure 5.9-11. This allows comparison of performance to be made across the coatings that were studied.

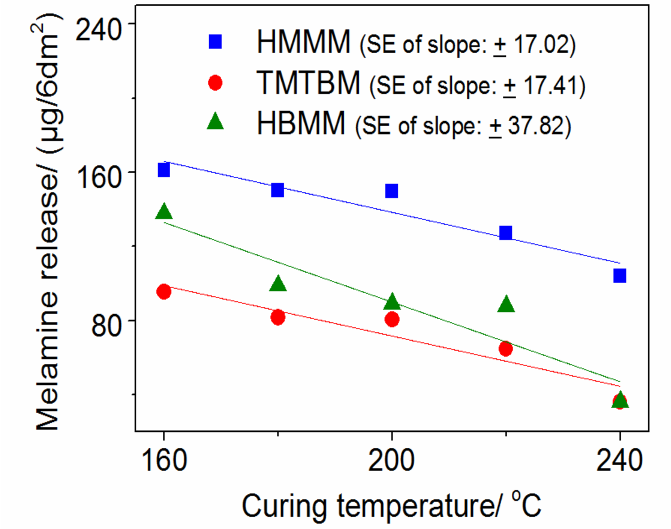


Figure 5.9-11: Epoxy phenolic coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

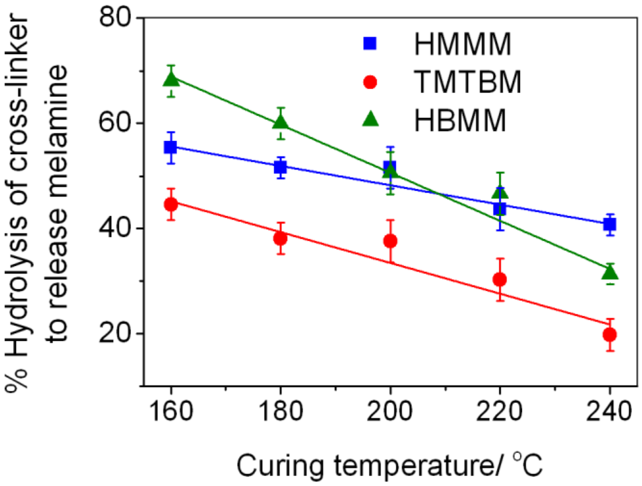


Figure 5.9-12: Epoxy phenolic coatings containing a different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

From the data given in Figure 5.9-11, Figure 5.9-12 and the other figures presented in this Section, the following discussion points arise:

- The temperature of curing has an effect of on the amount of melamine that is released from the coatings, after retorting in a 10% (v/v) aqueous ethanol food simulant. This part of the total study has established that curing the coatings at temperature that is greater than the commercially used 200°C, for 10 minutes, would give a route to lowering the extent of melamine release.

- The results indicate that the cross-link density of the coatings is increased with an increase in the curing temperature, making it more difficult for any melamine to be generated and so migrate. When cured at 160°C (40°C lower than the industrial standard), the required cross-link density is would not be achieved, making subsequent melamine migration from the coating more likely. This point is further discussed in Section 5.10.

- The extent of the hydrolysis depends on the type of cross-linker that is used in the formulation. The TMTBM cross-linked coatings gave less hydrolysis of cross-linker to melamine than did the HMMM cross-linked coatings or the HBMM cross-linked coatings.

5.10. Surface energetics and wetting of coatings—the effects of curing time and of curing temperature

Table 5.10-1 contains the results obtained from surface tension measurements. 3% (v/v) aqueous acetic acid was used as a model for a more protic solvent and to represent the more acidic food simulant. 10% (v/v) aqueous ethanol was used in the contact angle tests.

Table 5.10-1: Surface tension values (Nm^{-1}) of extraction solutions

	Measurement				
	1st	**2nd**	**3rd**	**Average**	**S.D**
Deionised water	72.1	71.2	73.0	72.1	0.9
3% (v/v) aqueous acetic acid food simulant	64.4	64.8	64.9	64.7	0.3
10% (v/v) aqueous ethanol food simulant	52.0	53.2	53.4	52.9	0.8

The surface tension of water (72.1 Nm^{-1}) was greater than that of 3% (v/v) aqueous acetic acid and 10% (v/v) aqueous ethanol, as expected. Introducing ethanol into pure distilled water, lowers its surface tension, (Rao and Leja, 2004). These results provide a basis to understanding the wetting characteristics of cured coating surfaces, a point that is of relevance when the coatings come into contact with the food simulants and with foods.

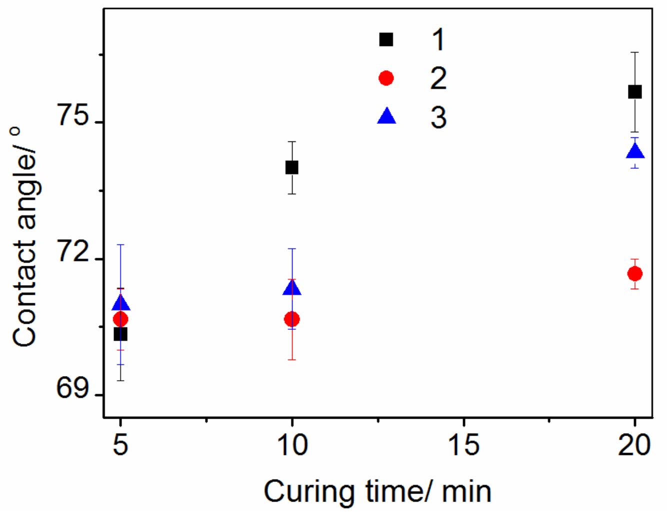


Figure 5.10-1: Variations in the contact angle of the cured coatings with curing time from hexamethoxymethyl melamine (HMMM) cross-linked coatings, cured at 200 °C; 1: unpigmented epoxy anhydride coating, 2: PW2-pigmented epoxy anhydride coating and 3: epoxy phenolic coating

According to Figure 5.10-1, although there is a considerable spread in the repeatability, there is a reasonable indication that the 10% (v/v) aqueous ethanol food simulant exerted the greater surface interaction (wetting) with those coatings that were cured for shorter time. This finding agrees with the results given in Section 5.9, where melamine release and cross-linker hydrolysis were shown to decrease with an increase in the curing time. The findings can be summarised as follows:

- Since each coating class gave values of contact angles that were different from those of another class of coating, the surface wettability properties of each coating would be expected to be different. This finding agrees with the results given in Section 5.4 to Section 5.9.

- The more the coatings were cured, the more the system was locked, the greater the barrier properties and the consolidation. Thus, the opportunities for melamine release would be more reduced. The results suggest that the change in curing time and the change in surface wetting are related. This finding concurs with the results shown in Section 5.9.

With respect to the effect on surface energetics of changes in the curing temperature, relevant results are shown in Figure 5.10-2.

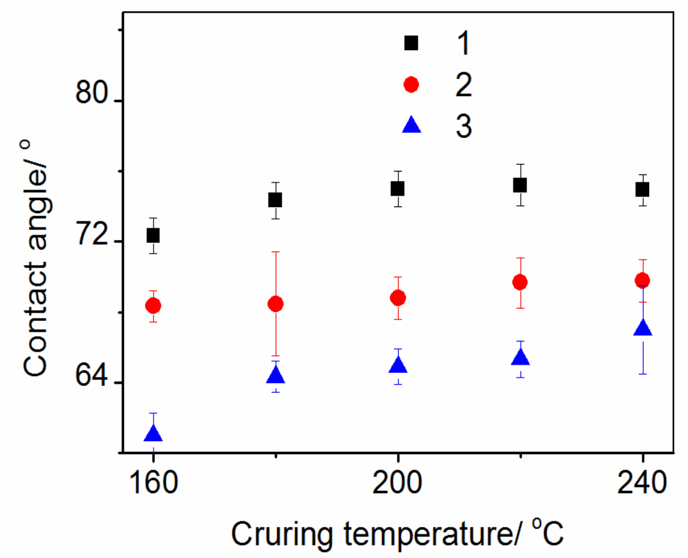


Figure 5.10-2: HMMM cross-linked coatings, cured for 10 minutes; 1: unpigmented epoxy anhydride coating, 2: PW2-pigmented epoxy anhydride coating and 3: epoxy phenolic coating. Tests carried out with 10% (v/v) aqueous ethanol

Figure 5.10-2 shows that the 10 % (v/v) aqueous ethanolic food stimulant more those coatings that were cured at lower temperatures. For the 10 % (v/v) aqueous ethanolic food simulant treatment, the lower the curing temperature, the more the fluid simulant interacted with the surface, (lower values of contact angle were obtained). The results also show that each coating class had surface wettability properties that were different from the other coating classes. Thus, with respect to the interaction of the 10% (v/v) food simulant with the coatings, wetting in unpigmented epoxy anhydride coatings > wetting in PW2-pigmented epoxy anhydride coatings > wetting in epoxy phenolic coatings.

In Section 5.9, it was shown that melamine release from coatings, after retorting in a 10% (v/v) aqueous ethanolic simulant, decreased with increase in the curing temperature. The greater the curing temperature, the more the system was “sealed”. Clearly, for the optimum performance characteristics of the dried/cured coatings to be realised, optimised conditions of curing, namely the curing time, the curing temperature and wet film thickness of the coating need to be adopted.

5.11. Drawbacks associated with increasing the curing time or increasing the curing temperature

Figure 5.11-1 to Figure 5.11-3 show the results obtained from the surface spectrophotometric measurements that were carried out on the cured, coated panels. These coatings were cured at the standard 200 °C, for various time periods.

The wavelength region of 400-700 nm (visible region of the electromagnetic spectrum) was used so that the measurements to be correlated with the visual assessments that were made on the panels when monitoring/observing the uniformity of different areas of the coated panels, indirectly establishing the uniformity of the consequences of the curing process.

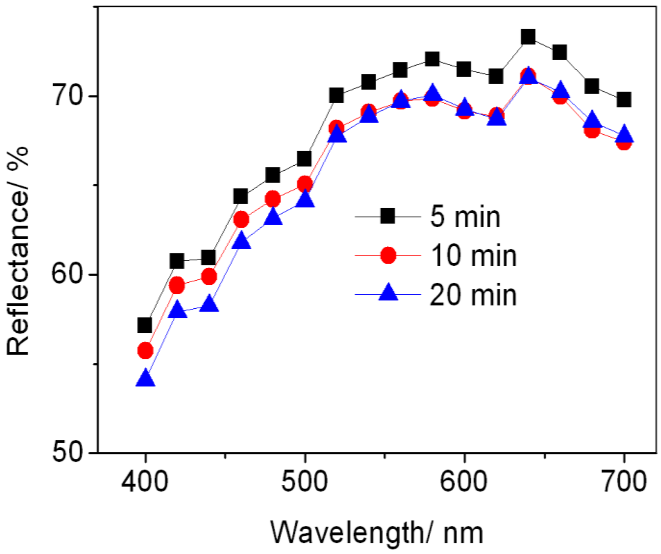


Figure 5.11-1: Surface reflectance behaviour of HMMM cross-linked unpigmented epoxy anhydride coatings, cured at 200 °C, for various stated time periods

The spectrophotometric measurements that were carried out on the panels show that an increase in the curing time, at the standard 200 °C, affects the surface reflectance of the coatings.

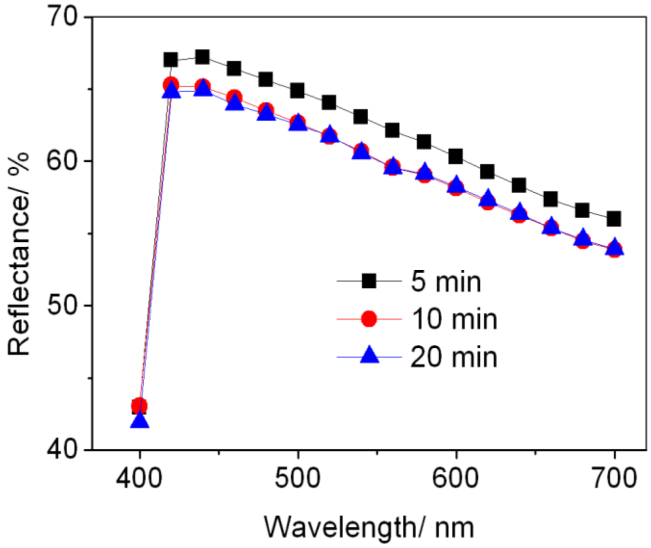


Figure 5.11-2: Surface reflectance behaviour of HMMM cross-linked PW2-pigmented epoxy anhydride coatings, cured at 200 °C, for various stated time periods

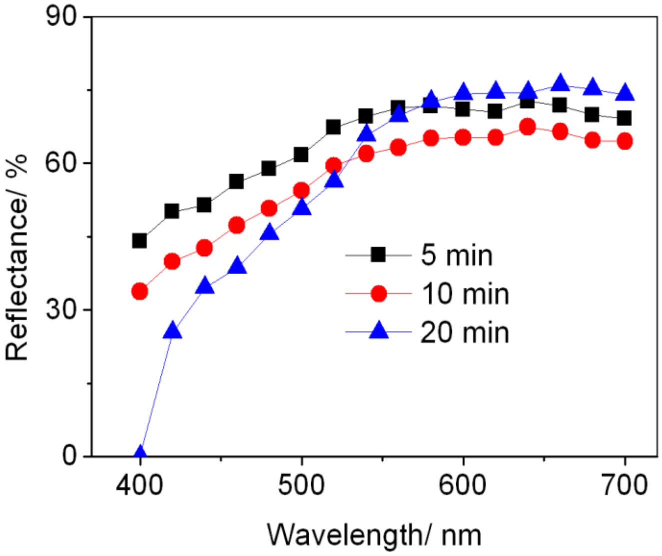


Figure 5.11-3: Surface reflectance behaviour of HMMM cross-linked epoxy phenolic coatings, cured at 200 °C, for various stated time periods

Figure 5.11-1 to Figure 5.11-3 show that, in each case, there was a significant difference between the reflectance properties of the coatings that were cured for a shorter time and those coatings that were cured for a longer time, at the standard 200 °C curing temperature. In addition, the behaviour of one coating type differs from that exhibited by another. This behaviour depends on the bulk binder used in formulating the coatings and on whether or not the TiO_2 pigment was used. Both coatings represented by Figure 5.11-1 and Figure 5.11-3 prior to curing were clear and unpigmented. The coatings in Figure 5.11-2 contained TiO_2 pigment particles, showing entirely different surface reflectances than those exhibited by the clear coatings. The reflectance spectra in Figure 5.11-2 were each dominated by the scattering behaviour of the TiO_2 pigment particles.

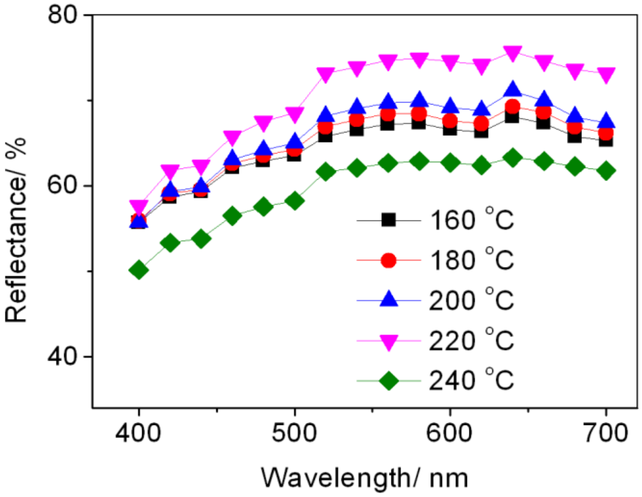


Figure 5.11-4: Surface reflectance behaviour of HMMM cross-linked unpigmented epoxy anhydride coatings, cured for 10 minutes, at various temperatures

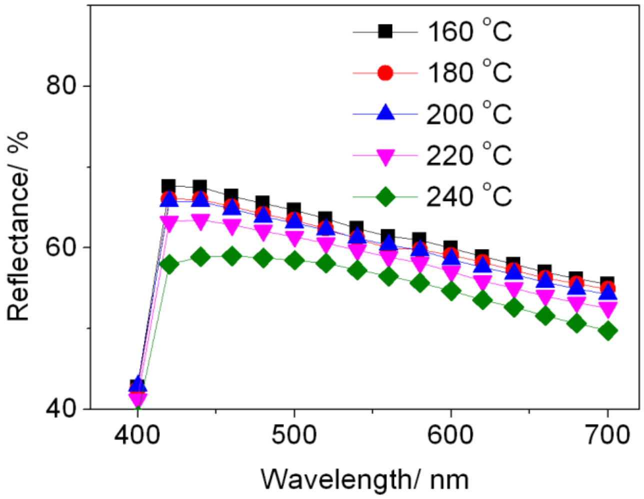


Figure 5.11-5: Surface reflectance behaviour of HMMM cross-linked pigmented epoxy anhydride coatings, cured for 10 minutes, at various temperatures

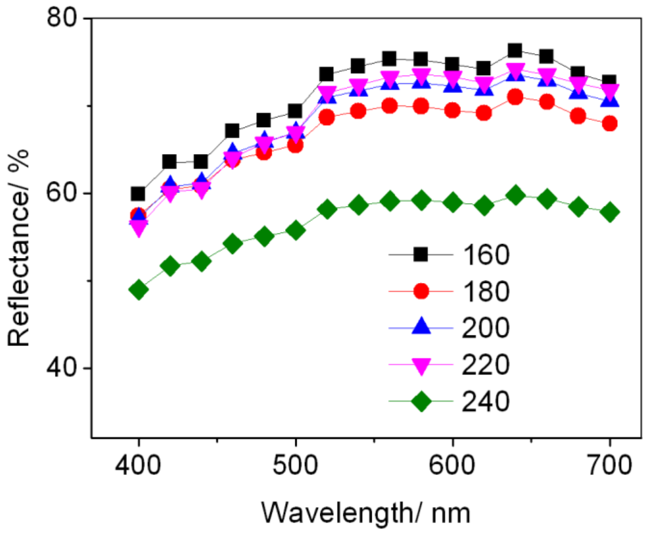


Figure 5.11-6: Surface reflectance behaviour of HMMM cross-linked epoxy phenolic coatings cured for 10 minutes at various temperatures

From the findings in Figure 5.11-4 to Figure 5.11-6, the following conclusions can be drawn:

- The surface reflectance properties of each of the coatings studied changed when the curing temperature was changed (was increased or decreased from a standard value). Generally, the greater the curing temperature, the less was the reflection from their surfaces and the duller the surface.

- Section 5.9 showed that an increase in the curing temperature can help to lower melamine migration from the coatings. However, such an action could prove be problematic for the industry since the overall appearance of the coatings would be changed.

- With respect to the PW2-pigmented coatings, both reflectance studies and physical observations showed that an increase in the curing temperature up to 240^{o}C, caused the coatings to exhibit a yellowish appearance.

- The surface reflectance behaviour of coatings was significantly affected by type of binder used in the formulation and by the presence of TiO_2 pigment particles.

- Surface reflectance measurements, using spectrophotometers can give a method for monitoring the appearance and the exchange of colour changes that result from changes to the curing conditions.

5.12. The effect of a two-step curing procedure on melamine release

These studies and those described in Section 5.13 out because it sometimes occurs that a coating can receive a two-step cure. For example, if the metal gets first a base coat and then a top coat, clearly the base coat is passed through the curing oven twice. Also, if a metal has an external coating/decoration applied, the interior coating may go through the oven twice, depending on the application sequence (i.e internal followed by external (2 stovings) or external followed by internal (1 stoving)).

The effects of interrupting a single curing session or of breaking a curing cycle into two separate sessions with "resting" of the coating in between the two sessions are shown in Table 5.12-1 to Table 5.12-2.

Table 5.12-1: Unpigmented epoxy anhydride coatings, cross-linked with hexamethoxymethyl melamine (HMMM), cured at 200°C, showing the effect of a two-step curing procedure on melamine release in μg/6dm^2 and on the percentage of the cross-linker hydrolysis

1st curing	Resting time	2nd curing	μg/6dm^2	% Hydrolysis
10 min	0	0	542 ±6	71.2 ±1.8
7.5 min	2 min	2.5 min	547 ±11	71.9 ±2.3
2.5 min	2 min	7.5 min	547 ±7	71.9 ±2
5 min	2 min	5 min	541 ±5	71.2 ±1.6
5 min	5 min	5 min	544 ±3	71.6 ±1.1
5 min	10 min	5 min	588 ±4	77.3 ±1.5

Table 5.12-2: Pigmented epoxy anhydride coatings, cross-linked with hexamethoxymethyl melamine (HMMM), cured at 200°C, the effect of a two-step curing procedure on melamine release in μg/6dm^2 and on the percentage of the cross-linker hydrolysis

1st curing	Resting time	2nd curing	μg/6dm^2	% Hydrolysis
10 min	0	0	373 ±6	32.1 ±2
7.5 min	2 min	2.5 min	389 ±3	33.5 ±1.1
2.5 min	2 min	7.5 min	389 ±4	33.5 ±1.8
5 min	5 min	5 min	389 ±6	33.5 ±2

Table 5.12-3: Epoxy phenolic coatings cross-linked, with hexamethoxymethyl melamine (HMMM), cured at 200°C, the effect of a two-step curing procedure on melamine release in μg/6dm^2 and on the percentage of the cross-linker hydrolysis

1st curing	Resting time	2nd curing	μg/6dm^2	% Hydrolysis
10 min	0	0	148 ± 4	50.9 ±2
7.5 min	2 min	2.5 min	146 ± 5	50.8 ±2
2.5 min	2 min	7.5 min	148 ±6	51.0 ±2.2
5 min	5 min	5 min	147 ±4	50.9 ±1.9

The results show that breaking the cure session, with resting of the coatings in between the two sessions, does not have any significant effect on the total amount of melamine that is released from the cured coatings, after retorting the coatings in the 10% (v/v) aqueous ethanolic food simulant. It also allows the conclusion, that should the curing session be interrupted intentionally or unintentionally (e.g. a power failure) for a short period of time, provided that, in total, the coatings is cured for the required time at the appropriate temperature, the melamine migration behaviour of the coatings would not be affected.

5.13. Effects of a wet-on-dry coating deposition procedure for specified, overall coating thicknesses

The results obtained from the study of the effect of a two-step coating deposition procedure (wet-on-dry), used for a specified overall coating thickness, are presented in Table 5.13-1 to Table 5.13-3.

The following points are relevant to interpretations and to the provision of an understanding of the results given in Table 5.13-1 to Table 5.13-3.

- The term “double coat on the same side”, (DCSS) refers to two layers of coating being present on the same side of the tinplate substrate, with the same film thickness (e.g. 6gsm). The second layer was applied and cured after the curing of the first layer. DCSS gives the same food contact area as the single coat (SC).

- The term “single coat on each side”, (SCES) refers to two layers of coating being present, with the same film thickness (e.g. 6gsm), each on one side of the tinplate substrate, applied and cured separately. Thus, one of the coating layers received a double cure. SCES gives a food contact surface that is double that of a single coat (SC).

With respect to the results expressed in melamine release units (µg/6dm^2), a comparison needs to be made between the DCSS and the SC and between the SCES and the SC. Thus, in Table 5.13-1 for example, with respect to the HMMM cross-linked coatings, the results imply the following:

- The SC approach released 117 µg/6dm^2 in comparison to the 147 µg/6dm^2 released by the DCSS approach. Therefore, the second top layer in the only released about 30 µg of melamine per 6dm^2 of coating. Thus, the total cross-linker hydrolysis in the DCSS was less than that achieved by the SC procedure.

- The SC approach released 117 µg of melamine per 6dm^2 of coating in comparison to the 79 µg/6dm^2 released by the SCES approach. It is worth noting that both the SC and SCES give the same area of coating that will be exposed to the same volume of food simulant. However, the SCES has double the amount of coating that the SC has. The results imply that, in the SCES system, the coating layer that received the single cure released about 59 µg/6dm^2 while the layer that received a double cure released only 21 µg of melamine per 6dm^2 of coating.

The interpretations shown for the results in Table 5.13-1 can be related to the results presented in Table 5.13-2 and Table 5.13-3. From these findings, the following points are relevant:

- In the DCSS approach, the upper coating layer serves as a barrier to the lower layer, hence limiting the amount of melamine arising from the lower layer, during the autoclaving procedure. This observation could be of value since, in an ideal situation, an increase in the wet coating thickness would lower the rate of diffusion (migration) of substances from the bulk of the coating, (Embuscado and Huber, 2009b).

- The double cure that one layer in each of the DCSS and the SCES approaches receives, reduces the overall hydrolysis of the cross-linker components of the coatings after retorting, in comparison to that achieved by the SC procedure, for the same overall coating thickness.

- Although the SCES approach offers a possibility of reduced cross-linker hydrolysis, the procedure may have limited industrial application (if any). This is because, in the filled can, only one side of the substrate comes into contact with food.

- To limit melamine release/migration from coatings into a foodstuff or into food simulants, the strategy of the application of double layers can be of a benefit. The second layer needs to be applied and cured after the curing of the first layer, all targeting the total film weight thickness, needed to achieve the desired/required performance properties.

Table 5.13-1: Unpigmented epoxy anhydride coatings, cured at 200 °C for 10 minutes using different cross-linkers; HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Cross-linker	Coating application	Total film thickness	Melamine release/ μg/6dm^2	% Hydrolysis of cross-linker
HMMM	Single coat	6 gsm	376 ±6	49.3 ±2
HMMM	Double coat on the same side	12 gsm	480 ±5	31.6 ±1
HMMM	Single coat on each side	12 gsm	219 ±5	28.8 ±0.8
TMTBM	Single coat	6 gsm	177 ±3	31.8 ±1
TMTBM	Double coat on the same side	12 gsm	214 ±4	19.2 ±1
TMTBM	Single coat on each side	12 gsm	104 ±5	18.7 ±1
HBMM	Single coat	6 gsm	242 ±5	53.1 ±1.1
HBMM	Double coat on the same side	12 gsm	337 ±6	37.1 ±2
HBMM	Single coat on each side	12 gsm	149 ±3	32.6 ±0.5
DBMB	Single coat	6 gsm	87 ±5	10.6 ±1
DBMB	Double coat on the same side	12 gsm	87 ±4	5.3 ±0.9
DBMB	Single coat on each side	12 gsm	49 ±3	5.9 ±0.4

Table 5.13-2: PW2-pigmented epoxy anhydride coatings, cured at 200 °C for 10 minutes using different cross-linkers; HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Cross-linker	Coating application	Total film thickness	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
HMMM	Single coat	12 gsm	302 ±4	26.0 ±1.2
HMMM	Double coat on the same side	24 gsm	396 ±5	16.9 ±1.6
HMMM	Single coat on each side	24 gsm	190 ±6	16.4 ±2
TMTBM	Single coat	12 gsm	199 ±3	23.3 ±1
TMTBM	Double coat on the same side	24 gsm	253 ±5	14.8 ±2
TMTBM	Single coat on each side	24 gsm	116 ±4	13.5 ±1.3
HBMM	Single coat	12 gsm	264 ±4	37.3 ±1
HBMM	Double coat on the same side	24 gsm	285 ±6	20.2 ±2
HBMM	Single coat on each side	24 gsm	149 ±3	21.1 ±1
DBMB	Single coat	12 gsm	87±3	6.9 ±1
DBMB	Double coat on the same side	24 gsm	86 ±2	3.4 ±0.5
DBMB	Single coat on each side	24 gsm	42 ±2	3.4 ±0.6

Table 5.13-3: Epoxy phenolic coatings, cured at 200 °C for 10 minutes using different cross-linkers; HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Cross-linker	Coating application	Total film thickness	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
HMMM	Single coat	6 gsm	117 ±5	40.1 ±2
HMMM	Double coat on the same side	12 gsm	147 ±6	25.2 ±3
HMMM	Single coat on each side	12 gsm	79 ±4	26.5 ±2
TMTBM	Single coat	6 gsm	110 ±13	51.4 ±4.5
TMTBM	Double coat on the same side	12 gsm	117 ±6	27.3 ±3
TMTBM	Single coat on each side	12 gsm	58 ±5	27.2 ±2
HBMM	Single coat	6 gsm	98 ±5	55.7 ±2
HBMM	Double coat on the same side	12 gsm	114 ±4	32.4 ±2
HBMM	Single coat on each side	12 gsm	57 ±3	32.6 ±1
DBMB	Single coat	6 gsm	84 ±4	26.6 ±2
DBMB	Double coat on the same side	12 gsm	82 ±4	12.9 ±2
DBMB	Single coat on each side	12 gsm	41 ±2	12.9 ±1

5.14. The effects of the presence of the TiO_2 pigment (PW2) in epoxy anhydride coatings

The results from the studies carried out to investigate the effect of the presence or absence of TiO_2 pigment particles in epoxy-anhydride coatings are shown in Table 5.14-1.

In the table, the results are expressed in normalised form showing the %hydrolysis of each cross-linker, in order to allow for comparison to be made of the cross-linker contribution to coating hydrolysis.

Table 5.14-1: The effect/benefit of using PW2-TiO_2 pigment in epoxy anhydride coatings, each containing a different cross-linker; HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Cross-linker type 0.5% of formulation	Melamine release/ (µg/6dm^2)		% Hydrolysis of cross-linker to release melamine	
	With TiO_2	Without TiO_2	With TiO_2	Without TiO_2
HMMM-1	404 ±6	622 ±4	35 ±1	74 ±1
HMMM-2	392 ±3	525 ±4	34 ±2	70 ±2
HMMM-3	418 ±2	567 ±5	36 ±2	75 ±1
HBMM-1	217 ±2	321 ±7	31 ±2	71 ±1
HBMM-2	423 ±5	655 ±6	54 ±4	96 ±5
HBMM-3	249 ±4	373 ±6	36 ±2	81 ±1
MMTC-1 (TMTBM)	227 ±5	497 ±6	23 ±6	79 ±3
MMTC-2	242 ±2	294 ±8	28 ±2	53 ±2
MMTC-3	317 ±3	224 ±7	37 ±3	40 ±4
MMTC-4	193 ±4	371 ±3	15 ±2	34 ±2
DBMB	79 ±2	80 ±8	6 ±2	10 ±3

According to the results given in Table 5.14-1, when the PW2-TiO_2 particles were excluded from the coatings, the amount of melamine that was released through hydrolysis increased significantly. This observation was consistent across the eleven coatings, each of which contained a different grade of the amino cross-linker, (Section 2.4 and Table 2.2-2).

TiO_2 particles are used as a catalytic support in various applications, (Li et al., 2003). Such catalytic involvement could be relevant to the observed behaviour of the pigmented epoxy anhydride coatings. Thus, the polar, hydrophilic surface of the TiO_2 particles is contributing to the polymerisation process that occurs between the melamino cross-linkers and the epoxy-anhydride polymeric binders that exist within the coating, (see Section 2.6.3). In this way, a greater cross-link density could be achieved, resulting in the lower melamine release observed.

Generally, the hexamethoxymethyl melamine (HMMM) cross-linked coatings and the hexabutoxymethyl melamine (HBMM) cross-linked coatings gave a similar hydrolysis pattern. This pattern was different from that exhibited by the methylol melamine-type (MMTC) cross-linked coatings and the dibutoxymethyl benzoguanamine (DBMB) cross-linked coatings. Differences in the results when different grades of the same cross-linker type were used arise because of differences in the cross-linker composition. This can be seen clearly in the TGA results shown in Section 2.8.6. The TGA patterns correlate with the behaviour of the cross-linkers shown in Table 5.14-1. Accordingly, the following discussion points are relevant:

- HMMMs and HBMMs have similar thermal decomposition patterns, Section 2.8.6. Accordingly, in Table 5.14-1 the HMMMs and the HBMMs have similar hydrolysis patterns, in pigmented cross-linked coatings and in unpigmented cross-linked coatings. This implies that, the release of melamine from the retorted coatings was influenced by both thermal events and chemical events, (thermally induces changes).

- Both the MMTC and the DBMB give similar thermal decomposition patterns and hydrolysis patterns. Both cross-linkers, in the two sets of coatings, gave lower melamine release and less overall hydrolysis than occurred with the HMMMs and the HBMMs. Thus, the chemistry of each cross-linker type plays a major role in the hydrolysis. Both MMTC and DBMB contain methylol functionality, having greater tendency to react during curing, leading to greater cross-link density than can be achieved by HMMM or HBMM, (Jacobs, 1997). Therefore, MMTC cross-linked coatings and the DBMB cross-linked coatings are less susceptible to cross-linker hydrolysis during the retorting of the coatings than are the HMMM and the HBMM cross-linked coatings.

- The dibutoxymethyl benzoguanamine (DBMB) cross-linker gave the least melamine release and cross-linker hydrolysis. DBMB has a limited tendency to hydrolyse to melamine since the melamine that is released arises from melamino impurities in the DBMB cross-linker. The bulk of the DBMB cross-linker composition is based on benzoguanamino components, (Inchem.org, 2001).

5.15. The effects of different grades of TiO_2 pigments on melamine release

Pigments generally operate on the basis particle shape, particles size and particle size distribution. For any particular application purpose, when the size or the shape of the pigment particles is changed, it would be expected that the properties of the material would change. This change would be to the colour, dispersion quality, dispersion stability, chemical properties and physical properties of the product. Three grades of TiO_2 pigment (Section2.6) were used in selected coatings, being subjected to identical treatments to investigate if, on the basis of particle size and the particle size distribution, the pigment grades could be used interchangeably with respect to melamine release.

The effects of the use of different TiO_2 pigment-grades on the amount of melamine that is generated and released in the epoxy-anhydride coatings, cross-linked with the HBMM cross-linker, are presented in Figure 5.15-1 to Figure 5.15-3.

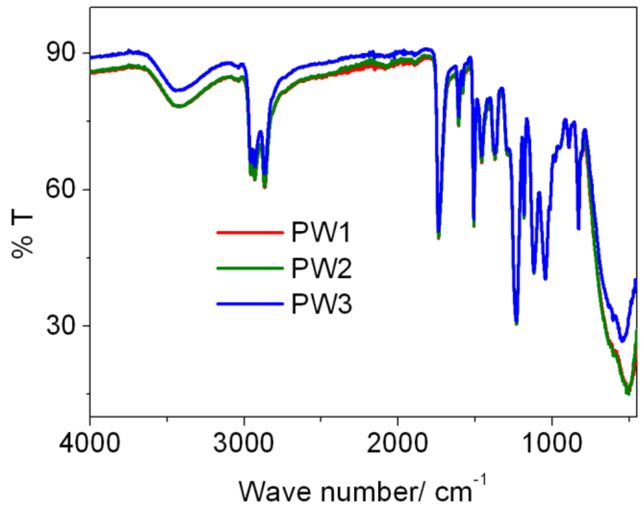


Figure 5.15-1: HBMM containing epoxy anhydride coatings, cured at 200 °C for 10 minutes, each containing a different grade of the pigment white (PW), i.e. the TiO_2 particles

The FT-IR data, Figure 5.15-1, show that the wet coatings, each containing a different grade of TiO_2, did not differ significantly in their interaction with infrared radiation. Figure 5.15-2 and Figure 5.15-3 indicate that the three pigment grades exhibit very similar behaviour in the amount of melamine that was released from the coatings. It should be recalled that the average size of their particles, in the three pigment grades, their size distribution and their zeta potential values did not vary considerably.

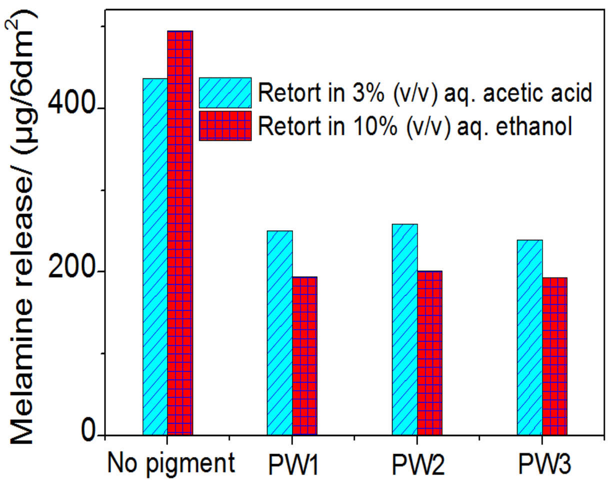


Figure 5.15-2: Effect of the pigment white (PW) species, i.e. the TiO_2 particle grade, on melamine release after retorting in the aqueous simulants, from HBMM cross-linked epoxy anhydride coatings

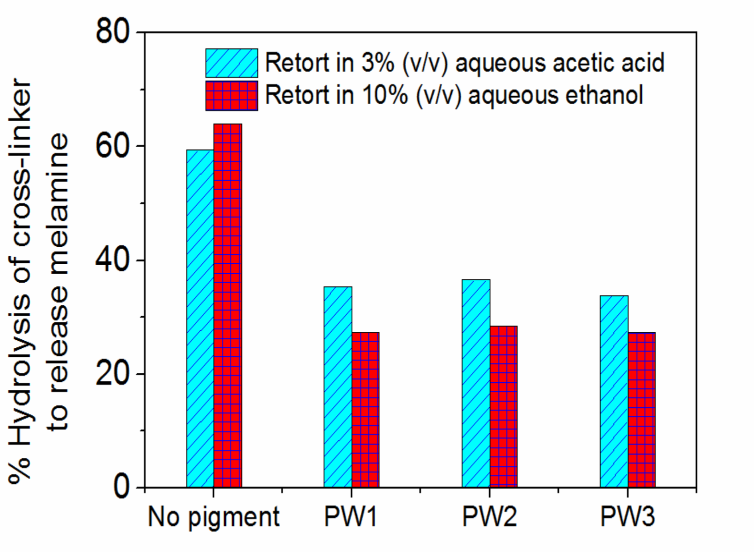


Figure 5.15-3: Effect of the pigment white (PW) species, i.e. TiO_2 particle grade, on the extent of cross-linker hydrolysis (to release melamine) after retorting in the aqueous simulants, from HBMM cross-linked epoxy anhydride coatings

The results show that the release of melamine from the epoxy coatings occurs when either of the food simulants was used, i.e., the 3% (v/v) aqueous acetic acid or the 10% (v/v) aqueous ethanol. There was more release of melamine when the 3% (v/v) aqueous acetic acid food simulant was used because of its greater acidity, although both food simulants are protic solvents, (Brown, 2013). The 3% (v/v) aqueous acetic acid showed more surface interaction with the coatings than the 10% (v/v) aqueous ethanol, when contact angle studies were carried out.

In an overall assessment, the three pigment grades exhibit similar properties and effectiveness, similar size distribution and similar zeta potential values. In a comparative manner, the presence of each of the three pigment grades reduces melamine release from the coatings. Further discussions are provided in Section 5.14.

5.16. The influence of controlled ageing on the properties of fluid, TiO_2 pigmented epoxy anhydride coatings

For can coatings, a six months shelf life is typically set as a criterion for fitness of purpose. In this study, storage periods of two weeks were used to represent the range of times it takes for the coatings to be transported to users, (Valspar UK, 2011). Storage times of 20 weeks and 40 weeks were considered to represent the time it takes for the coatings to be used up in can making processes.

Figure 5.16-1 and Figure 5.16-2 show the results that were obtained from investigations of the ageing behaviour of fluid pigmented epoxy anhydride coatings. The influence of the controlled ageing of the coatings was monitored in terms of melamine release and in terms of cross-linker hydrolysis.

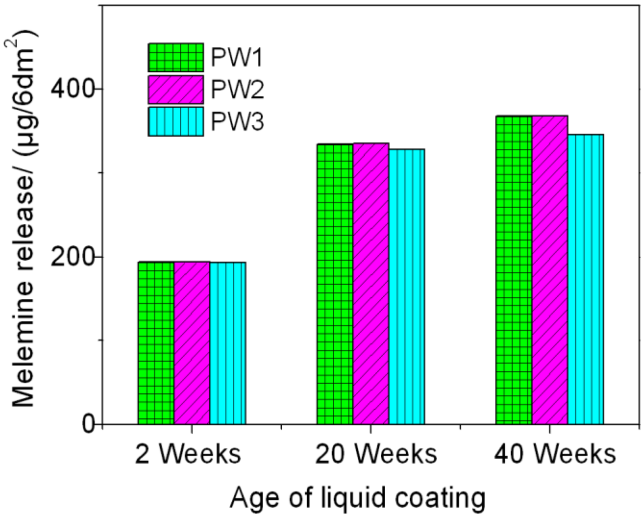


Figure 5.16-1: Effect of wet ageing on the extent of melamine release, from HMMM cross-linked epoxy anhydride coatings

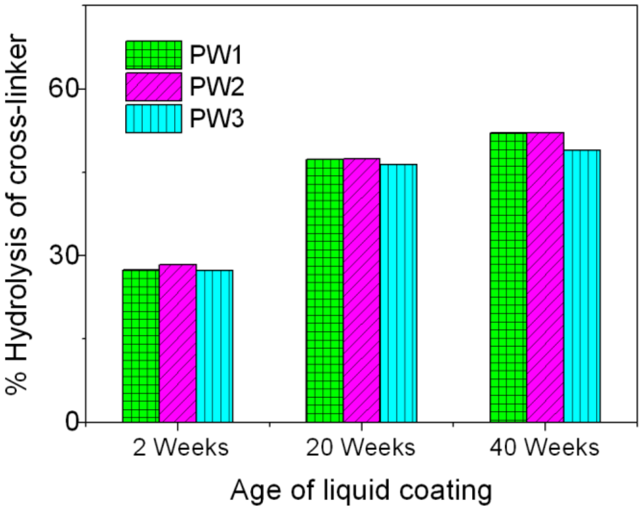


Figure 5.16-2: Effect of wet ageing on the extent of cross-linker hydrolysis to yield melamine, from HMMM cross-linked epoxy anhydride coatings

The results show that all of the pigmented coatings studied underwent wet ageing, as observed by considering the melamine release from the epoxy anhydride coatings. In each case, both the release of melamine and the hydrolysis of the cross-linker increased as a consequence of the ageing. The results show that during storage, the pigmented epoxy anhydride coatings, each containing a different pigment grade all behaved very similarly. These results indicate that the three pigment grades can be used interchangeably with respect to the melamine release behaviour that arises during the hydrolysis of the cured coatings. Even with the ageing effect, the melamine released by the coatings was well below the current European acceptable limit of 2.5 mg/6dm^2, (European Union, 2011b). However, since any release of melamine is unwanted, the issue of the ageing effect with respect to melamine release needs to be addressed. Also, the significance of components in the coatings, the mixing quality and the pigmentation would need to be considered. Such ageing should become a component of all “fitness for purpose” related testing.

5.17. Stability of the release products in retorted, isolated food simulants

The results obtained from the studies that were carried out to establish the stability of melamine, of benzoguanamine and of formaldehyde after each was released from the coatings into the 10% (v/v) aqueous ethanolic food simulant are shown in Table 5.17-1 to Table 5.17-3.

The test results (Table 5.17-1) show that the melamine content of the retorted isolated food stimulant does not change up to the period of four weeks that was studied, during storing under laboratory conditions. Thus, during this storage period, the melamine that is contained in the 10% (v/v) aqueous ethanol simulants is stable and therefore does not degrade or react with other components that might be present in the simulant.

The results in Table 5.17-1 confirm previous conclusions, (Section 5.14) showing the benefits from the presence of the TiO_2 pigment in the coatings that are seen by comparing the hydrolysis behaviour of the three coatings. The PW2-pigmented coating gave lower cross-linker hydrolysis (about 35 %) than the coatings that did contain any pigment (52- 62 %).

Table 5.17-1: Stability of melamine, present in the retorted, isolated food simulants, isolated following the retorting of several epoxy coatings, cross-linked with the hexamethoxymethyl melamine (HMMM cross-linker)

Coating type	Age of retorted simulant	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
Unpigmented epoxy anhydride coatings	1 day	462 ±4	60.8 ±0.5
	1 week	458 ±8	60.3 ±0.7
	4 weeks	478 ±5	62.9 ±1.1
Pigmented epoxy anhydride coatings	1 day	405 ±6	34.9 ±0.6
	1 week	407 ±5	35.0 ±1.2
	4 weeks	407 ±8	34.9 ±0.4
Epoxy phenolic coatings	1 day	157 ±8	54.1 ±0.8
	1 week	158 ±8	54.3 ±0.5
	4 weeks	157 ±11	54.1 ±0.6

Table 5.17-2: Stability of benzoguanamine, present in retorted, isolated simulants, isolated following the retorting of dibutoxymethyl benzoguanamine (DBMB) cross-linked, PW2-pigmented epoxy anhydride coatings

Age of retorted simulant	Benzoguanamine release/ µg/6dm^2	% Hydrolysis of cross-linker
1 day	364 ±4	19.4 ±1.1
1 week	371 ±2	20.3 ±0.6
2 weeks	368 ±4	19.8 ±1.2

Table 5.17-3: Stability of formaldehyde, present in retorted, isolated simulants, from retort of HMMM cross-linked, pigmented epoxy anhydride coatings

Age of retorted simulant	Formaldehyde release/ µg/6dm^2	% Hydrolysis of cross-linker
1 day	8.9 ±0.3	10.7 ±0.5
1 week	8.8 ± 0.5	10.7 ±0.8
2 weeks	8.5 ±0.6	10.4 ±1

The results shown in Table 5.17-2 and Table 5.17-3, respectively indicate that benzoguanamine and formaldehyde were also stable in the simulants, for up to two weeks of storage under ambient conditions. During this time period, there would be no ageing with respect to melamine, benzoguanamine and formaldehyde in the sealed, isolated food simulants from which the coated metal panels were been removed.

These findings are significant since they provide an understanding of whether or not under the conditions of the study, melamine might have a tendency to undergo hydrolysis to derivative compounds such as ammeline, ammelide and cyanuric acid, (see Section 1.10.3.1.1.). The findings are also relevant to indicating the potential formation of the melamine-cyanuric acid complex, MCA, (see Section 1.10.3.1.1). The results obtained imply that the MCA complex is not formed since the concentration of melamine in the retorted food simulants did not change.

5.18. Stability of the isolated retort solutions after additional heating, with respect to further release of melamine

The results from the studies carried out to establish the stability of melamino derivates, in an ethanolic food simulant, after the simulant had undergone further heating, are shown in Table 5.18-1 and Table 5.18-2.

Table 5.18-1: Stability of melamine, after re-heating of isolated simulant following the initial retorting of the stated epoxy coatings

Coating type	Procedure	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
Unpigmented epoxy anhydride coatings	Coating retort	438 ±4	57.6 ±4
	Simulant re-heating	431 ±5	57.4 ±4
PW2-pigmented epoxy anhydride coatings	Coating retort	401 ±8	34.3 ±4
	Simulant re-heating	394 ±5	33.9 ±3
Epoxy phenolic coatings	Coating retort	165 ±8	56.1 ±2
	Simulant re-heating	131 ±9	48.1 ±3

Table 5.18-1 gives the results from the additional reheating of the isolated 10% (v/v) aqueous ethanol food simulants, showing that the concentration of melamine did not change after re-heating. The results confirm previous conclusions, (Section 5.14) showing the benefit of the presence of the TiO_2 pigment in the coatings, seen by comparing the hydrolysis behaviour of the three coatings. The PW2-pigmented epoxy anhydride coating gave less cross-linker hydrolysis (about 34 %) that did those that did not contain a TiO_2 pigment, (58 %).

The overall results show that when the retorted, isolated food simulants were re-heated, the concentration of melamine in the simulants did not change. This implies that during the re-heating, any melamino derivates that might have been contained in the simulants were either stable or did not undertake hydrolysis to release more melamine.

Table 5.18-2: Stability of melamine, after the re-heating of the isolated stimulants, following initial coating retorting, in the PW2-pigmented epoxy anhydride coatings

Cross-linker used	Procedure	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
HMMM	Coating retort	411 ±5	35.4 ±5
	Simulant re-heating	394 ±9	33.9 ±4
HBMM	Coating retort	257 ±4	36.3 ±7
	Simulant re-heating	262 ±6	37.1 ±3
TMTBM	Coating retort	167 ±4	19.5 ±3
	Simulant re-heating	164 ±6	19.2 ±2
DBMB	Coating retort	72 ±7	5.8 ±4
	Simulant re-heating	73 ±6	5.8 ±3

The results show that under the conditions used study, melamine does not have a tendency to undergo hydrolysis to derivative compounds such as ammeline, ammelide and cyanuric acid, (see Section 1.10.3.1.1.) nor does it lead to the formation of the melamine-cyanuric acid complex, MCA, (see Section 1.10.3.1.1).

5.19. The design of epoxy coatings that give no release or limited release of melamine, benzoguanamine and formaldehyde

According to the findings of Sections 5.4 to 5.11, melamine, benzoguanamine and formaldehyde are released, through hydrolysis, from the composite epoxy coatings, during the retorting of the coatings in the selected food simulant at the elevated temperature of treatment and under aqueous conditions. Although the amounts that are released are within current European regulations, it has already been pointed out that the regulations are dynamic and that there are strong indications that the specific migration limits of melamine will be reduced from the current 2.5 mg/kg to 1 mg/kg, (Valspar UK, 2011). Clearly, it is feasible that the limit could be reduced further.

Thus, there is therefore a need to find a long term solution to the migration of melamine, of benzoguanamine and of formaldehyde from coatings when the “parent” compositions are used in can coatings. This means that a viable combination of formulation and curing strategies needs to be adopted by the industry, if the migration issue is to be continually realistically addressed and managed.

Based on the findings from this study, the reduced release/migration of melamine, benzoguanamine and formaldehyde could be achieved by:

- Using lower amounts of the amino cross-linker in the coatings relative to that currently used in the industry.
- Compared with current practice, curing the coatings at a higher temperature for a longer duration is recommended. However, care must be taken in choosing this option to ensure that no discoloration/change in the appearance in the coatings occurred and also no substrate degradation occurred.
- Using TiO_2 pigment particles in formulations. Their presence in the coatings helps to reduce the release/migration of melamine. Optimising the grade of TiO_2 should be attempted.
- To limit melamine release/migration from coatings into a foodstuff or into food simulants, the strategy of an application of double layers can be of a benefit. The second layer needs to be applied and cured after the curing of the first layer, all to the required total film weight thickness.

5.20. Conclusions

The release of melamine, of benzoguanamine and of formaldehyde is not affected by room temperature treatment of the coatings immersed in various extraction media. The results have shown that these treatments do not lead to the release of melamine from the coatings within the detection limit (LOD) or of quantification limit (LOQ).

The release of melamine from the epoxy coatings occurs when the 3% (v/v) aqueous acetic acid or the 10% (v/v) aqueous ethanol is used. There was more release of melamine when the 3% (v/v) aqueous acetic acid food simulant was used because of its lower pH and its greater surface interaction with the coatings.

The release of melamine, of formaldehyde and of benzoguanamine is influenced by the elevated temperatures under aqueous conditions, being dependent on specific conditions. In all cases, the amounts of melamine and formaldehyde that were released into food simulants were within current approved limits set by the European regulatory organisations.

The coatings that were cross-linked with the commercial benzoguanamino cross-linkers released both melamine and benzoguanamine. The release of melamine arises from “impurity” melamino components that were contained in the benzoguanamino cross-linker.

The chemistry of the cross-linker action determines the extent of the release, based on the functionality of the cross-linker and its potential for participation in cross-linking reactions, during the curing of the coatings. Those cross-linkers containing the methylol functionality have a lower potential to release melamine, benzoguanamine and formaldehyde than those cross-linkers that contain alkylated functional groups.

Generally, the greater the amount of amino cross-linker that is used in the coatings, the greater is the amount of melamine that is released when the cured coatings are retorted in ethanolic food simulants. However, the amount of the cross-linker that is used in the coatings does not have a significant effect on either the hardness of the coatings or the thermal degradation pathway.

Increasing the curing temperature, in all cases, strongly reduces the amount of melamine that is released/detected in the resultant, retorted coatings. Increasing the curing time has a minimal effect on the amount of melamine that is detected from retorted coatings.

The presence of the TiO_2 pigment was beneficial, helping to reduce the extent of melamine release and migration from retorted coatings into the 10% (v/v) aqueous ethanolic food simulant. Moreover, the results show that the three coatings that each contained one option of the three pigment grades gave very similar melamine release behaviour. The results indicate that three pigment grades can be used interchangeably with respect to reducing melamine release. Ageing of liquid coatings increased the melamine release behaviour of the coatings.

The use of “wet on dry” coating and curing procedures can help to lower the amount of melamine that is released from the coatings into the 10% (v/v) aqueous ethanol food simulant. The concentration of the migrant species, after release into the 10% (v/v) aqueous ethanol simulant did not change with additional heating of the simulants, provided that the metal panels are removed. However, should the metal panel be included during the additional heating, more migrant species are released.

Chapter 6: Poly(ester) coatings— study of the release and migration of melamine, of benzoguanamine and of formaldehyde

6.1. Introduction

This chapter relates to studies that were carried out on selected food contact poly(ester)-based coatings, namely poly(ester)-urea coatings and poly(ester)-acrylic coatings.

The poly(ester)-urea coatings and the poly(ester)-acrylic coatings represent a newer technology branch relative to epoxy coatings technology. Poly(ester)-based coatings are used in food-based applications. They show excellent adhesion, good mechanical properties and chemical resistance in various media. This study was aimed at reinforcing such good characteristics and providing an understanding of the potential for such coatings to release melamine, benzoguanamine and formaldehyde, when used in food contact-based applications.

Various experiments were carried out using selected representative cross-linkers in investigations of the tendency of the cured poly(ester) coatings to release melamine, benzoguanamine and formaldehyde after the coatings had been retorted in selected aqueous food simulants, at elevated temperatures. Retorting of the coatings at 131 ^{o}C for 1 hour was used to represent the food sterilisation process. The potential for these poly(ester) coatings to release low molecular weight compounds was also investigated through room temperature studies.

During the investigations, the effects of the cross-linker chemistry, the amount of cross-linker in the coatings, the curing conditions, the coating application procedures and the kinetics of the release processes were investigated. Also, the stability of the migrant species in retorted food simulants and their potential for further reaction after release, was investigated.

As described previously, (Chapter 5), the results obtained from all the migration studies are expressed in µg/6dm^{2}, (where 1ppb = 1µg/6dm^{2}), to establish whether or not there was a trend by which the performance of the various cross-linking compounds could be compared. The results were then converted into values of % hydrolysis of cross-linker to melamine. This was achieved by taking into account the molecular weight of each cross-linker, in addition to the thickness and the area of the coatings that were used, in each case.

Another factor to be borne in mind is the influence of the simulant (solution/solubility properties and chemical reactivities) on the release process. For this reason, the results should be interpreted on the basis of the standard 10% (v/v) aqueous ethanol food simulant that was used.

6.2. Release behaviour of poly(ester) coatings– the tendency to yield melamine, benzoguanamine and formaldehyde into various extractant solvents, at room temperature

The results obtained from the room temperature treatment of the cured poly(ester)-urea coatings and the poly(ester) acrylic coatings, in the different solvent systems, are presented in Table 6.2-1. The panels used were coated with HMMM-cross-linked poly(ester) coatings. These were then immersed in the selected solvents at room temperature, for 24 hours.

The results shown in Table 6.2-1 were consistent with those obtained from the study of the epoxy coatings, Section 5.2. The overall results show that following the immersion of coatings into one of the various solvents, at room temperature, (25 ^{o}C), there was no detectable release of migrants melamine, benzoguanamine and formaldehyde were not released after 24 hours. If there was any release, such release was below the limit of detection (<LOD) of the standard methods of analyses that were used. The limit of detection (LOD) values of the techniques used were 17 µg/6dm^2 for melamine, 15 µg/6dm^2 for benzoguanamine and 1 µg/6dm^2 for formaldehyde.

Table 6.2-1: Room temperature treatment of poly(ester) coatings

"Solvent"	TSP of "solvent"	Melamine release	Benzoguanamine release	Formaldehyde release
D.I Water	47.9	<LOD	<LOD	<LOD
Acetonitrile	24.6	<LOD	<LOD	<LOD
Dichloromethane	19.8	<LOD	<LOD	<LOD
Chloroform	19.0	<LOD	<LOD	<LOD
Toluene	18.2	<LOD	<LOD	<LOD
Xylene	18.0	<LOD	<LOD	<LOD
3% Acetic acid	–	<LOD	<LOD	<LOD
10% Ethanol	–	<LOD	<LOD	<LOD

TSP: total solubility parameter $(MPa)^{1/2}$ and LOD: limit of detection

6.3. The effect of cross-linker chemistry on melamine release from cured, retorted poly(ester) coatings

Table 6.2-2 shows the amounts of melamine that several poly(ester) coatings released after each was retorted in the 10% (v/v) aqueous ethanol food simulant. It should be recalled that the amounts of melamine released from all of the coatings are expressed in migration units, in µg/6dm^2, in order for comparison to be made with the 2.5 mg/6dm^2 allowed limit of melamine in food contact materials, (European Union, 2011b)..

In Table 6.2-3, the results are expressed in terms of the percentage of each cross-linker that was hydrolysed during the retorting of the coatings, in the 10% (v/v) aqueous ethanol food simulant. Based on the results in Table 6.2-3, the performances of the coatings and of the cross-linkers that they contain can be compared.

It can be concluded from the results in Table 6.2-3 that under all of the conditions of formulation, application, curing and retorting, to which both the poly(ester)-urea coatings and the poly(ester)-acrylic coatings were subjected, the amount of melamine released was below the current European SML acceptable limits.

Table 6.2-2: Amount of melamine released from the poly(ester) coatings that were cross-linked with the stated different amino cross-linkers, cured for 12 minutes at 195 °C, retorted in 10% (v/v) aqueous ethanol, at 131 °C, for 1 hour

	Melamine release/ µg/6dm^2	
Cross-linker	Poly(ester)-urea coatings	Poly(ester)-acrylic coatings
HMMM-1	333 ±5	1254 ±3
HMMM-2	338 ±7	1332 ±3
HMMM-3	345 ±2	1471 ±2
HBMM-1	246 ±5	444 ±4
HBMM-2	233 ±7	396 ±2
HBMM-3	215 ±8	463 ±5
MMTC-1 (TMTBM)	328 ±4	322 ±5
MMTC-2	248 ±2	314 ±4
MMTC-3	241 ±5	318 ±2
MMTC-4	344 ±3	372 ±3
DBMB	133 ±2	240 ±3

Table 6.2-3: % Hydrolysis of cross-linker, occurring as a consequence of autoclaving the poly(ester) coatings that were cross-linked with the stated different amino cross-linkers, cured for 12 minutes at 195 °C, retorted in 10% (v/v) aqueous ethanol, at 131 °C, for 1 hour

	% Hydrolysis of cross-linker to melamine	
Cross-linker	Poly(ester)-urea coatings	Poly(ester)-acrylic coatings
HMMM-1	9 % ±0.4	11 % ±0.8
HMMM-2	9 % ±0.6	11 % ±0.5
HMMM-3	9 % ±0.4	13 % ±0.2
HBMM-1	11 % ±0.5	6 % ±0.8
HBMM-2	10 % ±1	6 % ±1
HBMM-3	9 % ±1	7 % ±1
MMTC-1 (TMTBM)	10 % ±0.4	4 % ±0.4
MMTC-2	8 % ±0.6	4 % ±0.3
MMTC-3	9 % ±0.5	4 % ±0.3
MMTC-4	8 % ±2	3 % ±0.6
DBMB	3 ±0.5	2 ±0.6

The members of each cross-linker class gave similar melamine release behaviour. Differences between the behaviour of individual cross-linkers in each particular group, arise because of differences in the degrees of their substitution, brought about during the manufacture of each cross-linker. The amounts of melamine that were released by hexamethoxymethyl melamine (HMMM)-cross-linked poly(ester)-acrylic coatings were significantly greater than those released by their poly(ester)-urea counter parts, because of greater loading of cross-linker in the former class (Section 3.3.6). However, the overall hydrolysis of the cross-linkers in the two sets of coatings was comparable because of similarities in the chemistries of the base poly(ester) polymeric binders that were used in the coating formulations.

The lower hydrolysis achieved using the methylol melamine-type cross-linkers (MMTC) and the dibutoxymethyl benzoguanamine cross-linker (DBMB) arises due to reactivity differences between them and the alkylated cross-linkers, HMMM and HBMM. Both the MMTC and the DBMB cross-linkers contain the methylol functionality allowing them to develop more cross-linking during curing as a result of the availability of the highly reactive $–CH_2OH$ functional groups. It is an established fact that ether functional groups (C–O–C), in HMMM and HBMM are less reactive than hydroxyl functional groups (–OH), as contained in the MMTC and DBMB cross-linkers, (Jacobs, 1997). There is also a tendency, during the curing of the coatings, for the alkylated cross-linkers to lose their etherifying alcoholic functional group, allowing for them to cross-link with the bulk binder through $–CH_2OH$. Methylol-type cross-linkers will directly enter into cross-linking reaction since they do not need to lose any alcoholic group. This point is further discussed in Section 7.7.

In all cases, the dibutoxymethyl benzoguanamine (DBMB)-cross-linked coatings gave the least release of melamine, through hydrolysis. Compared to the other cross-linkers, the DBMB contains the least amount of active melamino component that could potentially be hydrolysed. As explained in Section 2.8.3, DBMB is predominantly based on benzoguanamino chemistry. Any melamine release therefore has its origin in the melamino impurities (or the small amount of melamine as an additive) that the DBMB cross-linker contained.

6.4. The kinetic aspects of the release of melamine from cured, retorted poly(ester) coatings

The results derived from a partial kinetic study of the release of melamine from poly(ester) coatings are shown in Figure 6.4-1 to Figure 6.4-4. For each coatings class, the results are expressed in terms melamine release units and in the percentage of the cross-linker component of each coating that was hydrolysed, during the retorting procedures that were carried out at 131 ^{o}C.

Even when the various coatings in each poly(ester) class were retorted beyond the standard 131 ^{o}C for 1 hour, with respect to European regulations, the amounts of melamine that the coatings released did not exceed the current allowance limit, (European Union, 2011b). It should be recalled that the 131 °C for 1 hour retort is the standard used to represent extreme food sterilisation. Therefore, under the conditions studied, the coatings would not present any safety concerns should they be used in food contact applications.

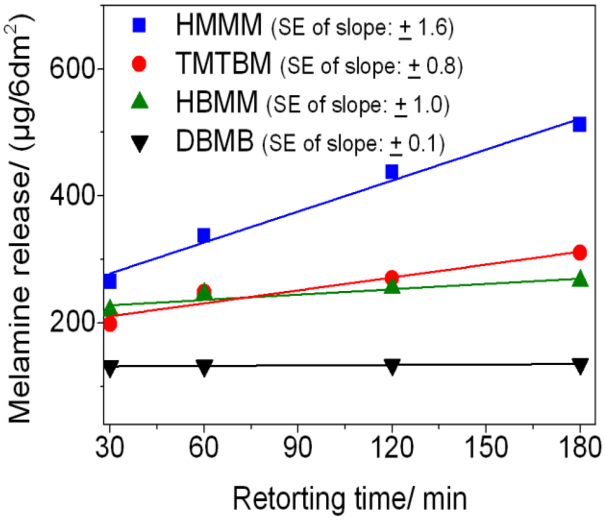


Figure 6.4-1: Poly(ester)-urea coatings containing one of the different selected cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

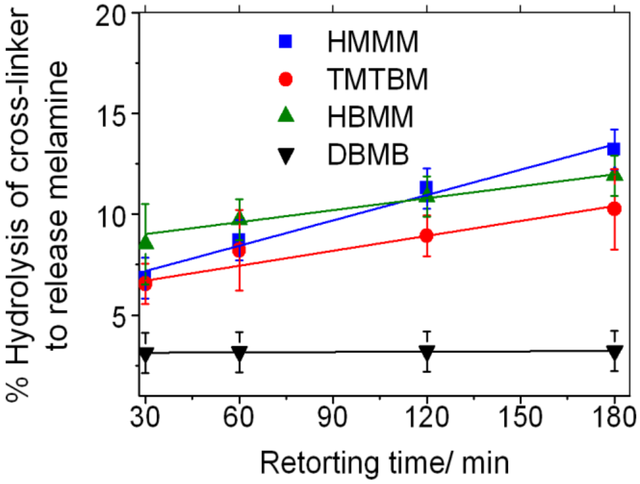


Figure 6.4-2: Poly(ester)-urea coatings containing one of the different selected cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

The more apparent observations that can be made from studying the data in Figure 6.4-1 and Figure 6.4-2 are summarised below:

- There is a potential for melamine release from poly(ester)-urea coatings into the food when the canned food undergoes autoclaving and/or sterilisation during processing. The longer the period under which the high temperature treatments are applied, the greater is the tendency of the coatings to release melamine, until all of the melamine is released.

- The rate of release is proportional to the amount available for release.

- If Figure 6.4-1 and Figure 6.4-2 were each extrapolated to the zero retorting time, the results would indicate that in each case, that melamine was already available for release even before retorting of the coatings commenced. This point agrees with the findings in Section 6.15, where it was shown that the generation of melamine might have commenced during the curing of the coatings. However, any melamine that might have been released during the curing process must have been locked in the coating as a result of film consolidation through curing. This available melamine could be extracted if the coatings are subjected to elevated temperature retorting under aqueous conditions. It has already been shown that the room temperature treatment of the coatings in “solvents” does not lead to any release of melamine, (Section 6.2).

- The melamine release kinetics are largely dependent on the chemistry of each cross-linker. The TMTBM and the DBMB cross-linkers possess methylol functional groups while the HMMM and the HBMM contain alkylated groups. The reactivity of the two different groups differs, (Jacobs, 1997). This point was covered in detail in Section 6.3.

- When the dibutoxymethyl benzoguanamine (DBMB) cross-linker was used in the coatings, any melamine available for extraction was released during the first 30 minutes of the retorting procedure. It should be recalled that this cross-linker has a limited capacity to hydrolyse to melamine, since the bulk of the cross-linker composition is based on benzoguanamino chemistry, (Inchem.org, 2001). This point was discussed in detail in Section 6.3.

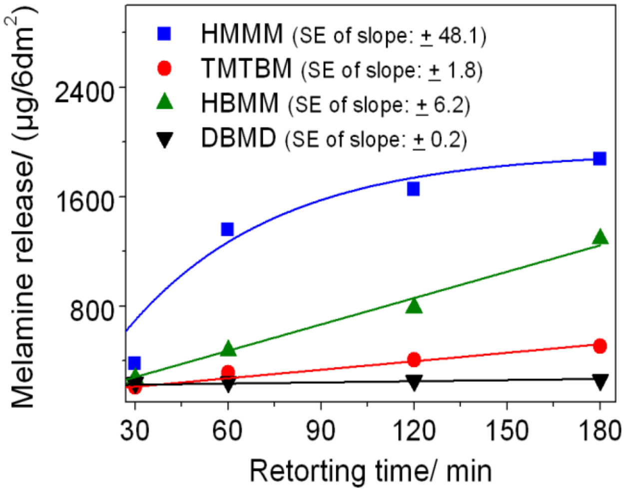


Figure 6.4-3: Poly(ester)-acrylic coatings containing one of the different selected cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

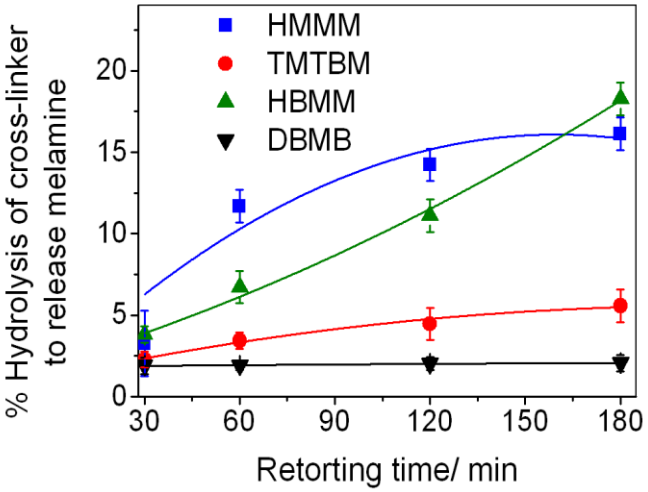


Figure 6.4-4: Poly(ester)-acrylic coatings containing one of the different selected cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

With most of the poly(ester)-acrylic coatings, melamine release into the 10% (v/v) ethanolic food simulant increased with an increase in the retorting time, the exception being when the dibutoxymethyl benzoguanamine (DBMB) cross-linker was used, Figure

6.4-3. As stated earlier, this melamine release is related to the impurities/additive in the benzoguanamine cross-linker, (Inchem.org, 2001).

The overall results mean that there is a potential for melamine release from amino coatings into the food when the canned food components undergoes autoclaving and/or sterilisation. The longer the period under which the high temperature treatments are applied, the greater is the tendency of the coatings to release melamine, until all of the melamine is released. The rate of release is proportional to the amount available for release.

The role that the cross-linker chemistry plays in the release of melamine and the hydrolysis of the cross-linker components of the coatings to yield melamine was discussed in details in Section 6.3.

6.5. Kinetic aspects of the release of benzoguanamine from cured, retorted coatings

The results from the study of the retort-time-dependent release of benzoguanamine from the poly(ester) coatings are shown in Figure 6.5-1.. In Figure 6.5-2, the results depict the percentage of the cross-linker component of each coating that was hydrolysed during the retort procedures, carried out at 131 °C.

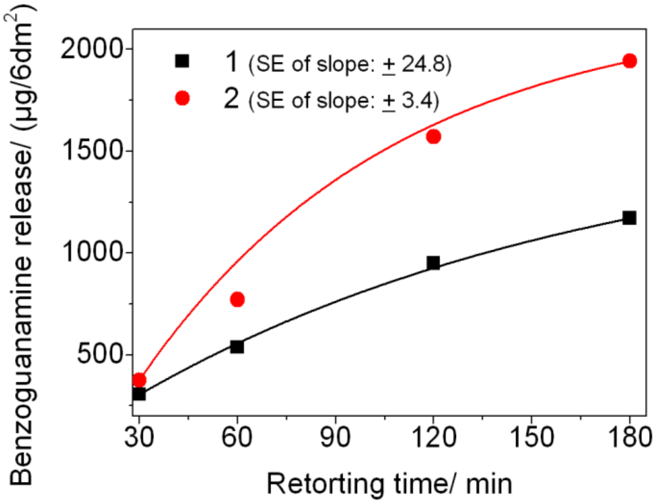


Figure 6.5-1: Dibutoxymethyl benzoguanamine (DBMB) cross-linked coatings, 1: poly(ester)-urea coating and 2: poly(ester)-acrylic coating

In all cases, the amount of benzoguanamine released from the coatings during retort procedures increased with an increase in retorting time. Under the conditions for which the coatings were studied, the amounts released were within the current approved legislations, (European Union, 2011a). The results show that there is a potential for benzoguanamine release, from the poly(ester) coatings into the food, when the coatings are used in cans. The rate of cross-linker hydrolysis to benzoguanamine is proportional to the amount available for release.

The amount of benzoguanamine that was released by each coating depends on the amount of the dibutoxymethyl benzoguanamine (DBMB) cross-linker that was used in formulation, according to industry specifications, (Figure 6.5-1). In Section 3.3.5 and Section 3.3.6 it was shown that 5% of cross-linker and 10% of cross-linker were used in the total formulation (much higher levels than in of the epoxy coating formulations), respectively for the poly(ester)-urea coatings and the poly(ester-acrylic coatings. Bearing this in mind, the results in Figure 6.5-1 show that the two poly(ester) coatings behave similarly.

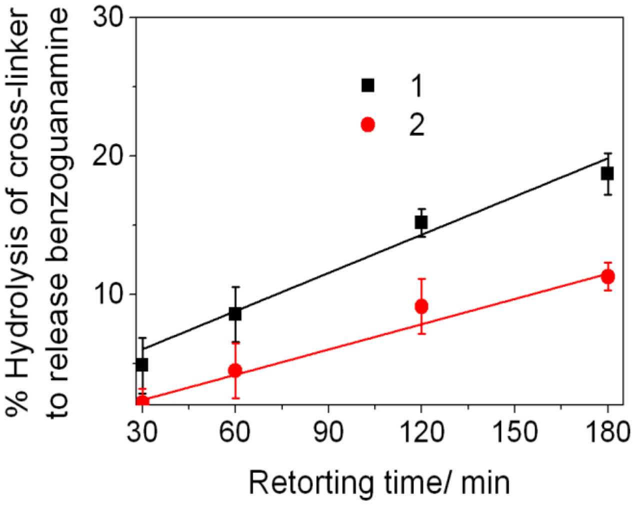


Figure 6.5-2: Dibutoxymethyl benzoguanamine (DBMB)-cross-linked coatings, 1: poly(ester)-urea coating and 2: poly(ester)-acrylic coating

Both Figure 6.5-1 and Figure 6.5-2 show that the release of benzoguanamine and the hydrolysis of a dibutoxymethyl benzoguanamine (DBMB) cross-linked coating depend on the retorting time. According to Figure 6.5-2, [Hydrolysis of cross-linker in poly(ester)-

urea coating] > [Hydrolysis of cross-linker in poly(ester)-acrylic coating]. The differences in hydrolysis at the 131 ^{o}C for 1 hour are minor. Thus, under food sterilisation conditions, the behaviour of the DBMB in both coating types is similar.

6.6. Kinetic aspects of the release of formaldehyde from cured, retorted poly(ester) coatings

The effect of retorting time on the release of formaldehyde from the poly(ester) coatings can be seen in Figure 6.6-1 to Figure 6.6-4. For each coating, the results are expressed in terms of formaldehyde release units and in the percentage of the cross-linker component of each coating that was hydrolysed during the retorting procedures, carried out at 131 ^{o}C.

The release of formaldehyde increased with an increase in the retorting time. The extent of the release depended on the chemistry of the amino cross-liker that was used in formulation and reactivity of each cross-linker compound during the curing of the coatings. In all cases, the rate of formaldehyde release is proportional to the amount available for release. Thus, one would expect a maximum in the release profile as the amount for release becomes exhausted.

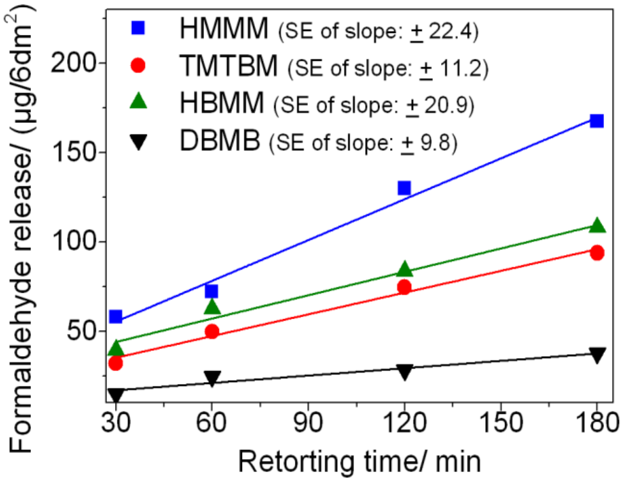


Figure 6.6-1: Poly(ester)-urea coatings containing the selected different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

The release behaviour of formaldehyde from the various poly(ester)-urea coatings is described in Figure 6.6-1. The figure shows the release of formaldehyde by the retorted coatings into the 10% (v/v) aqueous food depends on the retorting time. In order to explain the contribution of cross-linker chemistry to the release process and to compare the slopes of the graphs, Figure 6.6-2 should be considered as the normalised version of Figure 6.6-1. This is because, in assembling Figure 6.6-2, the differences in film thickness and in solids content of all of the coatings were taken into account.

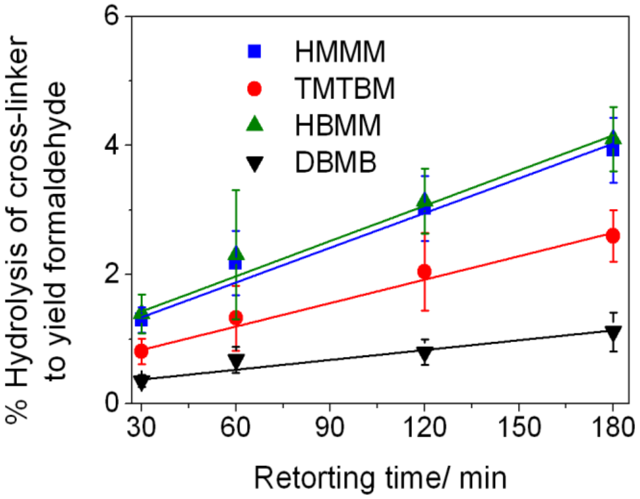


Figure 6.6-2: Poly(ester)-urea coatings containing the selected different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

According to Figure 6.6-2, the order of hydrolysis of the cross-linker component of the coatings, to release formaldehyde, was [HMMM cross-linked coatings] = [HBMM cross-linked coatings] > [TMTBM cross-linked coatings] > [DBMB cross-linked coatings]. Previously, TGA studies indicated that both the HMMM and the HBMM exhibit similar decomposition profiles leading to the formation of melamine and formaldehyde, Section 2.8.6. It is not surprising therefore, that, the two cross-linkers show similar formaldehyde release. The HMMM and the HBMM cross-linked coatings show a similar overall hydrolysis pattern because they have comparable chemical functionality since. Both are etherified, amino cross-linkers. The TMTBM and the DBMB cross-linked coatings gave less hydrolysis of cross-linker to formaldehyde because, during curing, a greater extent of cross-linking reaction was achieved compared to when the other cross-linkers were used.

The DBMB cross-linked coating gave the lowest release of formaldehyde and lowest extent of cross-linker hydrolysis. Compositionally, the DBMB has only two formaldehyde-forming groups, whereas the three other cross-linkers, possess four groups with formaldehyde formation capability.

The corresponding formaldehyde release behaviour of the various poly(ester)-acrylic coatings are presented in Figure 6.6-3 and Figure 6.6-4. All of retort tests were carried out using the 10% (v/v) aqueous food simulant, at the food sterilisation temperature of 131 °C.

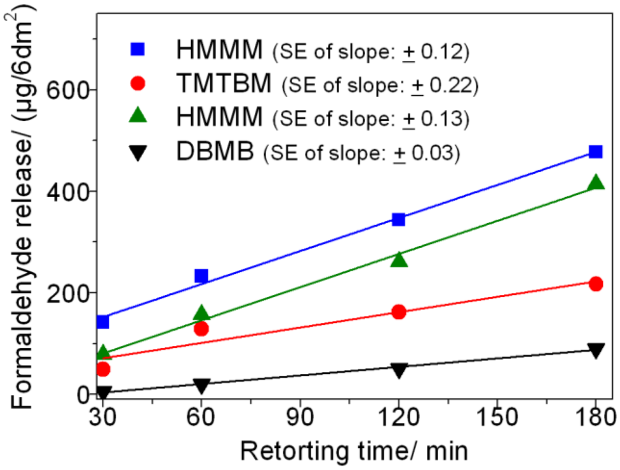


Figure 6.6-3: Poly(ester)-acrylic coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

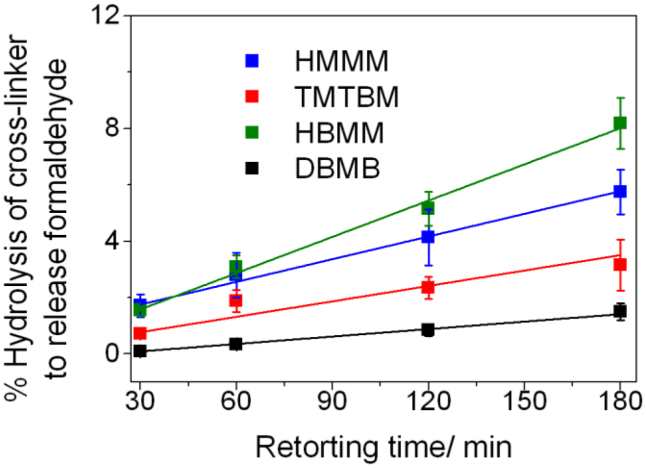


Figure 6.6-4: Poly(ester)-acrylic coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

In support of the findings given in Sections 6.4 and 6.5, the results shown in Figure 6.6-3 and Figure 6.6-4 confirm the potential of the two poly(ester) coatings to undergo hydrolysis, leading to the release of formaldehyde into the 10% (v/v) aqueous ethanolic food simulant. Thus, during the industrial processing of canned foods, the longer the period over which the high temperature treatments are applied, the greater would be the tendency of such coatings to release formaldehyde. Further relevant considerations are:

1. The kinetics of the hydrolysis to formaldehyde can be considered to be complex. Formaldehyde formation/release increases with an increase in retorting time. Thus, the formaldehyde release process continues until the source of formaldehyde, from the cross-linker, is exhausted.

2. The extent of the release and the extent of the cross-linker hydrolysis is dependent on the type and the chemistry of the amino cross-linker that is used in formulating the coatings. This point was covered in Section 6.3.

3. In all cases, the amounts of formaldehyde that the coatings release did not exceed the 15 mg/6dm^2 limit, easily complying with current European regulations, (European Commission, 2005b).

4. Point 3 remains true even when the poly(ester)-acrylic coatings are retorted for longer than the standard 1 hour at the 131 ^{o}C food sterilisation temperature.

6.7. The effect of the amount of amino cross-linker used in formulations on the performance of the poly(ester) coatings

Figure 6.7-1 to Figure 6.7-6 contain the results obtained from various studies into the performance properties of poly(ester) coatings when the amounts of amino cross-linker in the coatings were varied. For each coating, the results are expressed in terms of melamine release units and in terms of the percentage of the cross-linker component of each coating that was hydrolysed during the retort procedures, carried out at 131 ^{o}C, for 1 hour.

Figure 6.7-1 shows that with respect to cross-linker content of the coatings, the melamine release process exhibited by the coatings follow a time dependent profile. The amount released depends on the concentration of cross-linker that the coatings contain. When 5% of a cross-linker is used in the poly(ester)-urea coatings and when 10% of a cross-linker is used in poly(ester)-acrylic coatings, the amounts of melamine that can possibly be released, using the conditions under which the coatings were studied, do not exceed the current European regulations.

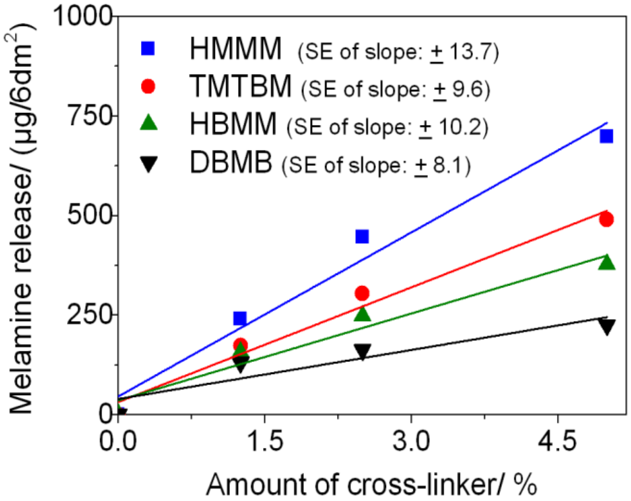


Figure 6.7-1: Poly(ester)-urea coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

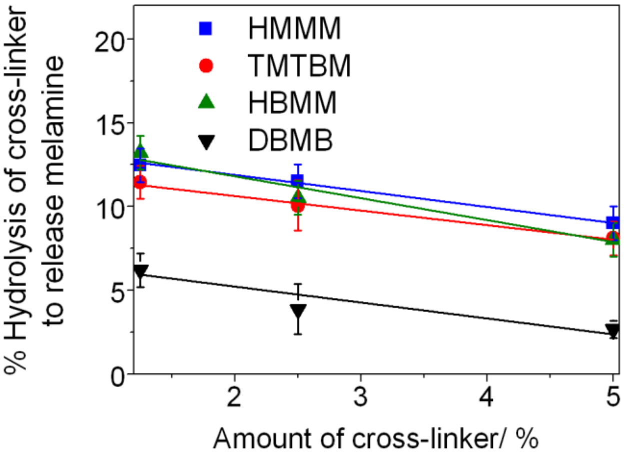


Figure 6.7-2: Poly(ester)-urea coatings containing one of the selected different cross-linker, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

The results given in Figure 6.7-1 and Figure 6.7-2 show that the melamine release from, for the poly(ester)-urea coatings increased with an increase in the amount of cross-linker in the coating, even though the extent of hydrolysis changes only slightly with variations in the cross-linker content. Figure 6.7-2 show that the hydrolysis of the cross-linker component of the poly(ester)-urea was in the order [Hydrolysis of HMMM cross-linked coating] = [Hydrolysis of HBMM cross-linked coating] = [Hydrolysis of TMTBM cross-linked coating] > [Hydrolysis of DBMB cross-linked coating]. In all four cases, the hydrolysis was well below that achieved by epoxy coatings largely because of the excellent barrier properties of the poly(ester) coating. As explained in previous sections, impurities/by-products arise in the benzoguanamine cross-linker synthesis, (Inchem.org, 2001).

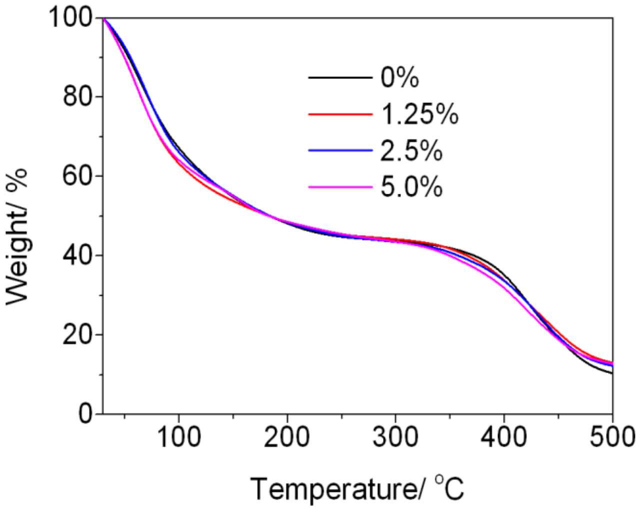


Figure 6.7-3: Poly(ester)-urea coatings containing different amounts of the cross-linker (hexamethoxymethyl melamine, HMMM)

An increase in the cross-linker content of the coatings up to 5%, does not significantly change the thermal decomposition of the coatings, (Figure 6.7-3). Such action did not affect the hardness of the coatings. The above findings agreed with the findings in Section 5.8. The thermal behaviour of the coatings is dominated by the polymeric binders that they contain. When the cross-linker contents of the coatings were increased, the hardness values of the coatings remained at 176 HU.

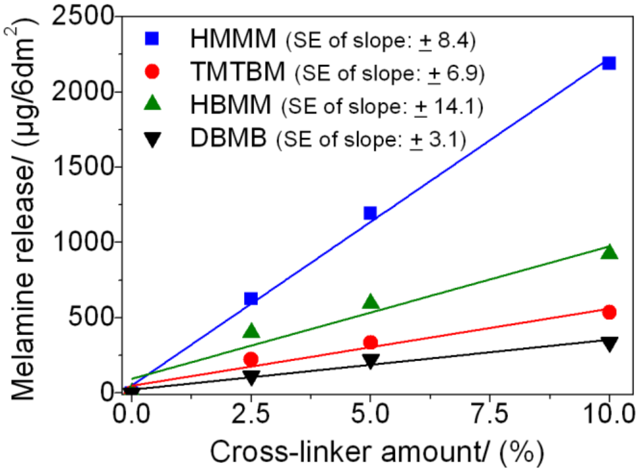


Figure 6.7-4: Poly(ester)-acrylic coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

The trends in Figure 6.7-4 agree with those shown Figure 6.7-1. The amount released into the 10% (v/v) aqueous ethanolic food simulant depends somewhat on the amount of original cross-linker in the coatings. Figure 6.7-5 shows that in all four cases, the extent of hydrolysis was well below that achieved by the epoxy coatings, largely because of the excellent barrier properties of the poly(ester)-acrylic coatings. The difference in the extents of melamine release or the extents of cross-linker hydrolysis depends largely on the choice of the cross-linker. This point was covered in detail in Section 6.3, where the contribution of the cross-linker’s chemistry on the release process was discussed.

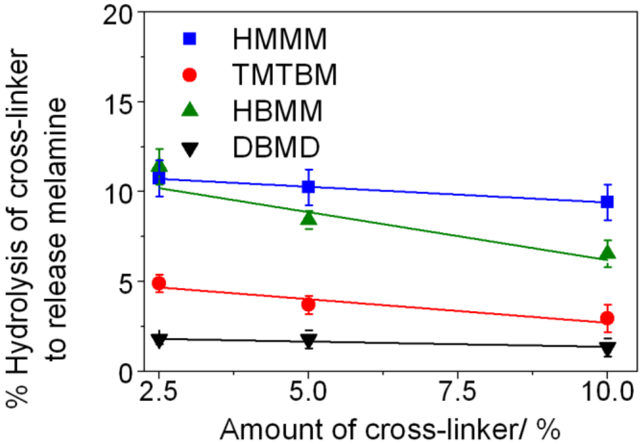


Figure 6.7-5: Poly(ester)-acrylic coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

Figure 6.7-6 shows that when the amount of the cross-linker in the poly(ester)-acrylic coatings was increased, the thermal degradation pathways of the coatings did not change uniformly. Only minor changes to the solids content of the coatings were observed. In addition, the hardness values of the coatings did not change, centred around 146 HU for the poly(ester)-urea coatings and 107 HU for the poly(ester)acrylic coatings, demonstrating the influence of the binder and the binder-cross-linker relationship on the hardness of the resulting composite coating.

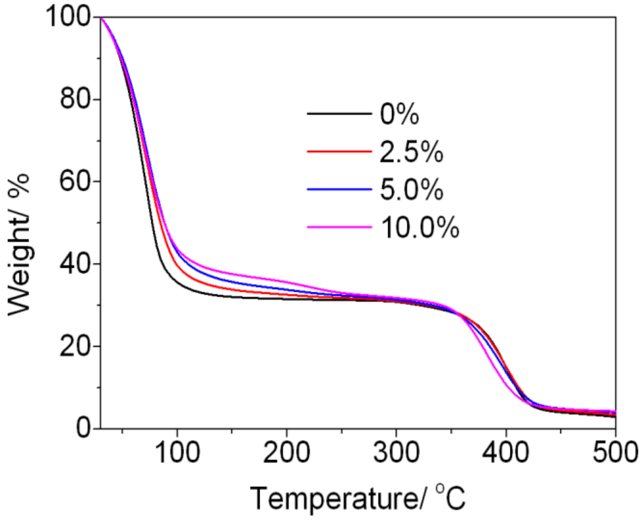


Figure 6.7-6: Poly(ester)-acrylic coatings containing different amounts of cross-linker (hexamethoxymethyl melamine, HMMM)

6.8. The effects of curing time and of curing temperature on the release of melamine

The influence of the curing time on melamine release from the poly(ester) coatings into the ethanolic food simulant is clearly shown in Figure 6.8-1 to Figure 6.8-4. The corresponding results relating to the influence of curing temperature on melamine release from the poly(ester) coatings into the 10% (v/v) aqueous ethanol food simulant are shown in Figure 6.8-5 to Figure 6.8-8.

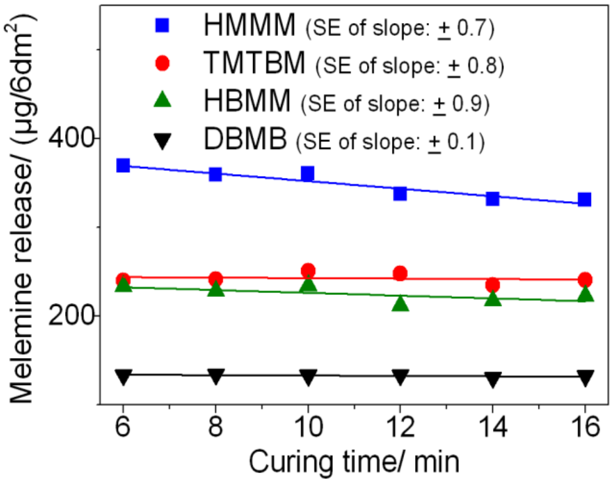


Figure 6.8-1: Poly(ester)-urea coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

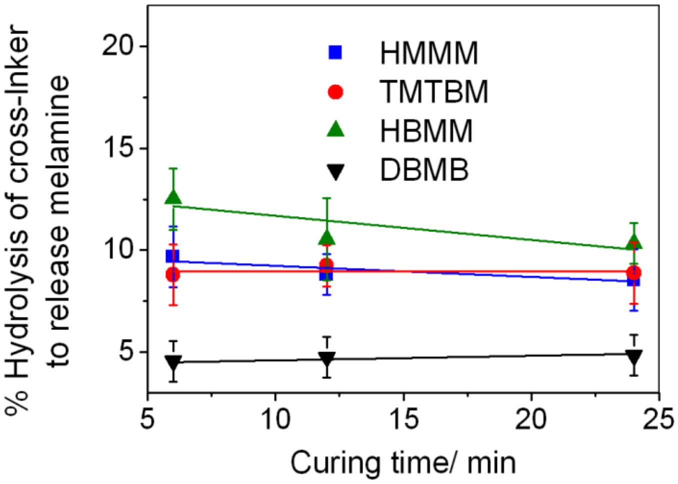


Figure 6.8-2: Poly(ester)-urea coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

Figure 6.8-1 and Figure 6.8-2 show the effect of curing time on the release of melamine and on the hydrolysis of cross-linker component of poly(ester)-urea coatings. Figure 6.8-2 is the normalised version of Figure 6.8-1. Thus, the results show that [Hydrolysis by HBMM cross-linked coatings] > [Hydrolysis by HMMM cross-linked coatings] = [Hydrolysis by TMTBM cross-linked coatings] > [Hydrolysis by DBMB cross-linked coatings]. This order was achieved because of the differences in the potentials for the cross-linkers to react during curing and their resistance to hydrolysis. TMTBM and the DBMB, are the more reactive amongst the three cross-linkers on the basis of possessing a more labile methylol functional group as opposed to the ether groups of the HMMM and the HBMM, (Jacobs, 1997). This contribution of cross-linker chemistry on the release process was discussed in detail in Section 6.3.

For the poly(ester)-urea coatings that were studied, according to Figure 6.8-1 and Figure 6.8-2, an increase in the curing time at the standard curing temperature has a limited effect on melamine release and on the hydrolysis of the cross-linkers. It is very likely that standard 12 minutes curing might have been sufficient for the coatings to achieve a sufficient cross-link density. The additional period that the coatings were kept in the oven therefore had a limited effect on network/film formation. These findings agree with those described in Section 5.9, relating to epoxy phenolic coatings.

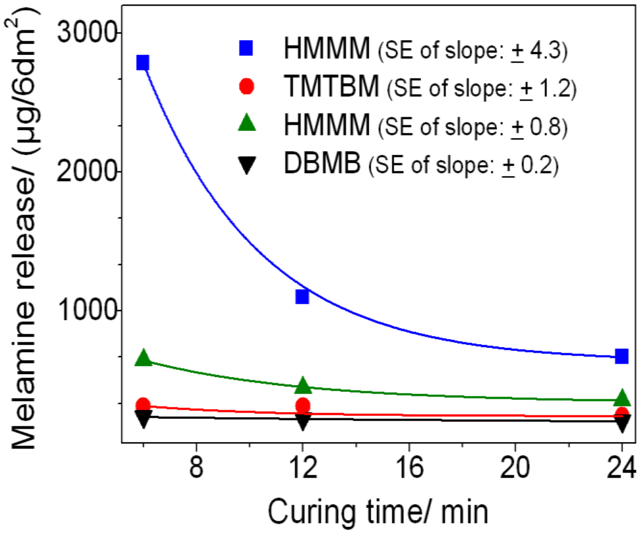


Figure 6.8-3: Poly(ester)-acrylic coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

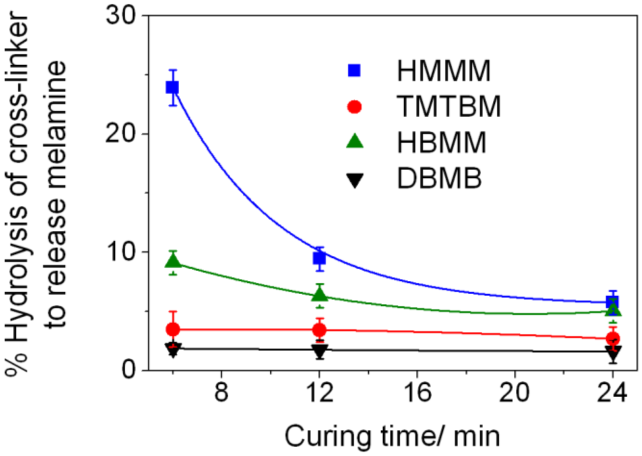


Figure 6.8-4: Poly(ester)-acrylic coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

The corresponding results for the effect of curing time on melamine release from the poly(ester)-acrylic coatings are shown in Figure 6.4-3 and Figure 6.4-4. According to the results, an increase in the curing time at the standard curing temperature has a limited effect on melamine release and on hydrolysis of the cross-linker component of the coatings. The interpretations agree with those for the epoxy phenolic coatings, Section 5.9. Due to inherent composition of the HMMM cross-linker, its compatibility with the bulk coating, whether or not sufficient mixing was achieved during formulation, the HMMM cross-linked coating did not achieve sufficient cross-linking after curing for 6 minutes. Thus, the greatest amount of melamine was released in this instance.

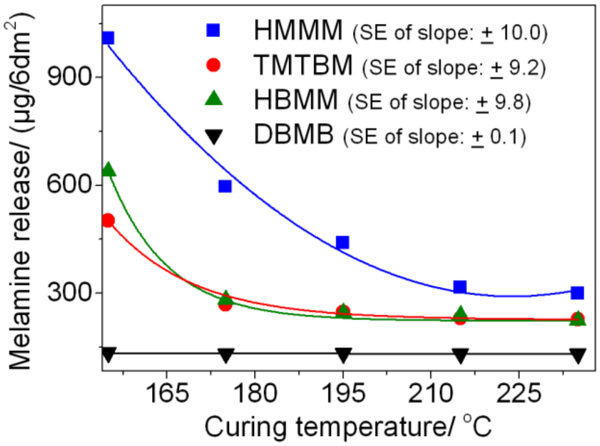


Figure 6.8-5: Poly(ester)-urea coatings containing one of the selected different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

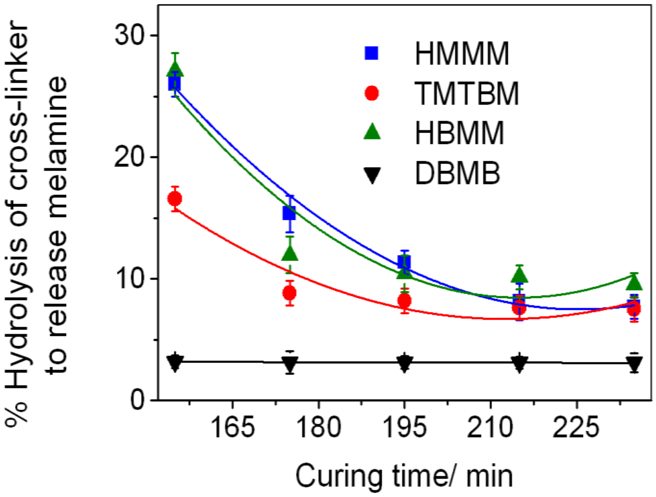


Figure 6.8-6: Poly(ester)-urea coatings containing one of the selected cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

From the results shown in Figure 6.8-5 to Figure 6.8-8, it can be concluded that increasing the curing temperature, generally reduces the amount of melamine that is released from both the poly(ester)-urea coatings and the poly(ester) acrylic retorted coatings. The extent of cross-linker hydrolysis was reduced when the curing temperature was increased, in stages from 155 ^{o}C to 235 ^{o}C, for the standard 12 minutes of curing time. The melamine release achieved by poly(ester)-urea coatings compares with that achieved by the poly(ester)-acrylic coatings. A close analysis of the two sets of results shows that:

- Except for the HMMM cross-linked poly(ester)-acrylic coatings, under all of the curing conditions through which the coatings were formulated, applied, cured and retorted, the amount of melamine released was well below the current European acceptable limit of 2.5 mg/6dm^{2} for food contact materials, (European Union, 2011b). As shown in Figure 6.8-7, the HMMM cross-linked poly(ester)-acrylic coatings could not meet the SML of 2.5 mg/6dm^{2}. However, the curing temperatures were below the industry 195 ^{o}C coating.

- The poly(ester)-urea coatings gave less overall release of melamine at each stage of the process compared with the amount released by poly(ester)-acrylic coatings. This arises because of difference in the concentration of cross-linker that used formulation amongst the coatings, Section 3.3.5 and Section 3.3.6. However, the overall pattern of melamine release was similar. Both coatings contained similar binder compositions.

- Curing the coatings for the standard time of 12 minutes at a higher temperature allows for more cross-linking to be achieved, resulting in a more inter-locked structure, making it more difficult for melamine to be released during the retorting of the coatings in the 10% (v/v) aqueous ethanol food simulant.

- TMTBM cross-linked coatings gave less hydrolysis of the cross-linker to melamine than did the HMMM cross-linked coatings or the HBMM cross-linked coatings. During curing, a greater cross-linking extent would have been achieved compared to when the HMMM and the HBMM cross-linkers were used. TMTBM contains highly reactive methylol groups in comparison to the HMMM and the HBMM, both of which contain a less reactive ether functionality, (Jacobs, 1997).

- It has been established that curing the coatings at temperature that is greater than the commercially used 195 °C, for a consistent 12 minutes, would give a route to lowering the extent of melamine release.

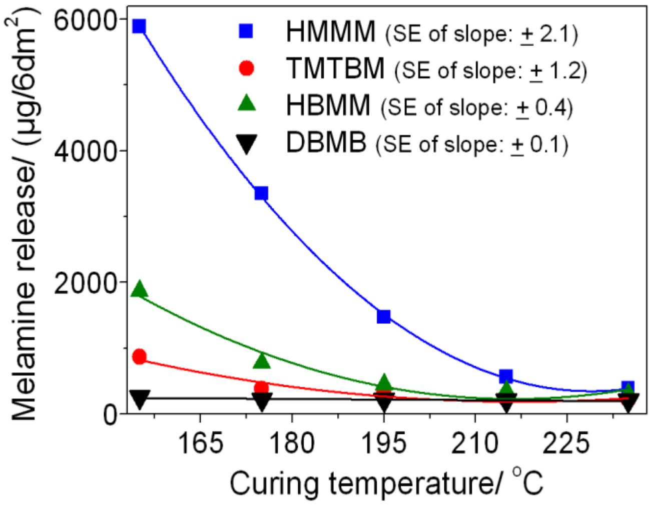


Figure 6.8-7: Poly(ester)-acrylic coatings containing one of the different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

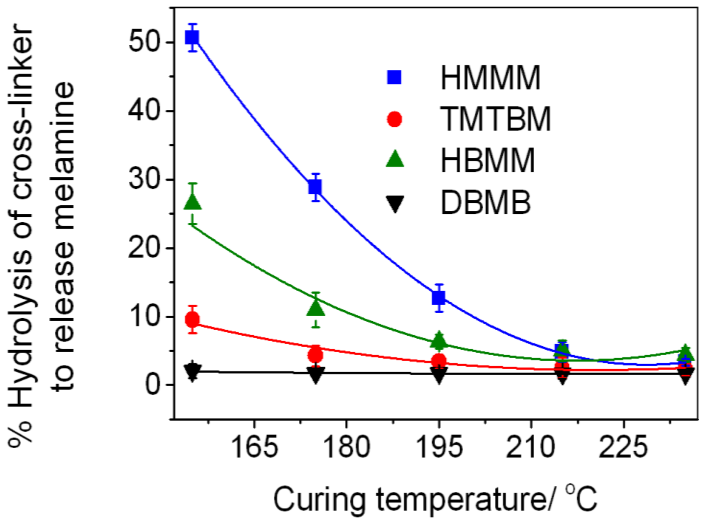


Figure 6.8-8: Poly(ester)-acrylic coatings containing one of the different cross-linkers, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

6.9. Surface energetics and wetting of coatings—the effects of curing time and of curing temperature

The results from the contact angle studies, carried out to investigate the extent of interaction between the 10% (v/v) aqueous ethanolic food simulant and the surface of the coatings that had been cured under various conditions are shown in Figure 6.9-1 and Figure 6.9-2.

Figure 6.9-1 shows that the 10% (v/v) aqueous ethanol food simulant exerted greater surface interaction with those coatings that were cured for the shorter times. This finding agrees with the results given in Section 6.8, where the melamine release from the coatings and the HMMM cross-linker hydrolysis decreased with an increase in the curing time. The following points are worthy of notice:

- Since each coating class gave values of contact angles that differed from another class of coating, the surface wettability properties of each coating would be expected to be different. The values of contact angle were similar. The differences are not significant.

- The more the coatings were cured, the denser was the cured products, the chances of melamine release being more reduced. The results suggest that the change in curing time and the change in surface wetting can be correlated.

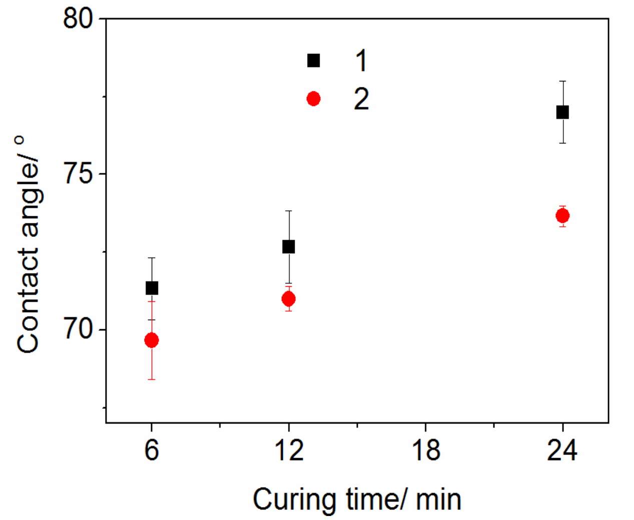


Figure 6.9-1: Hexamethoxymethyl melamine (HMMM) cross-linked coatings, cured at 195 °C; 1: poly(ester)-urea coating, 2: poly(ester)-acrylic coating. Tests carried out with 10% (v/v) aqueous ethanol food simulant composition

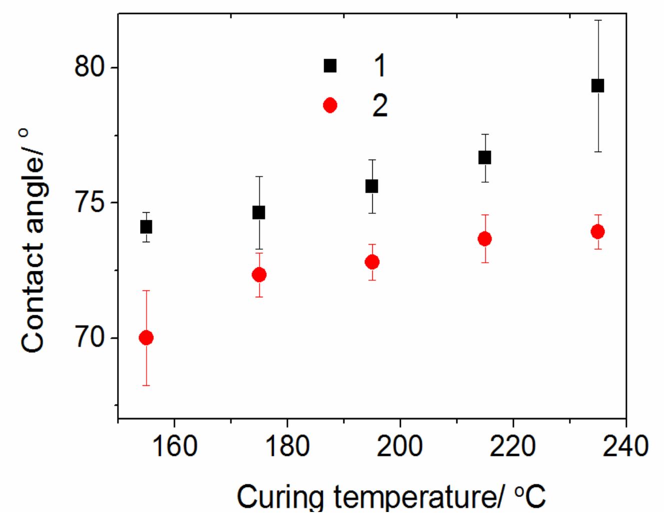


Figure 6.9-2: HMMM cross-linked coatings, cured for 12 minutes; 1: poly(ester)-urea coating, 2: poly(ester)-acrylic coating. Tests carried out with 10% (v/v) aqueous ethanol

The effects of the curing temperature on surface energetics are shown in Figure 6.9-2. The 10% (v/v) aqueous ethanolic food simulant exerted more interfacial interaction with the coatings that were cured at a lower temperature. In Section 6.8, it was stated that melamine was released most from those coatings that were cured for a lower temperature. The greater the curing temperature, the greater would be the cross-link density achieved in the coating. Thus, fewer migrants would be released because of the lesser surface interaction between the food simulant and the coating.

6.10. Drawbacks associated with an increase in the curing time or an increase in the curing temperature

The results in this section concern an investigation into establishing whether or not an increase or a decrease of either the curing time or the curing temperature would affect the appearance of the coatings. Thus, changes in the reflectance, the lightening or the darkening of the coatings were monitored. The results help to provide some prediction and of the appearance of coatings, as a quality control measure.

Figure 6.10-1 to Figure 6.10-4 relates to the poly(ester)-urea coatings and the poly(ester)-acrylic coatings that were cured at the standard 195 °C for various time periods. The wavelength region of 400-700 nm (visible region of the electromagnetic spectrum) was used so that the measurements to be correlated with visual assessments of the panels when monitoring/observing the uniformity of different areas of the coated panels, indirectly establishing the uniformity of the consequences of the curing process.

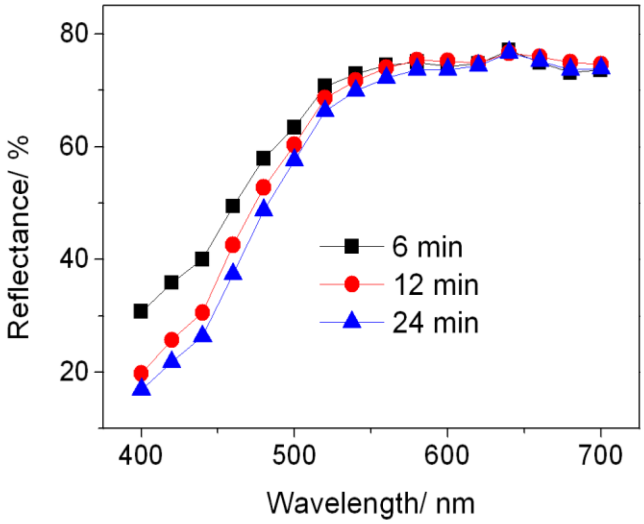


Figure 6.10-1: Surface reflectance behaviour of HMMM cross-linked poly(ester)-urea coatings, cured at 195 °C, for various time periods

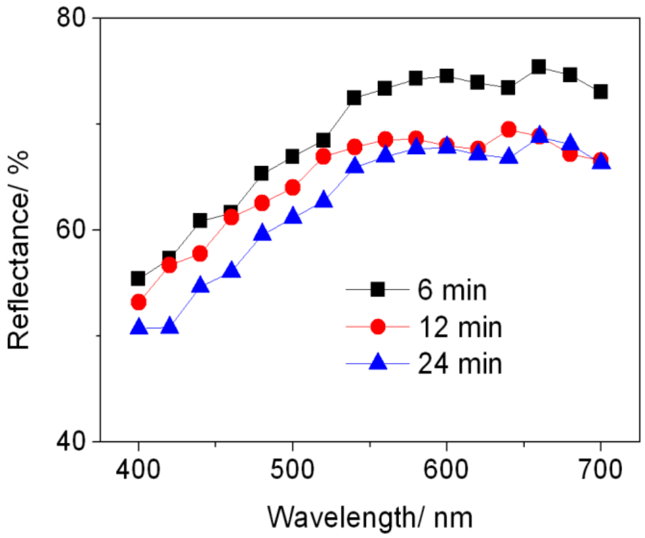
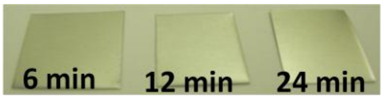
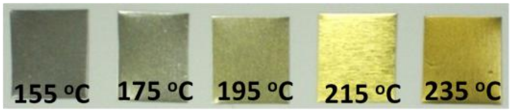
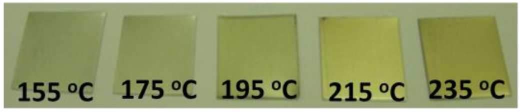


Figure 6.10-2: Surface reflectance behaviour of HMMM cross-linked poly(ester)-acrylic coatings, cured at 195 °C, for various time periods

The spectral reflectance curves shown in Figure 6.10-1 to Figure 6.10-4 indicate that changes in the curing conditions affect the reflectance characteristics of the coatings. The reflectance from the coatings decreased when the curing time was increased. The data given in Figure 6.10-3 and Figure 6.10-4 show a decrease in reflectance with an increase in the temperature at which the coatings were cured. The changes can be attributed to molecular weight increase, structure development, film formation, cross-linking and interlocking in the coatings, as a consequence of increasing either the curing time or the curing temperature. Such surface reflectance changes can prove to be a challenge for the industry, unless controlled.

Table 6.10-1 displays coatings for which visual examinations of the panels were conducted. These coatings were treated across an increasing curing time, at the standard 195 °C. On the left of Table 6.10-1, there is a display of coatings that were cured for various time periods at the 195 °C curing temperature. On the right of Table 6.10-1, there is a display of coatings that were cured at various temperatures for the 12 minutes. Changes in visual appearance of the coatings were most apparent when the curing temperatures were increased. The results concur with those shown in Figure 6.10-3 and Figure 6.10-4.

Table 6.10-1: Visual assessment of HMMM cross-linked poly(ester) coatings; the effect of an increase in curing time and curing temperature on panel appearance

Poly(ester)-urea 	Poly(ester)-acrylic 
Poly(ester)-urea 	Poly(ester)-acrylic 

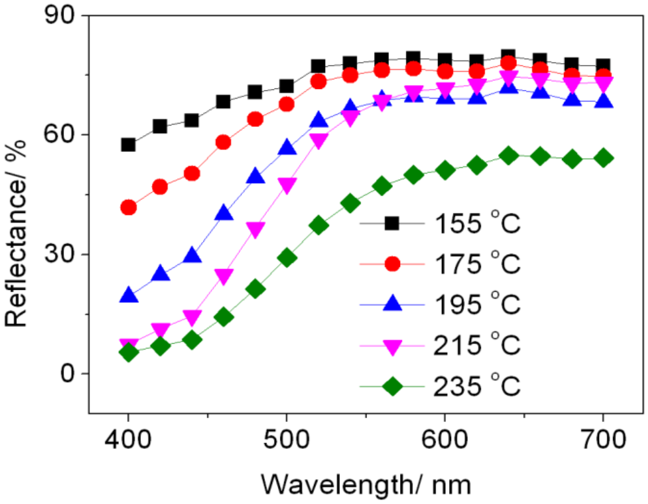


Figure 6.10-3: Surface reflectance behaviour of HMMM cross-linked, poly(ester)-urea coatings, cured for 12 minutes, at various temperatures

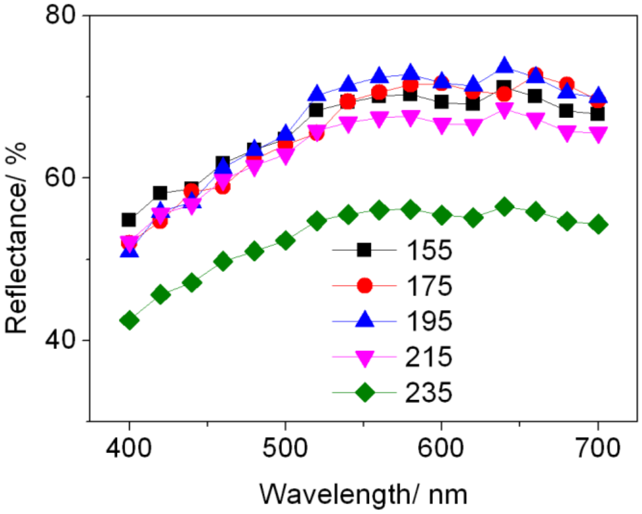


Figure 6.10-4: Surface reflectance behaviour of HMMM cross-linked, poly(ester)-acrylic coatings, cured for 12 minutes, at various temperatures

The following points are noteworthy:

- The surface reflectance properties of each of the coatings studied changed when the curing conditions were changed. Generally, the greater the curing temperature, the less was the reflection from their surface and the duller their surface appears.
- An increase in the curing temperature can help lower melamine migration from the coatings into aqueous food simulants. However, such action would prove to be a challenge for the industry since the overall appearance of the coatings could change. Such an action can also have adverse effects on the substrate. These points would require continues monitoring.
- The extent of the surface reflectance of the coatings is significantly dependent on the chemistry of curing. Accordingly, surface reflectance procedures, using spectrophotometers, provide a viable quality control method for monitoring the appearance of the surfaces and the degree of change that occurs when the curing conditions are changed.

6.11. The effect of a two-step curing procedure on melamine release

The rationale for these two-step studies is given in Section 5.12 . The results are shown in Table 6.11-1 and Table 6.11-2.

Table 6.11-1: Poly(ester)-urea coatings, cross-linked with HMMM, cured at 195 °C. Results expressed as melamine release in µg/6dm^2 and as the percentage of the cross-linker hydrolysis

1st curing	Resting time	2nd curing	µg/6dm^2	% Hydrolysis
12 min	0	0	346 ±4	8.9 ±0.2
8 min	2 min	4 min	380 ±4	9.8 ±0.2
6 min	2 min	6 min	389 ±3	10.1 ±0.2
6 min	5 min	6 min	349 ±2	9.1 ±.1
6 min	10 min	6 min	368 ±4	9.5 ±0.2

Table 6.11-2: Poly(ester)-acrylic coatings, cross-linked with hexamethoxymetheyl melamine (HMMM), cured at 195 °C. Results expressed as melamine release in μg/6dm^2 and as the percentage of the cross-linker hydrolysis

1st curing	Resting time	2nd curing	μg/6dm^2	% Hydrolysis
12 min	0	0	1173 ±5	10.1 ±0.3
8 min	2 min	4 min	938 ±4	8.1 ±0.2
6 min	2 min	6 min	1080 ±3	9.3 ±0.2
6 min	5 min	6 min	1043 ±4	9.0 ±0.3
6 min	10 min	6 min	1042 ±4	9.0 ±0.4

The results show that breaking the curing session, with resting of the coatings in between the two sessions, does not have any significant effect on the total amount of melamine that is released from the cured coatings. On retorting of the coatings in the 10% (v/v) aqueous ethanolic food simulant, the hydrolysis of the cross-linker to melamine remained relatively the same. Therefore, provided that the coatings are eventually cured for the total required time, at the appropriate temperature, the melamine migration behaviour of the final coatings will be unaffected.

6.12. Effects of a wet-on-dry coating deposition procedure for specified, overall coating thicknesses

The results obtained from the study of a two-step coating deposition procedure (wet-on-dry) as opposed to the traditional one-step deposition and curing procedure, targeting a specified overall coating thickness, are presented in Table 6.12-1 and Table 6.12-2. The following points are relevant to the interpretation of these results.

- Double coat on the same side, (DCSS). This term refers to two layers of coating, on the same side of the tinplate, with the same film thickness (e.g. 8 gsm). The second layer was applied and cured after the curing of the first layer. DCSS has the same food contact area as the single coat (SC) system.

- Single coat on each side, (SCES). This term refers to two layers of coating, with the same film thickness (e.g. 8 gsm), each on one side of the tinplate substrate applied and cured separately. Thus, one of the coating layers received a double cure. SCES therefore has a food contact surface that is double that of a SC system.

With respect to the results that are expressed in melamine release units (µg/6dm^2), a comparison needs to be made between the DCSS and the SC systems and between the SCES and the SC systems. In Table 6.12-1 for example, with respect to the HMMM cross-linked coatings, the results imply the following:

- The SC released 337 µg/6dm^2 in comparison to the 383 µg/6dm^2 that were released by the DCSS system. Therefore, the second top layer in the only released about 38 µg of melamine per 6dm^2 of coating. Thus, the total cross-linker hydrolysis in the DCSS was less than that achieved by the SC procedure.

- The SC released 337 µg of melamine per 6dm^2 of coating in comparison to the 198 µg/6dm^2 released by the SCES. It is worth noting that both the SC and SCES had the same area of coating exposed to the same volume of food simulant. However, the SCES had double the amount of coating that the SC had. The results imply that in the SCES system, the coating layer that received single cure released about 168 µg/6dm^2 while the layer that received a double cure released only 59 µg of melamine per 6dm^2 of coating.

The interpretations of the results in Table 6.12-1 conveniently relate to the results presented in Table 6.12-2. Thus, in conclusion, the following points are relevant.

- When using a “wet-on-dry” procedure the coating film thickness doubles. However, the release of melamine through hydrolysis, after the retorting of the coatings in the 10% (v/v) aqueous ethanolic food simulant, does not change accordingly (i.e. double).

- In the DCSS procedure, the melamine that was released comes predominantly from the upper layer. There is an indication that the upper coating layer serves as barrier to the bottom layer. Also one should note the fact that the lower layer receives double the cure time of the top layer, which was cured once. The doubling of the curing that the bottom layer received could have improved the interlocking of the components in the coating layer, reducing the ease of any migration behaviour.

- The double cure that one layer in each of the DCSS and the SCES received, reduced the overall hydrolysis of the cross-linker components of the coatings after retorting, in comparison to that achieved by the SC procedure, for the same overall coating thickness.

- Although the SCES procedure offers reduced cross-linker hydrolysis, the procedure may have limited industrial application (if any). This is because, in the can using processes, only one side of the substrate comes into contact with food.

- To limit the extent of melamine release/migration from the coatings into a foodstuff or into an aqueous food simulant, the strategy of applying double layers can be of a benefit. The second layer needs to be applied and cured after the curing of the first layer for the total film weight thickness needed to give the desired/required performance properties.

Table 6.12-1: Poly(ester)-urea coatings, cured at 195 °C for 12 minutes, containing one of the cross-linkers; HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

Cross-linker	Coating application	Total film thickness	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
HMMM	Single coat	8 gsm	337 ±4	8.7 ±0.5
HMMM	Double coat on the same side	16 gsm	383 ±5	4.5 ±0.5
HMMM	Single coat on each side	16 gsm	198 ±3	5.1 ±0.4
TMTBM	Single coat	8 gsm	224 ±3	7.4 ±0.3
TMTBM	Double coat on the same side	16 gsm	254 ±5	4.2 ±0.4
TMTBM	Single coat on each side	16 gsm	135 ±2	5.1 ±0.2
HBMM	Single coat	8 gsm	255 ±3	10.8 ±0.2
HBMM	Double coat on the same side	16 gsm	271 ±2	5.8 ±0.2
HBMM	Single coat on each side	16 gsm	143 ±2	6.1 ±0.2
DBMB	Single coat	8 gsm	198 ±3	4.7 ±0.2
DBMB	Double coat on the same side	16 gsm	203 ±3	2.4 ±0.2
DBMB	Single coat on each side	16 gsm	100 ±2	2.4 ±0.2

Table 6.12-2: Poly(ester)-acrylic coatings, cured at 195 °C for 12 minutes containing one of the cross-linkers; HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

Cross-linker	Coating application	Total film thickness	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
HMMM	Single coat	12 gsm	1353 ±8	11.6 ±0.9
HMMM	Double coat on the same side	24 gsm	2155 ±6	9.3 ±0.8
HMMM	Single coat on each side	24 gsm	1044 ±4	9.0 ±0.7
TMTBM	Single coat	12 gsm	312 ±3	3.4 ±0.2
TMTBM	Double coat on the same side	24 gsm	350 ±4	1.9 ±0.3
TMTBM	Single coat on each side	24 gsm	181 ±3	1.9 ±0.2
HBMM	Single coat	12 gsm	481 ±5	6.8 ±0.4
HBMM	Double coat on the same side	24 gsm	871 ±5	6.2 ±0.3
HBMM	Single coat on each side	24 gsm	393 ±4	5.6 ±0.3
DBMB	Single coat	12 gsm	232 ±3	1.8±0.2
DBMB	Double coat on the same side	24 gsm	221 ±2	0.9±0.2
DBMB	Single coat on each side	24 gsm	125 ±3	0.8±0.1

6.13. Stability of the release products in retorted, isolated simulants

Melamine has a tendency to undergo hydrolysis and form sequentially ammeline, ammelide and finally cyanuric acid under appropriate conditions, (Section 1.10.3.1). Table 6.13-1 to Table 6.13-4 show results that were obtained from the studies carried out to investigate the stability of melamine, benzoguanamine and formaldehyde, in those 10% (v/v) aqueous ethanolic food simulants that remained after/from the retorting of the cured poly(ester)-urea coatings and the cured poly(ester)-acrylic coatings.

Table 6.13-1: Stability of melamine after release into 10% (v/v) aqueous ethanolic simulants, from poly(ester)-urea coatings, using different cross-linkers

Cross-linker used	Age of retorted simulant	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
HMMM	1 day	337 ±4	8.7 ±0.8
	1 week	333 ±4	8.6 ±0.7
	2 weeks	339 ±5	8.7 ±1
HBMM	1 day	248 ±2	8.2 ±
	1 week	243 ±4	8.1 ±
	2 weeks	244 ±3	8.1 ±
TMTBM	1 day	246 ±2	10.4 ±0.4
	1 week	245 ±2	10.4 ±0.4
	2 weeks	248 ±6	10.5 ±1
DBMB	1 day	133 ±1	3.2 ±0.2
	1 week	131 ±2	3.1 ±0.2
	2 weeks	137 ±3	3.3 ±0.3

The results in Table 6.13-1 concern solutions that were obtained from retorting poly(ester)-urea coatings developed from different options of amino cross-linker. The results do not show any change in the amount of melamine produced in the 10% (v/v) aqueous ethanolic solutions, contained in closed containers. Thus, the stored 10% (v/v) aqueous ethanolic simulants did not age with time at room temperature, with respect to melamine production/change. For the storage period that was considered, under the conditions used, the results suggest that melamine does not hydrolyse to form the analogous compounds ammeline, ammelide or cyanuric acid. Thus, it can be inferred that in the retorted/isolated, 10% (v/v) aqueous ethanolic simulants, melamine-cyanuric acid complex (MCA) was not formed

Table 6.13-2 presents additional results that were obtained from different poly(ester)-based coatings developed from the hexamethoxymethyl melamine (HMMM) cross-linker. The results confirm the observations made above, which is the inference that melamine is stable under the retorting conditions used.

Table 6.13-2: Stability of melamine, present in retorted, isolated simulants, from the retorting of HMMM cross-linked poly(ester) coatings

Coating type	Age of retorted simulant	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
Poly(ester)-urea coatings	1 day	337 ±3	8.7 ±0.2
	1 week	333 ±2	8.6 ±0.3
	4 weeks	339 ±2	8.7 ±0.2
Poly(ester)-acrylic coatings	1 day	2165 ±5	9.4 ±0.7
	1 week	2155 ±7	9.1 ±1
	4 weeks	2151 ±4	9.1 ±0.8

Table 6.13-3 and Table 6.13-4 show the results that were obtained from the studies carried out to investigate the stability of benzoguanamine and of formaldehyde in the 10% (v/v) aqueous ethanolic food simulants that remained after/from the retorting of the cured poly(ester)-acrylic coatings.

Table 6.13-3: Stability of benzoguanamine, present in retorted, isolated simulants, from the retorting of DBMB cross-linked, poly(ester)-acrylic coatings

Age of retorted simulant	Benzoguanamine release/ µg/6dm^2	% Hydrolysis of cross-linker
1 day	770 ±4	4.9 ±0.4
1 week	772 ±6	5.0 ±0.5
2 weeks	769 ±4	4.9 ±0.4

Table 6.13-4: Stability of formaldehyde, present in retorted, isolated simulants, from the retorting of HMMM cross-linked, poly(ester)-acrylic coating

Age of retorted simulant	Formaldehyde release/ µg/6dm^2	% Hydrolysis of cross-linker
1 day	234 ±3	2.8 ±0.3
1 week	236 ±3	2.8 ±0.3
2 weeks	212 ±4	2.6 ±0.4

Benzoguanamine and formaldehyde were stable in the aqueous ethanolic solutions, contained in closed containers. For the storage period that was considered in the analysis of each migrant, in the retorted/isolated 10% (v/v) aqueous ethanolic simulants, the amount of the migrant of did not change significantly. Thus, according to the results, one would not expect any significant re-formation of cross-linker derivatives.

6.14. Stability of the isolated retort solutions after further heating, with respect to the further release of melamine

The results from the studies carried out to establish the stability of melamino species that were contained in the retorted aqueous ethanolic food simulants, after the simulants had undergone further heating, are shown in Table 6.14-1 and in Table 6.14-2. The objective of the investigations was to monitor any change in melamine concentration in the retorted food simulants, should further heating of the simulants lead to more or to less melamine being present.

Table 6.14-1: Stability of the extracted melamine, after re-heating of isolated 10% (v/v) aqueous ethanolic simulants, following, initial retorting of the poly(ester) coatings, cross-linked with the hexamethoxymethyl melamine (HMMM) cross-linker

Coating type	Procedure	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
Poly(ester)-urea coatings	Coating retort	350 ±5	9.1 ±1
	Simulant re-heating	347 ±6	8.9 ±1
Poly(ester)-acrylic coatings	Coating retort	1259 ±11	10.9 ±1
	Simulant re-heating	1075 ±8	9.3 ±1

Table 6.14-2: Stability of the extracted melamine, after re-heating of isolated 10% (v/v) aqueous ethanolic simulants, following, initial retorting of the poly(ester)-acrylic coatings

Cross-linker used	Procedure	Melamine release/ µg/6dm^2	% Hydrolysis of cross-linker
HMMM	Coating retort	1259 ±8	10.9 ±1
	Simulant re-heating	1091 ±11	9.6 ±1
HBMM	Coating retort	430 ±2	6.1 ±0.4
	Simulant re-heating	424 ±6	6.0 ±0.4
TMTBM	Coating retort	383 ±2	4.2 ±0.2
	Simulant re-heating	396 ±3	4.4 ±0.2
DBMB	Coating retort	241 ±3	1.9 ±0.1
	Simulant re-heating	230 ±3	1.8 ±0.1

The results presented in Table 6.14-1 and Table 6.14-2 are consistent with the results obtained for the epoxy coatings, shown and discussed in Section 5.18. When the retorted, isolated 10% (v/v) aqueous ethanol food simulants were reheated, the amount of melamine in the simulants did not change. This implies that during the reheating, both melamine and any melamino derivates, that might have been contained in the simulants, were stable. Furthermore, the results imply that under the prevailing conditions melamine did not hydrolyse to form its analogues, ammeline, ammelide or cyanuric acid.

6.15. The release and generation of melamine and formaldehyde during the curing of the selected poly(ester) coatings

In Section 5.7, it was stated that there was much less migration of to formaldehyde than there was either melamine or benzoguanamine. One explanation could be that, during curing, part of the formaldehyde from the cross-linker is (already) lost from the coating, under the influence of the heat and therefore is not available for subsequent migration.

When questioned, Valspar noted that the volatile fumes, containing solvent etc., from the curing ovens were either scrubbed or burnt (in the gas-fired ovens) and so no information on potential melamine and formaldehyde release by evaporation was readily available. Therefore, some limited experiments were conducted in this work.

In Section 4.4.6.5, it was stated that certain procedures can be carried out to simulate the curing of the selected coatings. However, the methods used were not identical to commercial curing processes. Thus, a softer coating was obtained than would otherwise have been the case. Nevertheless, such results can still be used as a guide to whether or not formaldehyde might be released during the heating of the coating. The results obtained using hexamethoxymethyl melamine (HMMM) cross-linked poly(ester) coatings are shown in Table 6.15-1 to Table 6.15-2.

Table 6.15-1: Analysis of distillates showing the amount of melamine that was detected from the poly(ester) coatings after the distillate was tested for any melamine presence

Coating type	melamine release/ µg/mL	% Hydrolysis of cross-linker
Poly(ester)-urea coatings	150	1.1
Poly(ester)-acrylic coatings	200	1.2

Table 6.15-2: Analysis of distillates showing the amount of formaldehyde that was detected from the poly(ester) coatings after the distillate was tested for any formaldehyde presence

Coating type	Formaldehyde release/ µg/mL	% Hydrolysis of cross-linker
Poly(ester)-urea coatings	0.5	0.02
Poly(ester)-acrylic coatings	2.2	0.04

The results show that in the distillate that was isolated after the distillation of the coatings, formaldehyde was detected. The fact that melamine was also detected during the analysis, in an amount that was above the residual melamine level of the cross-linker, could indicate that, both formaldehyde and melamine were generated during the distillation process, Section 4.4.6.5. A further investigation was carried out to monitor the process (also in Section 4.4.6.5). The results are shown in Figure 6.15-1 and Figure 6.15-2. The data in the figures were obtained via a qualitative analysis procedure. However, these data should be treated in a semi-quantitative manner since the methods used have not been validated fully.

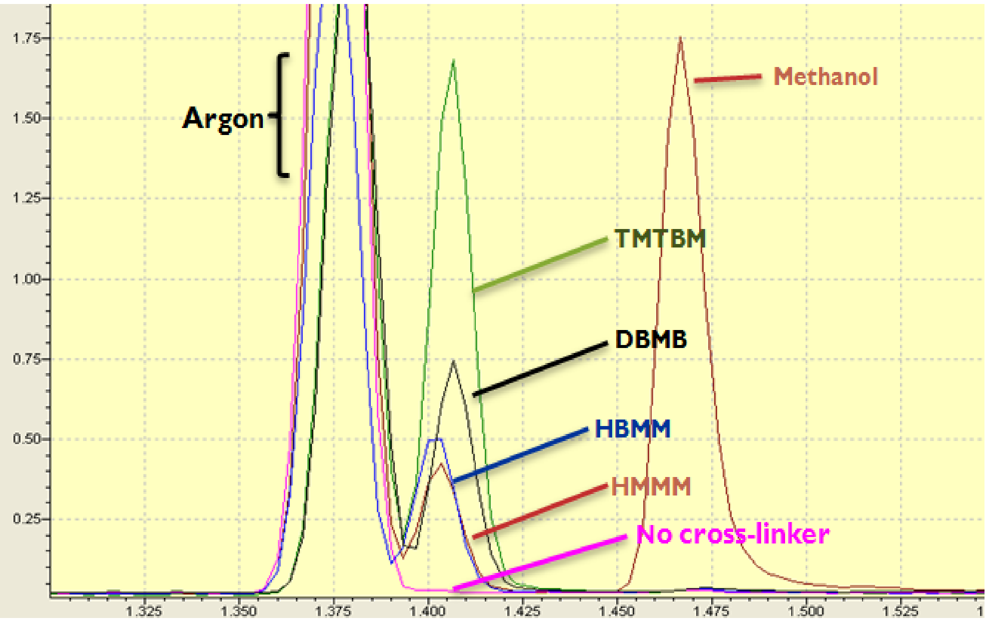


Figure 6.15-1: Poly(ester)-acrylic coatings, containing different cross-linkers, cured at 195 ^{o}C for 12 minutes. The peaks near 1.415 min indicate the formaldehyde that was released by the coatings, each containing a different cross-linker. The peaks are labelled on the basis of the cross-linker that was used in each coating formulation, HMMM: hexamethoxymethyl melamine, TMTBM: trimethylol tributoxymethyl melamine, HBMM: hexabutoxymethyl melamine and DBMB: dibutoxymethyl benzoguanamine

Figure 6.15-1 shows that formaldehyde was released during the curing of the coatings, confirming earlier suggestions, (Sections 6.4 to Section 6.6). In the figure, the peaks near 1.415 min represent the formaldehyde that was released by the coatings, each containing a different cross-linker. In the case of the HMMM cross-linked poly(ester) acrylic coating, methanol, the etherifying alcohol was also released. In the case of the HBMM cross-linked poly(ester) acrylic coating, butanol, the etherifying alcohol was detected.

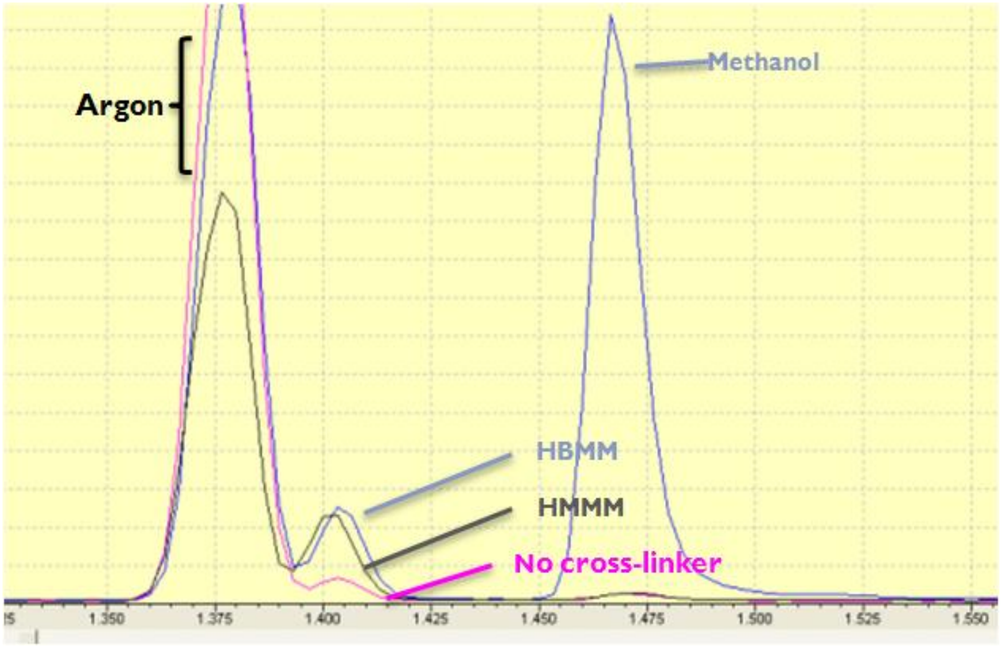


Figure 6.15-2: Poly(ester)-urea coatings, containing different cross-linkers, cured at 195 °C for 12 minutes. The peaks near 1.415 min indicate the formaldehyde that was released by the coatings, each containing a different cross-linker. The peaks are labelled on the basis of the cross-linker that is used in each coating formulation. HMMM: hexamethoxymethyl melamine and HBMM: hexabutoxymethyl melamine

Figure 6.15-2, representing the coating that contained no cross-linker shows a formaldehyde peak at 1.415 min. This is because the coating was formulated using a urea-formaldehyde polymeric binder, Section 3.3.5. It appears that during the curing of the coatings, as a result of the thermal treatment in each coating, the etherified part of the cross-linker was broken-down into formaldehyde and into the appropriate alcohol, either methanol or butanol. These suggestions are in agreement with TGA studies that were carried out, (Section 2.4.7), where it was shown that a thermal process can lead to formaldehyde release and to melamine release, from the cross-linkers, (Moore and Donnelly, 1963).

The results are vital to the provision of an understanding of the mechanism of the breakdown process of the cross-linked coatings, which leads to the formation of melamine and formaldehyde. This point is covered in detail in Section 7.7.

6.16. The design of poly(ester) coatings that give either no release or limited release of melamine, benzoguanamine and formaldehyde

With regards to limiting the amounts of melamine, benzoguanamine and formaldehyde that might be generated from retorted coatings, curing at a higher temperature for a longer time should be considered. Poly(ester)-urea coatings and poly(ester)-acrylic coatings could be cured at 215 ^{o}C for 16 minutes, instead of the current standard practice of 195 ^{o}C for 12 minutes. Such conditions would have only a limited effect on the visual appearance of the coatings and would not negatively compromise either the hardness or the flexibility of the coatings.

With regards to cross-linker choice, the trimethoxymethyl melamines offer much in the route to the reduction of melamine, benzoguanamine and formaldehyde release from the coatings that arise during retorting, sterilising, or pasteurising.

6.17. Conclusions

In the cases studied, the amount of melamine that was released and subsequently migrated into the aqueous ethanolic food simulants was within the current approved limits, set by the European regulatory organisations. The results show that the extraction/migration process is influenced by the temperature of the thermal treatment, by the aqueous conditions and by the presence of an acidic (proton donor) food simulant.

All of the cured coatings released melamine, benzoguanamine and formaldehyde, to an extent that was appropriate to the coating, after being retorted in the 10% (v/v) aqueous ethanolic food simulant. This release and subsequent migration was the result of the de-crosslinking of the coatings and the hydrolysis of the amino cross-linkers obtained. The benzoguanamino cross-linked coatings released both melamine and benzoguanamine. This melamine release arises because of the melamino impurities that are contained in the supplied benzoguanamino cross-linker.

The cross-linker action determined the extent of any release, based on the functionality of the cross-linker and its potential for participation in cross-linking reactions, during the curing of the coatings. The cross-linkers containing the methylol functionality have a lower potential to release melamine, benzoguanamine and formaldehyde than do the cross-linkers that contain alkylated functional groups.

The results show that increasing the curing temperature, in all cases, strongly reduces the amount of melamine that is generated in the retorted coatings. Increasing the curing time also reduces the amount of melamine that is released from the retorted coatings.

The “wet-on-dry” procedure significantly reduced the amount of melamine that was released from the retorted poly(ester) coatings through cross-linker hydrolysis, in comparison to a “single coat” procedure, for the same overall coating thickness. This procedure offers an attractive solution to the problem of melamine release/migration from coatings.

Generally, the greater the amount of amino cross-linker that is used in the coatings, the greater are the amounts of melamine that were released when the cured coatings are retorted in 10% (v/v) aqueous ethanolic food simulant. However, the amount of the cross-linker that is used in the coatings does not have a significant effect on either the hardness of the coatings or the thermal degradation pathways.

The overall results show that the concentration of the migrant species, after release into the aqueous ethanolic simulants remains the same, with time, and does not change on the additional heating of the simulants, provided that the metal panels are removed.

Chapter 7: General Discussion/Summary

This research project concerned the migration of melamine, benzoguanamine and formaldehyde from retorted coatings that contain melamine cross-linkers. Also considered were the factors that affect the migration processes, the factors that can limit the migration processes and the benefits of using certain strategies to arrest melamine migration from the coatings into aqueous ethanolic food simulants.

Here, are considered the relevance of the findings and a comparison of the behaviour of epoxy coatings and poly(ester) coatings with respect to the release of melamine, benzoguanamine and formaldehyde.

7.1. Release of melamine, benzoguanamine and formaldehyde as a consequence of the retorting the coatings

In Chapters 5 and 6 it was stated that when melamino cross-linked coatings are retorted in aqueous food simulants, at elevated temperatures, melamine, benzoguanamine or formaldehyde are released into the food simulants. There is therefore, a potential for the released migrant species to migrate into contained food. In the food canning industry, pressure cooking and sterilisation of canned foodstuffs occur. This provides opportunity for the migration events to be supported. The current study has shown that, under the current industrial process conditions, the amounts of the migrant species that can potentially be released into the contained food are within current European regulations. Nevertheless, there is a drive for continuous improvement and innovation within the industry, to reduce levels even further,

From a comparison of the epoxy coatings and the poly(ester) coatings that were cross-linked with either a melamino compound or a benzoguanamino compound, the relative amount/speed of cross-linker hydrolysis is:

Hydrolysis of the cross-linkers in epoxy coatings >>> Hydrolysis of cross-linkers in poly(ester) coatings

From the epoxy coatings and the poly(ester) coatings that were cross-linked with a melamino compound, the extent of the release into the 10% (v/v) aqueous ethanolic food simulant (in migration concentrations) can be summarised as follows:

Release of melamine (µg/6dm^2) >> Release of formaldehyde (µg/6dm^2)

When a benzoguanamine cross-linker was used in the coatings, the relative release was: Release of benzoguanamine (µg/6dm^2) >> Release of melamine (µg/6dm^2) >> Release of formaldehyde (µg/6dm^2).

The amount of formaldehyde that was released during the retorting of the coatings was below expectations, probably because formaldehyde was lost during the oven curing of the coatings. It is well known in industry that formaldehyde is generated during the curing cycle and rigorous workplace limits are in place. When a benzoguanamino cross-linked coating was used, as expected, the release of melamine was much less than the release of benzoguanamine; this limited melamine release arose because of the presence of melamino impurities (or perhaps a small level of melamine as an additive) in the benzoguanamine-based cross-linker.

7.2. Action of the migrant compounds in the aqueous food simulants after coatings retorting

After the retorting of coatings in the aqueous food simulants, the amount of the migrants (melamine, benzoguanamine or formaldehyde) in the simulants remained the same, after the coatings had been removed. If the retorted food simulants were isolated, sealed and stored, the amount of the migrant compounds remained the same even when the isolated food simulants underwent further thermal treatments. This is interpreted as meaning that the cross-linker component in the coating hydrolyses and releases formaldehyde plus melamine and/or benzoguanamine directly into the food simulant. There is no evidence for an alternative route, which is a partial hydrolysis giving rise to a migration of soluble low molecular weight oligomers that subsequently hydrolyse further in the simulant to release the free species. To be strict in the interpretation, if this alternative route does operate, then the hydrolysis in solution must be very fast in comparison to the release from the coating so that no significant quantity of the soluble intermediate builds-up.

In addition to the action of the food simulant on the coating, one needs to consider the action of the coating and its migrants on the food or other contents of the can containers. Clearly, this will depend considerably on the nature of the contents and on the stability of the contents. This means that there will always need to be alertness/watching briefs when variants to coating options are considered or additives are used.

It has been shown (Section 5.2 and Section 5.15) that the release of melamine from epoxy coatings occurs when either 3% (v/v) aqueous acetic acid or 10% (v/v) aqueous ethanol is used as a food simulant. Slightly more was released when the 3% (v/v) aqueous acetic acid food simulant was used, because of its greater acidic properties. The 3% (v/v) aqueous acetic acid gave more surface interaction with the coatings than did the 10% (v/v) aqueous ethanol, as shown from contact angle studies.

7.3. Dependence of migrant release on cross-linker type

The extent of the release of melamine, benzoguanamine and formaldehyde is influenced by the type of amino cross-linker and its chemistry. Cross-linkers containing the methylol functionality (–CH_2OH group), gave rise to less melamine, benzoguanamine and formaldehyde than did the alkylated cross-linkers, such as HMMM and HBMM. With the methylol-type cross-linkers, more interlocking was achieved, making it more difficult for migration to occur.

From the differences in the action of the cross-linkers in the coatings, on the extent of the hydrolysis, viable options have been identified for use in formulation strategies and performance optimisations.

7.4. Time-temperature correlations— effect on migrant release

The curing temperature and the curing time affected the extent of melamine that was released when the cured coatings were retorted in aqueous ethanolic food stimulants.

The extent of cross-linker hydrolysis decreased, in all cases, when the curing temperature had been increased. Also an increase in the curing time lowered the extent of hydrolysis to melamine; this was especially so with the epoxy-based coatings. The 10% (v/v) aqueous ethanol food simulant has been shown to give lesser interactions with those coatings that were cured for longer times or at a greater temperature, compared with curing that had occurred for a shorter time or at a lesser temperature. When the curing temperature was increased from 160 ^{o}C, in stages, to 240 ^{o}C, hydrolysis of the cross-linked epoxy coatings was reduced by nearly 60%.

As might be expected, the amount of melamine that the coatings released depended on the amount of melamino cross-linker that was used in formulating the coatings. However, the hydrolysis of the coatings was independent of the amount of cross-linker. In certain instances, the more of the cross-linker that was used in the coatings, the less was the hydrolysis of the overall coatings. Also, in such coatings, the cross-linker affected the hardness of the coatings.

The overall assessment of both the epoxy coatings and the poly(ester) coatings showed that when the melamino cross-linkers were excluded from the formulations, there was no melamine migration issue. It was evident that, even without the cross-linkers, a solid, cross-linked coating film was achieved. Thus, the other binder components, in each coating, had the potential to form a cross-liked network. What was an important and a surprising finding of this work, is just how extensive hydrolysis of the cross-linker can be (up to 90% in certain coatings) and yet the coatings can still perform the function required of them in industrial use. The question could be asked - if they could be omitted from the formulations entirely? It seems likely that as well as acting as (possibly secondary-) cross linkers, they may play an additional role(s) in the application and curing mechanisms - for example for reasons of dispersion, wetting or catalysing the curing.

7.5. Melamine migration from a benzoguanamino cross-linked coating

Melamine was released from all of the retorted coatings that were cross-linked with a benzoguanamino cross-linker. If the benzoguanamino cross-linker had been free from starting product contamination, melamine should not have been a release product. Experimental investigations revealed that the melamine release arose from melamino "impurities" in the benzoguanamino cross-linker that was supplied, indicating incomplete synthesis of the benzoguanamine from melamine.

The results demonstrate the importance of using "pure" cross-linkers in curing. This would require a thorough melamine stripping/removal step to be included in the manufacturing process, but this is today a costly option. This is an important recommendation, presenting a worthwhile challenge for the industry.

7.6. The benefits of using TiO_2 pigment particles in epoxy-anhydride coatings

Melamine release tests have shown that incorporating TiO_2 particles into epoxy-anhydride coatings lowers the amount of melamine that the coatings release after they are retorted, in both the aqueous acidic food simulant and the aqueous ethanolic food stimulant. In particular, the action of the TiO_2 particles is considered to arise because of the surface treatment and the inherent interactivity of the pigment particles rendering the pigment surfaces hydrophilic, providing additional structure to the product arising from the curing of the coatings.

The three pigment grades had very similar characteristics as was their effect on the behaviour of the coatings. Even for the aged liquid coatings, the contribution of the pigments to the ageing process, with respect to melamine release, was very similar. In industry, therefore, the three different grades of the TiO_2 pigment could be used interchangeably, for the same purpose. It would be interesting to ascertain whether or not such interventions would be achieved using other pigmentary particles (organic types and inorganic types) and other particles that are not pigments (e.g. fillers, such as chalk). However, whatever is used must comply with food contact regulations or guidelines. This point relates to the broadening of the applications of the developed coatings technology.

7.7. Suggested coating hydrolysis pathway

The pathways through which the cross-linkers hydrolyse has been established and documented, (Bauer, 1982). The results from several investigations (Chapters 5 and 6) suggest a pathway through which the migrants are formed during this hydrolysis. TGA studies have shown that a thermal process can lead to formaldehyde release and to melamine release, at 200 °C and at 400 °C, respectively, from the cross-linkers (Section 2.4.7, (Moore and Donnelly, 1963)). However, since both melamine and formaldehyde are released under the conditions in which the coatings are retorted, it is reasonable to state that the release process is dominated by hydrolysis events rather than the thermal events, although both explanations are applicable.

Here, the potential hydrolysis pathways through which the cross-linkers are converted into melamine and formaldehyde are considered using HMMM, HBMM and TMTBM as cross-linker examples, (Figure 7.7-1 to Figure 7.7-3). The reaction will proceed when either the 3 % (v/v) aqueous acetic acid food simulant, pH 3.5 or the 10% (v/v) aqueous ethanol food simulant, pH 6.5, is used, (Bauer, 1982). Both food simulants have protic solvent characteristics.

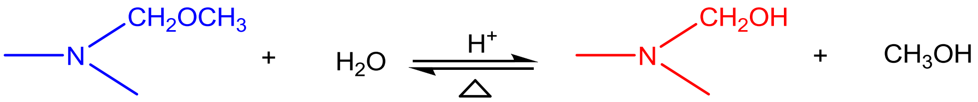


Figure 7.7-1: Scheme: The hydrolysis of hexamethoxymethyl melamine (HMMM), yielding a methylol melamine derivative, under aqueous conditions in the presence of an acid donor, in a controlled heating system

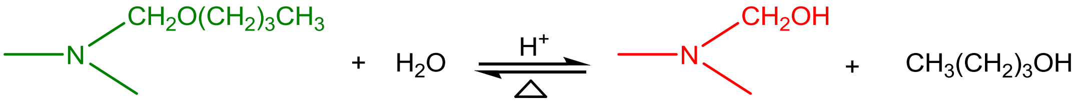


Figure 7.7-2: Scheme: The hydrolysis of hexabutoxymethyl melamine (HBMM), yielding a methylol melamine derivative, under aqueous conditions in the presence of an acid donor, in a controlled heating system

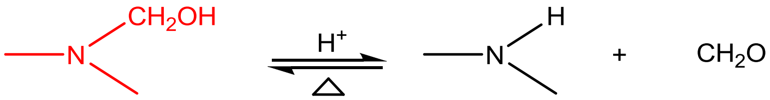


Figure 7.7-3: Scheme: The hydrolysis of a methylol melamino component (such as trimethoxy tributoxymethyl melamine, TMTBM) yielding methylol melamine derivative, under aqueous conditions in the presence of an acid donor, in a controlled heating system

The reaction involved in the hydrolysis of hexamethoxymethyl melamine (HMMM), yielding methylol melamine derivatives, under aqueous conditions in the presence of an acid donor, in a controlled heating system, is shown in Figure 7.7-1. In an analogous manner, Figure 7.7-2 shows the reaction involved in the hydrolysis of hexabutoxymethyl melamine (HBMM), yielding the methylol melamine derivative, under aqueous conditions in the presence of an acid donor, in a controlled heating system. Both reaction schemes correspond to literature reports of the hydrolysis of melamine derivatives, (Cordes and Bull, 1974, Clayden et al., 2012). Therefore, in the complete hydrolysis of HMMM to yield melamine, the reaction is thought to proceed in two steps, as shown in Figure 7.7-1 and Figure 7.7-3. The mechanism for the conversion proceeds in three steps. These are shown in Figure 7.7-4.

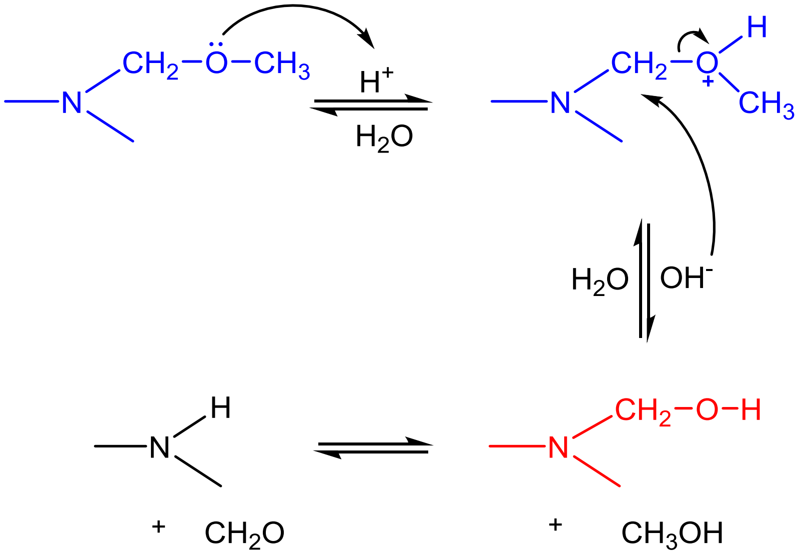


Figure 7.7-4: Scheme: The mechanistic pathway though which hexamethoxymethyl melamine (HMMM) is hydrolysed, yielding the methylol melamine derivative, under aqueous conditions in the presence of an acid donor, in a controlled heating system

For the amino cross-linked coatings, it can be appropriate to suggest that the cross-linker component in the coating undergoes hydrolysis, under the appropriate conditions, in the same manner as that of the bound cross-linker.

Through a three step schematic illustration, under the appropriate conditions, the mechanistic pathway through which a hexamethoxymethyl melamine (HMMM) cross-linked coating is hydrolysed, via retorting procedures, is shown in Figure 7.7-5 to Figure 7.7-7, seen as step 1 to step 3.

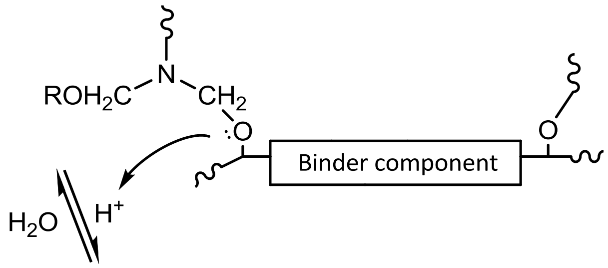


Figure 7.7-5: Step 1: Proton pick-up in a mechanistic scheme showing the pathway though which the hexamethoxymethyl melamine (HMMM) cross-linked coating is hydrolysed

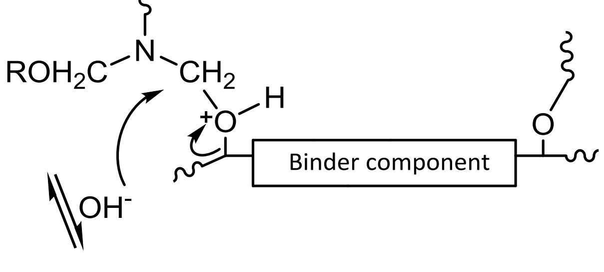


Figure 7.7-6: Step 2: Hydroxyl group attack in a mechanistic scheme showing the pathway though which the hexamethoxymethyl melamine (HMMM) cross-linked coating is hydrolysed

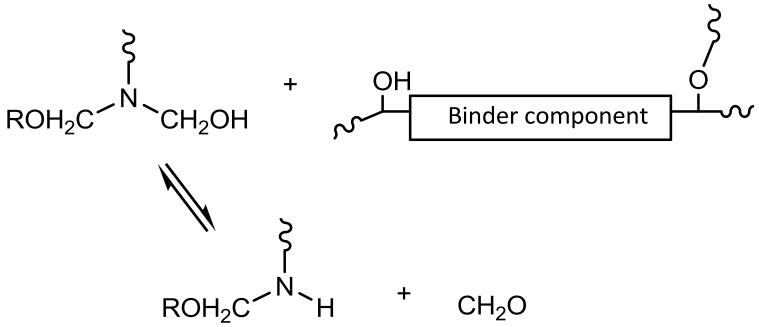


Figure 7.7-7: Step 3: Formation of melamine and of formaldehyde in a mechanistic scheme showing the pathway though which the hexamethoxymethyl melamine (HMMM) cross-linked coating is hydrolysed

In the first step, the coating takes up a hydrogen atom from the ionised water component of the food stimulant. This leads to its attachment to one of the lone pairs of the oxygen atom. This intermediate is unstable, giving a delocalisation of the charge, leading to step two. In step two, the hydroxyl ion attacks the intermediate leading to the formation of a methylol derivative. In step 3, as the reaction continues, formaldehyde and the corresponding melamino –NH group are formed.

Suggestions for further work

The three epoxy coatings and the two poly(ester) coatings studied in this research are among some major types of coating chemistries being used by the can coatings industry. Based on the feedback on this research from the concerned industries, other coating chemistries could also be investigated in a similar manner to that by which this project has been undertaken.

During this project, three grades of TiO_2 pigments were used in the studies. All of the three grades were surface treated. The presence of the pigment particles was beneficial to the coatings by lowering the amount of melamine that the coatings released. Further work might involve the study of the contribution of the extent of the surface treatment on reducing the melamine release from appropriate coatings. Also studies could be carried out using untreated TiO_2 pigment particles to investigate further the contributions of the surface treatments. To broaden the potential applications of this study, the range of pigments studied could be extended to include variants from the wide range of organic pigments and of inorganic pigments. Fillers and other 'safe' particulate systems could also be considered, providing they are approved for food contact applications.

Wet ageing affected the TiO_2 pigmented epoxy anhydride coatings with respect to melamine release, after their curing and the retorting in 10% (v/v) aqueous ethanolic food simulant. The coatings were aged under controlled laboratory conditions for up to 10 months. The study could be extended to include other clear, non-pigmented epoxy coatings and poly(ester) coatings.

As a further investigation, Thermo Mechanical Analysis (TMA) could be employed to establish the effect of the increase in curing time and the curing temperature on the mechanical properties of the coatings. Detailed kinetic studies could also be carried out to monitor the rate of the by-products degradation and the rates at which they are released into the aqueous food simulants.

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Appendix

The chemicals and supplied raw material samples were used following the COSHH regulations and MSDS advice. The advice was sought from suppliers if and when doubt arose. Appendix 1 here gives an example of such information presentation.