A SPECTROSCOPIC STUDY OF THE DEGRADATION OF POLYURETHANE COIL COATINGS

Submitted by

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Abstract

The degradation of polyurethane (PU) coil coatings were studied with step scan phase modulation photo-acoustic (SS-PM-PA) FTIR, confocal Raman mapping (CRM) and scanning electron microscopy (SEM). PU coatings were oven cured for 30 seconds to reach a peak metal temperature of 232°C. The cured coatings were exposed in a QUV A accelerated ageing test with exposure time intervals of 1200 hours and 4098 hours. Isophorone diisocyanate (IPDI) cross-linker gave lower cross-linking density and degradation rate to the PU coating compared to hexamethylene diisocyanate (HDI). Cyclic trimer (CT) isocyanate cross-linker gave higher durability compared to biuret (BI). A primary amide and urea entity rich top-film was formed at the surface of degraded PU coatings, with characteristic IR bands at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\). The decomposition of allophanate in exposed HDI-CT cross-linked PU coating was indicated. The degradation of BI core produced additional urea linkage compared to allophanate. \(\varepsilon\)-caprolactam (Capro) blocked isocyanate gave lower cross-linking density and higher degradation rate compared to methyl ethyl ketoxime (MEKO), and 3,5 dimethyl pyrazole (DMP). The addition of melamine and HALS (less than 5%) improved the durability of PU coatings. The melamine linkage was more sensitive to the degradation compared to the urethane linkage. The higher NCO/OH resulted in more rapid degradation product build-up at the surface of the PU coating in the meantime deterred the decomposition of amide II type linkage.

A FTIR peak fitting method was developed for generating degradation index plots, based on the knowledge of degradation chemistry of the PU coatings described above. The degradation rate correlation of the PU coatings exposed in the QUV A test and natural exposure sites including Liverpool, UK (LIV), Vereeniging, South Africa (SA) and Kuala Lumpur, Malaysia (KL) are demonstrated by using degradation index plot methods. The harshness of the natural exposure sites gives the order of KL > SA > LIV.
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List of abbreviations

BI biuret
Capro $\varepsilon$-caprolactam
Capro-HDI-CT Capro blocked HDI branch with CT core
Capro-PU PU coating cross-linked with Capro blocked isocyanate
CC clear-coat only
CCD charge-coupled device
CRM confocal Raman mapping
CT cyclic trimer
cyc cyclohexane ring
DMP 3,5 dimethyl pyrazole
DMP-HDI-BI DMP blocked HDI branch with BI core
DMP-HDI-CT DMP blocked HDI branch with CT core
DMP-PU PU coating cross-linked with DMP blocked isocyanate
DSP digital signal processor
EMMAQUA equatorial mount with mirrors for acceleration with water spray
ESR electron spin resonance
FTIR Fourier transform infrared spectroscopy
FWHH full width at half height
HALS hindered amine light stabilisers
HDI hexamethylene diisocyanate
I in-phase
ICS international chemometrics society
IPDI isophorone diisocyanate
IR infrared
KL Kuala Lumpur, Malaysia
LIV Liverpool, UK
LTD Long Term Development
List of abbreviations

MEKO methyl ethyl ketoxime
MEKO-HDI-CT MEKO blocked HDI branch with CT core
MEKO-IPDI-CT MEKO blocked IPDI branch with CT core
MEKO-PU PU coating cross-linked with MEKO blocked isocyanate
MF modulation frequency
NPA normalised peak area
OPD optical path difference
PA photo-acoustic
PAS photo-acoustic spectroscopy
PE polyester
PM phase modulation
PU polyurethane
PVC pigment volume concentration
Q quadrature
SA South Africa
SEM scanning electron microscopy
SIMS secondary ion mass spectrometry
SS step scan
Td deblocking temperature
TOP topcoat on primer
UV ultraviolet
XPS X-ray photo-electron spectroscopy
ZPD zero path difference
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1. Introduction

Coil coating paints have to be of a consistent quality in respect to the properties of workability, long service life and resistance to corrosion and adverse weather conditions [1, 2]. To achieve these demanding goals, great efforts have been made over the decades in the investigation of degradation chemistry of coatings [3]. As one of the most widely used paint technologies, polyester-melamine has been the subject of extensive attention in the last few years [4-6]. Over the same time period, the use of polyurethane (PU) technology in coil coatings has increased dramatically compared with other technologies [7]. However, there is a relative delay in chemical data collection and analysis relating to this technology and in particular the degradation chemistry. This project is designed to address this deficiency. The literature survey on the subject of the spectroscopic study of the degradation of PU coil coatings is given in Chapter 2.

The coil coating manufacturers have long relied on appearance-based measurements, such as gloss retention and colour change to monitor finish condition and durability of the coating. A limitation in using appearance-based measurements is the long period of time (years) required for significant changes to take place. The ability to realistically approximate the durability or service life performance of a coating system is becoming very important [8]. The more accurate the prediction, the better in terms of the risk management [9]. A sensitive spectroscopic technique has the advantage of allowing the early stages of degradation to be detected and therefore reduces the time required for the assessment. A great number of spectroscopic techniques have been applied for understanding PU degradation. Photo-acoustic step scan Fourier transform infrared (FTIR) spectroscopy has been demonstrated as a suitable technique for the study of the degradation chemistry of coil coatings [10, 11]. The advantages of this technique has been recognised in many aspects including non-destructive sampling and controlled probing depth for near-surface analysis [12]. Under the same technical category terms as vibrational spectroscopy, Raman spectroscopy is recognised as a complementary
technique to FTIR [13]. Confocal Raman coupled with a chemical imaging function has been shown to be a valuable tool for non-destructive chemometric studies of organic coating materials [11, 14]. In Chapter 4, the applicability of step scan phase modulation photo-acoustic (SS-PM-PA) FTIR technique on the depth profiling of TiO₂ pigment PU coil coatings is examined. In Chapter 5, the applicability of the confocal Raman mapping (CRM) chemometric method is verified by studying the content and distribution of Cyclic Trimer (CT) core of the isocyanate cross-linker at the surface of clear PU coil coatings. These two chapters are of importance on providing supportive information towards the further degradation study of PU coatings using SS-PM-PA FTIR and CRM techniques.

Due to the versatility of isocyanate cross-linker, commercial PU coatings can be very complex materials and consequently their durability can vary significantly [15]. The chemical changes of the PU systems is thought to occur prior to the physical degradation can be recognised throughout the weathering [16]. Thus, it is vital for paint designers to develop a better understanding of the chemical changes of the PU systems to improve the durability of PU coil coating products submitted to various environmental stresses. The degradation chemistry study on PU coil coatings by using spectroscopy techniques are discussed in Chapter 6 and Chapter 7. In Chapter 6, the impact of isocyanate structures on the degradation chemistry of PU coil coatings is investigated. The isocyanate branch structures including isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) and core structures including CT and biuret (BI) are varied. In addition to the degradation of urethane linkage as the predominant linkage within PU coatings, this study also elucidates the primary amide (-NH₂) and urea entity (-NH-(C=O)-N-) contained in urea, allophanate and to a less extent BI linkages involved degradation. In Chapter 7, the impact of isocyanate blocking agents to the film formation and the degradation of PU coil coatings are investigated. Three commercially available HDI-CT isocyanate cross-linkers with different blocking agents including ε-caprolactam (Capro), Methyl ethyl ketoxime (MEKO), and 3,5 Dimethyl Pyrazole
1. Introduction

(DMP) are studied. These two chapters address the chemical change pathway of the degradation of PU coil coatings by using spectroscopic techniques which are introduced in previous chapters.

The degradation rate of polymer materials can be quantitatively evaluated by using the degradation index plot method [3, 17, 18]. The FTIR technique has been commonly used to generate the degradation index data [19] for evaluating the degradation rate of the coil coating materials. The limitation of this technique is recognised as the overlapping nature of the IR band, which adds difficulties for accurate quantitative analysis [20]. The accuracy of the FTIR quantitative analysis can be improved by using peak fitting procedure [5, 6, 21-23]. In Chapter 8, the degradation index plots method is applied to correlate the degradation rate of the PU coatings exposed in QUV A tests and natural exposure sites including Liverpool, UK, South Africa and Kuala Lumpur. FTIR peak fitting method is used to generate data for establishing degradation index plots. The formulation of PU coating is varied with regards to the isocyanate cross-linkers. The degradation chemistry of the PU coatings under study has been extensively discussed in Chapter 6 and Chapter 7. This work develops the method which can be used to monitor the degradation rate of PU coatings quantitatively and with improved accuracy.

Chapter 9 discusses the impact of the addition of minor film formers (less than 5% wt.) including melamine and BI isocyanate, HALS additive and varied NCO/OH to the degradation of the clear PU coil coatings, in addition to isocyanate structures discussed in Chapter 6 and Chapter 7. The quantitative evaluation of the degradation rate of the PU coatings is made by using the degradation index plots method as discussed in Chapter 8.

Chapter 10 summarises the major conclusions drawn in previous chapters. The recommendations and the future work based on this study are discussed in Chapter 11.
2. Background

This chapter addresses the background knowledge on the subject of the spectroscopic study of the degradation of PU coil coatings, based on the extensive literature survey. Firstly, the production process, the paint and the applications for coil coating is introduced (Section 2.1). Secondly, the PU coating as one of the most important coil coating technologies is discussed including the aspects of the history and applications, the formation and degradation of PU polymers (Section 2.2). The components including isocyanate cross-linkers, polyester resins and pigments are further elaborated with regards to the formation of the PU coil coatings. The thermal- and photo- degradation mechanisms are introduced with regards to the degradation of the PU polymers. Thirdly, the weathering of the polymer material is mentioned in particular aspects of the natural and artificial exposure methods and the degradation rate evaluation method (Section 2.3). Finally, the theories of the spectroscopic characterisation techniques are introduced (Section 2.4). The theory of the infrared (IR) spectroscopy and step scan phase modulation photo-acoustic (SS-PM-PA) FTIR technique is particularly mentioned. The fundamental knowledge and the purpose on the FTIR peak fitting are discussed. The theories of the Raman spectroscopy and scanning electron microscope (SEM) are introduced. Some examples regarding other spectroscopic techniques however not employed in current study are also listed.

2.1. An introduction to coil coatings

2.1.1. The definition of coil coatings

From the industrial view, coil coating is a developed technique used in the continuous application of an organic coating (liquid paint or film) onto a metal substrate. This technology, based on the idea that it is easier to pre-paint a flat surface than post-paint an uneven surface through dipping or spraying, provides a multitude of colours together with specific finishes, surface textures and gloss appearances. The continuous painting
process ensures uniformity, maintaining the greatest consistency between each batch. The pre-painted metal produced is of consistent quality and with the properties of workability, long service lifetime and resistance to corrosion and adverse weather conditions. [24]

The organic coating paints can be divided into eight major categories including alkyds, acrylics, epoxies, polyester-melamines, PUs, polyester resin modified with silicone, polyvinyl chlorides and polyvinyl fluorides. Each has its own specific advantages. The most suitable system is chosen according to its cost expected performance and end use conditions. [2]

The metal substrate (steel or aluminium) is delivered in coil form from the rolling mills. Figure 2.1 shows a schematic diagram of coil coating line. The coil is positioned at the beginning of the line. It is then unwound at a constant speed and undergoes the various pretreatment and coating processes before being recoiled. Two strip accumulators found at the beginning and the end of the line enable the work to be continuous, allowing new coils to be added (and finished coils removed) by a metal stitching process without having to slow down or stop the line.

Figure 2.1 Schematic diagram of coil coating line [25]

The recoiled coating is then passed onto the profiling mills that continuously form the
coil into corrugated patterns or press finished blacks (depending on end use).

A two coat application of the paint system is most common (Figure 2.2). The first coat is the primer which is usually applied directly onto a freshly pre-treated metal surface. The role of the primer is to protect the metal substrate from corrosion and usually contains anti-corrosive pigments. The second coat is the finishing paint which provides the desired colour and appearance of the final coated system. The dry film thickness of the coatings is usually between 5 to 35 microns for a primer (most commonly 5 μm – 8μm) and 15 to 200 microns for the topcoat.

Figure 2.2 Cross-section of pre-painted galvanised steel [26]

2.1.2. The paints for coil coatings

Common paints for coil coating are made up with four main elements, base resins, solvents, pigments and additives. Base resins are usually synthetic petroleum-base products. They are selected according to the different functions required and are generally referred to by their generic name such as polyester, PU and epoxy. Solvents are also produced from petroleum, which solubilise and dilute the base resin, facilitate roller
application and then evaporate during the baking process. Pigments consist of either organic or mineral solids that determine the colour of the finished product. The most commonly used pigments are titanium dioxide (white), iron oxides (red, yellow, black), chrome oxide (green) and organic copper derivatives (blue and green phthalocyanines). Additives include catalysts, dispersing agents, lubrication waxes, and ultraviolet (UV) absorbers. [27]

2.1.3. The applications of coil coatings

Coil coating is increasingly used in different fields but can be divided into the following markets including construction, household electrical goods, transport, packaging and metal furniture. Nearly two thirds of all coil coated material produced in Europe goes into the construction industry wherein fabrication usually involves forming trapezoidal or similarly shaped profiles longitudinally in the pre-coated coil as it is unwound. [28]

2.2. An introduction to polyurethane (PU) coatings

2.2.1. History and applications of PU coatings

During the late 1930's, Otto Bayer and his co-workers pioneered the chemistry of polyisocyanates, a technology which led to the advent of PU coatings for a variety of applications [29]. Achieving both high UV durability and high levels of fabrication performance is often difficult and practically exclusive. The great benefit of PU chemistry is that, if properly formulated, it offers the potential of stepping away from this difficult balancing act and achieving films that can be hard, durable and flexible. The hydrolytic and photochemical stability of the urethane cross-link is considered superior to that of the melamine-polyester, which is known to undergo photo-enhanced hydrolysis [30].

PU coatings are available in both one- and two-pack forms. A two-component coating is
supplied with the polyol, pigments, solvents and additives in one pack and the free isocyanate in a second pack to be added and mixed just before use. A one-pack coating by contract is supplied with all the raw materials in the same container. The latter form is similar to the former one, except that the isocyanate groups are protected by a blocking agent which prevents the reaction with hydroxyl groups at low temperatures. The blocking agent is released during the baking process allowing the isocyanate groups to react with the hydroxyl groups of the resin. Blocked isocyanates are exclusively used in coil coatings since this assures the protections of limited shelf life which would be of a significant disadvantage in such a continuous process.

2.2.2. The chemistry of PU thermosets

PUs used for coil coating are thermoset polymers formed by the reaction between isocyanate cross-linker and polyester (PE) that contains hydroxyl groups, as shown in Scheme 2.1. The di- or tri-functional isocyanates are reacted with the nearby hydroxyl groups of the polyester resin, forming a three dimensional rigid PU network, as illustrated in Figure 2.3. The liquid resins became solid film through the co-condensation reaction. This process is termed as ‘curing’ of the coil coating. The choice of raw materials, both isocyanates and polyesters are very large enabling many combinations with a wide variety of properties of the PU coatings.

Scheme 2.1 The formation of PU by reacting isocyanate with polyester (PE)
2.2.2.1. The isocyanate cross-linkers for the PU thermosets

Core and branch structure of the isocyanate cross-linker

Polyisocyanates based on hexamethylene diisocyanate (HDI) are commonly used aliphatic isocyanate cross-linkers. The molecular structure of HDI is shown in Figure 2.4.

\[
\text{OCN} - (\text{CH}_2)_6 - \text{NCO}
\]

Figure 2.4 The molecular structure of hexamethylene diisocyanate (HDI)

Commercially available isocyanate cross-linkers are normally transformed into polymeric derivatives, such as biuret (BI) or cyclic trimer (CT), where the latter has been proved to be exceptionally stable owing to the presence of CT core structure [32]. The molecular structure of HDI polyisocyanate with BI and CT core structures are as shown in Figure 2.5 and Figure 2.6, respectively.
Finished coatings based on HDI-CT chemistry have significant advantages, including low viscosity, excellent colour, and low free monomer content compared to other polyisocyanates [33]. The CT core structure possesses an inherently higher thermal stability than that of the urethane linkage, and has been found to be the most stable structure obtained from isocyanates [34, 35]. The thermal resistance of the PU coating is found to be dependent upon the content of CT core structure within the coating formulation [36, 37]. Therefore, the quantitative evaluation of the content and distribution of CT core groups is expected to give an important indication of the thermal resistance of the PU coatings. Previous efforts have been made to evaluate the influence of CT core content to the flame-resistance PU system [36, 37]. However, the
instrumental methods used in these studies were based on non-imaging spectroscopic techniques. Merging spectroscopic imaging and chemometrics enhances the outcomes of instrumental technology and data analysis [38]. The application of a chemometric imaging method such as CRM is expected to provide valuable details on the content and distribution of the CT core structure, and, therefore, homogeneity of the PU coil coatings.

Another commonly used aliphatic isocyanate is isophorone diisocyanate (IPDI), in addition to HDI. The molecular structure of isophorone diisocyanate cyclic trimer (IPDI-CT) is shown in Figure 2.4. The HDI and IPDI are termed as the branch structure, in contrast to the core structure of the isocyanate cross-linker including BI and CT in this study.

Figure 2.7 The polyisocyanate of IPDI branch with Cyclic Trimer core structure (IPDI-CT)

Comparing to the backbone chain structure in HDI, the cyclohexyl ring in IPDI gives more significant steric influence due to its bulky structure, which may contribute to more rigid film formation and lower degradation rate [14, 39].
The formation of allophanate, urea and biuret moieties in PU coatings

The environmental condition of isocyanate-polyester cross-linking reactions may affect the ultimate PU coating formation and its subsequent degradation. Isocyanate-polyester cross-linking reactions may be interrupted by side reactions due to the present of ambient water [40]. As demonstrated in Scheme 2.2, when water is present during cross-linking reactions, a condensation reaction between the isocyanate and water produces unstable carbamic acid, which then forms CO$_2$ and primary amide. The latter then rapidly reacts with another isocyanate functionality to form a urea linkage. Also, urethane and urea linkages can further react with isocyanate to form allophanate and BI, respectively, because of their active hydrogen [40, 41]. Although the reactions forming allophanate and BI have been found to be slower than those reactions leading to the formation of urethane and urea linkages, the exceeded isocyanate may push the reactions towards products of allophanate and, to a less extent, BI. Therefore, in addition to the urethane linkage \((-\text{NH}-(\text{C}=\text{O})-\text{O}-)\), the primary amide \((-\text{NH}_2\)) and urea entity \((-\text{NH}-(\text{C}=\text{O})-\text{N}-)\) contained in urea, allophanate and to a less extent BI linkages can contribute to the subsequent degradation process, especially during the early degradation stage.

These side reactions are more likely to occur when PU coatings are cured in ambient with air-drying conditions. The humidity level is significantly low in coil coating applications with a curing temperature of approximately 232 °C compared to the ambient environment, and therefore these side reactions are minor effects compared to the formation of urethane linkages.
Scheme 2.2 The formation of allophanate, urea and biuret moieties in PU coatings. [40, 41]

**Blocking agent of the isocyanate cross-linker**

In PU coil coating applications, where curing is at higher temperatures, blocked isocyanate cross-linkers are preferably used to make one-pack PU paint [42, 43]. Isocyanates can be blocked by compounds such as ε-caprolactam, butanone oxime, phenol, or dimethylpyrazole. At elevated temperatures the blocked polyisocyanate liberates the blocking agent which may leave the film, and the polyisocyanate reacts with the polyester. There are two urethane linkage forming reaction mechanisms by which most blocked isocyanates can react with a nucleophile. In the elimination–addition reaction, the blocked isocyanate decomposes to the free isocyanate and the blocking group (Figure 2.8 (a)). The isocyanate then reacts with a nucleophile to form a final product. In the addition–elimination reaction, the nucleophile reacts directly with the blocked isocyanate to yield a tetrahedral intermediate followed by elimination
of the blocking agent (Figure 2.8 (b)). Generally, it has been assumed that the reaction proceeds by the elimination–addition pathway. However, in other cases, addition–elimination reaction has been proposed [44].

Figure 2.8 Curing of polyester polyisocyanates (principal reactions). (a) nucleophilic elimination-addition reaction, (b) nucleophilic addition-elimination reaction. PE = polyester, BI = blocking agent, R = rest of polyisocyanate. Metal catalyst (Lewis acid) enhances the electrophilicity of the C and the nucleophilicity of the O. [15, 45]

2.2.2.2. The polyester binders for the PU thermosets

Polyesters are polymers with more than one ester linkage per molecule prepared by esterification reaction of di-functional organic acids and di- or tri-functional polyols. In a typical PU coating, the polyester resin can account for between 70% - 90% of the total binder, thus it is clear that the final properties of the PU coating greatly depend on the hydroxylated resin used for the application. Specialised resins are prepared to meet different requirements, such as low or high molecular mass, linear or branched chains, -OH or –COOH functionality. Linear polyester with high molecular weight normally results in higher flexibility, whereas branched polyester results in higher cross-linking density [46]. The molecular structure of a polyester resin and hence the properties are determined by the choices of polyols and organic acids.
Many years of development have shown certain types of polyester resins demonstrate better outdoor long term performance, including hydroxylated polyesters, acrylic or acrylic-polyesters. Occasionally, alkyds, epoxies and polyethers are used for specific applications. More recently, further development work in the durability performance of the polyol reaction partner has led to the development of so called ‘super durable’ polyesters. In many cases this has been achieved by the use of cycloaliphatic monomers within the polyester. The advantage here is to use fully hydrogenated diacids and diols to achieve chain stiffness and yet to avoid the presence of UV absorbing chromophores. Naturally such an approach favours the use of cycloaliphatic polyisocyanates as cross-linking agents to maximise durability rather than the triazine based, melamine chemistry [47].

2.2.3. The pigments used for polyurethane (PU) coil coating

Pigments are insoluble fine particle size materials used in coatings to provide colour, to hide substrates, to modify the application properties of a coating, to modify the performance properties of films, and/or to reduce cost. Pigments are divided into four broad categories including white, colour, inert, and functional pigments. [48]

A large fraction of coatings contain white pigment. White pigments are used not only in white coatings, but also in a substantial fraction of other pigmented coatings to give lighter colours than would be obtained using colour pigments alone. The most important white pigment used in coatings is TiO$_2$ [49]. Two different crystal types are used: rutile and anatase. Rutile is used in larger volume primarily because it gives greater hiding power than anatase. On the other hand, rutile absorbs some violet light, whereas anatase absorbs almost no visible light. In most exterior applications, chalking must be minimised, and rutile TiO$_2$ is used. However, although rutile is less photoreactive than anatase, it is still sufficiently reactive to reduce exterior durability. The problem is minimised by treating the surface of the TiO$_2$ particles during pigment manufacture. The
most common surface treatments are silica (SiO$_2$) and/or alumina (Al$_2$O$_3$) [50].

Apart from white pigments, a wide variety of colour pigments is used in coatings. A number of considerations should be taken when selecting pigments, including colour, colour strength, opacity or transparency, ease of dispersion, exterior durability, heat resistance, chemical resistance, etc. [48].

**2.2.4. Minor film formers, additives and stochiometry variation for PU coil coatings**

**2.2.4.1. Melamine minor filmer**

Melamine can be added into PU formulations as a minor film former of the polyester-melamine-PU network [51]. The major benefit of using melamine as an additive is due to the high heat tolerance. By introducing the rigid triazine ring moiety into the main chain of PU, the polymer network demonstrated improved heat-resistance, water-resistance and mechanical properties [52]. Besides acting as a cross-linker, melamine and its derivatives were also widely used as flame retardant additives in different formulations such as PU foams. During combustion, the heat energy of the PU matrix could be absorbed by the melamine [35, 53]. In respect of weatherability, early work demonstrated that PU-acrylate clear-coats undergo a significantly slower photo-degradation than thermoset melamine-acrylate clear-coats [54]. A recent work showed that acrylic-urethane clear-coats were mainly sensitive to ageing induced by a photo-oxidative phenomenon, whereas acrylic-melamine clear-coats were sensitive to ageing induced by both photo-oxidative and hydrolytic phenomena [55], and the predominant phenomenon is the densification of the network through radical recombination, leading to an increase in thermoset hardness.
2.2.4.2. Hindered Amine Light Stabiliser (HALS) additives

Additives such as light stabilisers, cross linkers, fillers, surfactants and catalysts are used to control and modify the reaction process and performance characteristics of the polymer. HALS is one of the most important classes of light stabilisers. HALS acts as radical scavengers and peroxide decomposers [56], which destroys already formed radicals before damaging the PU network through consecutive reactions. The effectiveness of HALS is thought to have a direct link to the durability of the polymer system. A great deal of effort has been made to assess the longevity of HALS over the years [41, 57-63]. Early work used FTIR combined with ultraviolet spectroscopy [64], chemical stress relaxation [58] and computer analysis based GPC [61] to evaluate the HALS longevity associated weathering performance of clear-coats. Other analytical techniques such as ESR were used to assess the concentration of active HALS in weathered paint systems, although no simple indicator was found for monitoring the real amount of active HALS [57, 59, 63]. The protection time of HALS was theoretically predicted by taking into account the chemical and physical loss of the stabiliser due to evaporation, leaching or reaction with the radicals present, as well as the concentration of active stabiliser [60]. Additionally, the sustainability of HALS could also be affected by the weathering techniques used. When polymers were exposed to dry conditions, a complete loss of the stabiliser occurred through oxidative fatigue and migration out of the matrix, while extraction by water was the main process observed in wet conditions [41]. A recent work revealed that HALS stabilisers do not change the degradation mechanism of PU network but that they do decrease the rate of degradation and limit the increase in hardness [65].

2.2.5. The stochiometry variation (isocyanate to hydroxyl groups (NCO/OH))

The ultimate properties of the PU networks can be varied through a wide range by
altering the isocyanate/hydroxyl molar ratio (NCO/OH) [66]. When isocyanate is used in excess of the stoichiometric requirement, urea and allophanate formation take place in addition to the standard urethane formation, which are likely to undergo a number of competing reaction [67]. Many publications studied thermoplastic PU systems in terms of photo-oxidation by varying NCO/OH ratio, and it was found that the physico-mechanical and anti-corrosive properties of PU coatings can be improved by increasing the hard-segment density [68-70]. Nevertheless, the influence of NCO/OH stoichiometry towards the degradation of thermoset PU coatings can be rarely found.

2.3. The degradation of polyurethane (PU) coil coatings

2.3.1. The degradation modes of PU coatings

With regard to polymers, degradation is used to denote changes in physical properties caused by chemical reactions involving bond scission in the backbone of the macromolecule. In practice, degradation is usually subdivided in to various modes including thermal, mechanical, photochemical, radiation chemical, biological and chemical degradation [71]. Chemical degradation refers to processes which are induced under the influence of chemicals including moisture and solvents brought into contact with polymer. Thermal degradation refers to the case where the polymer, at elevated temperatures, starts to undergo chemical changes without the involvement of other compounds. Biologically initiated degradation relates to the chemical degradation when microbial attack is involved. Mechanical degradation generally refers to macroscopic effects brought about under the external stresses and shear forces. Light-induced polymer degradation, or photo-degradation, concerns the physical and chemical changes caused by irradiation of polymers with ultraviolet, visible light or near infrared. Radiation degradation refers to high energy radiations, such as X-rays, γ-rays, α-rays, etc., induced polymer alterations. There is strong inter-relationship between the various modes of polymer degradation. In regards to PU coil coatings, chemical hydrolysis, thermal- and photo- degradation are of major interests and should be further elaborated.
2.3.1.1. The comparison of the thermal degradation and oxidation of PU coatings

Thermal degradation and oxidation depend on temperature of exposure, oxygen supply and the polymer structure. In the presence of oxygen, most polymers undergo rapid chain scission reactions below their melting points. This is due to the reaction of macroradicals with oxygen to form hydroperoxides which themselves are unstable and break down rapidly forming more free radicals, hence the whole process becomes autocatalytic. A typical mechanism for the oxidation of polymer systems is given in Scheme 2.3. This scheme is often referred to as the Bolland-Gee mechanism [3].
2. Background

Initiation

\[ \text{POLYMER} \rightarrow R \cdot \]
\[ R \cdot +O_2 \rightarrow RO_2 \cdot \]
\[ RO_2 \cdot +RH \rightarrow ROOH + R \cdot \]

Propagation

\[ R \cdot +O_2 \rightarrow RO_2 \cdot \]
\[ RO_2 \cdot +RH \rightarrow ROOH + R \cdot \]

Chain branching

\[ ROOH \rightarrow RO \cdot +HO \cdot \]
\[ 2ROOH \rightarrow RO_2 \cdot +RO \cdot +H_2O \]
\[ RO \cdot +RH \rightarrow ROH + R \cdot \]
\[ HO \cdot +RH \rightarrow R \cdot +H_2O \]

Termination

\[ RO_2 \cdot +RO_2 \cdot \rightarrow \text{Inert products} \]
\[ RO_2 \cdot +R \rightarrow RO_2 R \]
\[ R \cdot +R \rightarrow RR \]

Scheme 2.3 A typical mechanism for the oxidation of polymer systems [3].

In this scheme, a macroradical is formed initially within the polymer network, due to the \( \pi \)-electron radicals on carbon atoms in \( \text{sp}^2 \) hybridizations yielded by most polymers [72]. The macroradical reacts with oxygen to form a peroxide radical (\( RO_2 \cdot \)). The peroxy radicals are reactive and so easily abstract a hydrogen atom either by an intra- or inter-molecular process to generate a hydroperoxide (\( ROOH \)) group and another macro radical site. The hydroperoxides in turn decompose resulting in the formation of alkoxy (\( RO \cdot \)) and hydroxyl (\( HO \cdot \)) radicals. Chain transfer reactions then take place resulting in further accelerated hydrogen atom abstraction reactions giving rise to more free radical species and the whole process becomes autocatalytic. Termination processes give in-chain peroxides and a series of recombination products.
It is also important to note that, although the polymer undergoes these types of degradation in an amorphous or a crystalline mode, the rate of diffusion of oxygen is faster in the amorphous material due to the higher free volume content within the polymer network. Therefore, the polymer in amorphous mode oxidises faster compared to the crystallised mode.

### 2.3.1.2. The photo-degradation and photo-oxidation of PU coatings

Most commercial organic polymers undergo chemical reactions upon irradiation with UV light, because they possess chromophoric groups (as regular constituents or as impurities) capable of absorbing UV light. This fact is important because the spectrum of the sunlight penetrating the earth atmosphere contains a portion of UV light (200 – 400 nm, 5% energy) [73]. Therefore, photo-reactions are usually induced when organic polymers are subjected to outdoor exposure, which often cause embrittlement, cracking, chalking and colour changes [71].

Commercial PU coatings can be very complex materials and consequently their light stability varies greatly. A series of papers published in the late 1990s investigated photo-oxidative degradation of aliphatic and aromatic PU coatings using IR spectroscopy [17, 74, 75]. It was found that thermo- and photo- oxidation processes often follow similar pathways. Irradiation with long wavelength (> 300 nm) provokes an UV induced oxidation on the methylene group in α position to the NH groups (α-CH₂). Induced oxidation of the methylene groups in α position to the carboxylate group of the urethane and induced oxidation of the methylene groups of the soft polyester segments were observed to be an important path of evolution. The oxidative reaction that follows was thought to lead to the formation of secondary peroxides and hydroperoxides, which might evolve further by reaction with water to form carboxylic acids. The main
photo-products may include peresters, primary urethanes, acetylurethanes, primary amides, acids, anhydrides and CO₂ [16]. The chemical change pathway of the degradation of the PU coatings is illustrated in Figure 2.9.
Figure 2.9 The chemical evolution pathway of the degradation of the PU coatings (Wilhelm and Gardette 1997; Wilhelm, Rivaton et al. 1998; Irusta and Fernandez-Berridi 1999; Yang, Yang et al. 2001)
2.3.1.3. **The chemical hydrolysis of PU coatings**

The extent of moisture absorption in a given polymer is a function of its hydrophilicity or chemical compatibility with water. Its role is usually to act as a plasticiser, decreasing the glass transition or softening temperature and yield strength of the polymer [62]. Rainfall, however, may act in concert with photo-initiated oxidation to produce chemical hydrolysis due to the acid rain effect [76], in addition to the erosion of the material, serving to wash away the embrittled surface layer so as to expose new material to direct sunlight [5].

2.3.2. **The Durability of PU coil coatings**

2.3.2.1. **The accelerated and natural weathering tests for ageing the PU coatings**

Most materials are subject to weathering. Synthetic polymers offer an impressive range of attractive properties and in many of their applications they are exposed to the outdoor environment. Whatever the application, there is often a natural concern regarding the durability of polymeric materials partly because if the useful lifetime can be predicted their maintenance and replacement can be planned. Prediction of lifetime is essential for the provision of realistic warranties and concomitant minimisation of commercial liabilities.

The deterioration of a material depends on how and to what extent it interacts with its surroundings, the outdoor environment, if considered in terms of sunshine, temperature, rainfall and wind. These parameters vary widely in duration, intensity and sequence. For most polymeric materials the main cause for the loss of properties is photo-oxidative attack, which is the combined action of oxygen and sunlight on their chemical structure. Absorbed moisture generally less damaging to polymeric materials than is sunlight, but
its effects may be important in certain cases, as introduced in Section 2.3.1.3.

\textit{Natural outdoor exposure}

Weatherability data is collected to provide guidance for designers to consider its outdoor application. Exposure trials are important means of evaluating the weatherability of a polymer. Panel trials in tropical and sub-tropical regions are of particular importance because almost invariably the high levels of temperature, humidity and solar radiation found in such regions have proved more aggressive to materials than those of other temperate zones \cite{77}.

Typical natural exposure trials include 3 – 10 years exposure in tropical locations. Artificial exposure tests have been developed aimed at reducing the time scale of natural exposure trials by increasing the combined UV radiation, temperature and water effects while trying to keep them properly balanced. One of the extensively used artificial exposure tests is the Equitorial Mount with Mirrors for Acceleration with Water Spray (EMMAQUA) \cite{78}. In the EMMAQUA test samples are mounted on the underside of a cross-member at the top of the machine and 10 highly polished aluminium mirrors are positioned so as to reflect the sun’s rays onto the target area above. The samples are automatically sprayed with water for 8 min during each hour of operation, which is claimed to correspond to wet climates. Sometimes a backing material is used to provide sufficient thermal insulation to cause samples to become appreciably hotter in the sun than they would without support. Tests are usually constructed under the radiation of 960 mJ/m$^2$ (total UV dosage), which is often equivalent to three years natural exposure in Florida, US.

\textit{Artificial weathering device exposure}

While it is preferable to have factual information on the actual long-term performance
outdoors of a material, reliable prediction of durability is recognised as being a necessary substitute in most cases for the confident outdoor application of polymer materials. These tests generally attempt to reproduce the sunlight-induced degradation processes by an artificial light source, such as carbon-arc source, xenon-arc source, fluorescent tube lamps, etc [78].

It is obviously important that the physical and chemical changes induced by artificial weathering should duplicate those resulting from outdoor exposure. A major advantage claimed for artificial weathering devices is that they can be employed to assess the relative stability of polymers, particularly members of the same polymer type. However, for a variety of reasons artificial tests can sometimes give weatherability ratings quite different from those found outdoors. Lack of agreement between the solar spectrum and that of the artificial light source is a common cause of poor correlation between the two modes of exposure [79]. Therefore, the value of artificial weathering test is a subject which has been debated for decades.

The QUV accelerated weathering tester has been wildly used to examine the durability of industrial coating materials. The QUV tester is designed to simulate outdoor weathering in a short period of time compared to natural exposure. A typical QUV A test exposes materials to alternating cycles of UV A light and moisture at controlled, elevated temperatures. It simulates the effects of sunlight, dew and rain using special fluorescent UV lamps, condensing humidity and/or water spray. [80, 81]

### 2.3.2.2. The degradation rate evaluation of the PU coatings

The common degradation products of a polymer coating contain carbonyl and hydroperoxides groups (Section 2.3). A typical formation of degradation products for polyethylene is displayed in Figure 2.10. The hydroperoxides build up initially by oxygen scavenging of the alky radicals and a maximum concentration and then fall off as they begin to decompose rapidly through the chain-branching steps. Here, more radicals
are produced as a consequence of hydrogen atom abstraction by the hydroxyl radicals. A single macroalkyl radical can result in the consumption of many oxygen molecules and the reaction accelerates rapidly resulting in the growth of carbonyl products which quickly form following chain-branching. The rate of oxidation eventually levels off due to a reduction in accessible reaction sites. [3] Polymers including PU normally have more complicated molecular structures and varied degree of crystallinity, which may vary the corresponding graph of degradation products formation. For example, the presence of a labile hydrogen atom could ease the oxidation to form peroxides [17]. Amorphous state is more susceptible to oxidation than crystalline polymers due to the faster speed of oxygen diffusion [18].

Figure 2.10 Typical graph of chemical product formation versus time of thermal oxidation for polyethylene. [3]

FTIR spectroscopy has been commonly used to monitor the degradation rate of cured coatings by the use of the following degradation index:
When organic polymers oxidise, carbonyl and hydroxyl groups are amongst the most prevalent products. They are easily detected by FTIR at the wavenumber near 1710 cm\(^{-1}\) and 3400 cm\(^{-1}\). The hydroxyl index curve can be plotted by using \([\text{OH, NH, COOH}]/[\text{CH}]\) area ratios in the FTIR spectra versus exposure time [19], as a common method to quantitatively evaluate the performance of polymer coatings as a function of photo-oxidation and hydrolysis. As shown in Figure 2.11, the \([\text{OH, NH, COOH}]\) peak area includes the hydroxyl, amine and carboxylic acid peak areas in the 2200 cm\(^{-1}\) – 3700 cm\(^{-1}\) region, and \([\text{CH}]\) peak area includes the methylenic peak area in the 2700 cm\(^{-1}\) – 3000 cm\(^{-1}\) region.

Figure 2.11 hydroxyl index is determined by the peak area ratio of \([\text{OH, NH, COOH}]/[\text{CH}]\) in the FTIR spectra. [12]
2.4. Spectroscopic characterisation to the degradation of PU coatings

2.4.1. Introduction

2.4.1.1. The purpose of spectroscopic characterisation

The coil coating manufacturers have long relied on appearance-based measurements, such as gloss retention and colour change to monitor finish condition and durability. The primary limitation in using appearance-based measurements to determine coating system durability is in the time required for significant changes to take place. Years may be required for significant appearance changes to take place in many outdoor environments. However, chemical, physical and mechanical changes can be reliably monitored well before appearance-based changes are sufficient to be measured. The demand for decreased cycle time in the development of new coating products requires that the coatings industry identifies methods to take advantage of these other property changes in predicting durability or service life.

The ability to realistically approximate the durability or service life performance of a coating system is becoming very important [8]. The more accurate the prediction, the better in terms of risk management. A sensitive technique has the advantage of allowing the early stages of deterioration to be detected and so reduces the time required for assessment. Over the years a variety of analytical techniques have been used for surface, interface and depth profiling analysis in the study of coil coating systems [82, 83]. The ability to obtain detailed chemical, physical and mechanical information for a given layer, or on a multi-layered system, will be increasingly important in designing future systems. A key advantage for these types of information is that changes can be identified and monitored well in advance of appearance changes being detectable.
2.4.1.2. The application of Fourier transform infrared (FTIR) and Raman vibrational spectroscopy to the PU degradation

FTIR analysis has had a long and successful history in surface and depth chemical composition analysis of paint/coating systems. More recently, Photo-acoustic spectroscopy (PAS) has gained much attention and popularity as a better indicator of real world performance in chemical analysis due to a unique combination of many features including non-destructive, non-contact measurement, simple sample preparation, dept profiling capability and high signal saturation limit [12].

While Raman spectroscopy has long been recognised as a valuable research technique in the years since the phenomenon was first observed by Dr. C. V. Raman in 1928 [84], it is only fairly recently that Raman has emerged as an important analytical tool for organic coating industries. Raman spectroscopy provides information on coating system materials that is similar, but often complimentary, to that obtained from IR spectroscopy. The two techniques provide a high level of information on molecular structure. Both monitor interactions between source radiation and matter that result in vibrational (energy level) transitions characteristic of inherent molecular substructures. [4]

Although both are vibrational spectrosopes, they differ most in their response to molecular symmetry. Raman is particularly useful in analysis of molecular structures that are more symmetrical, including polymer backbone, isolated/conjugated double bond, and certain organic pigment/dye unsaturated ring substructures. IR tends to be particularly useful in analysis of polymer side chain functional group, cross-linker, and additive substructures that are asymmetrical. This highlights the complementary nature of the Raman and IR techniques.
2. Background

2.4.1.3. **The step scan phase modulation photo-acoustic (SS-PM-PA) FTIR and confocal Raman (CRM)**

The degradation of polymer coatings are recognised as initially occurring near the PU coating surface at a depth of a few microns, owing to the more enhanced interaction between polymer film and environment factors including, oxygen, water, and pollutant at the surface than in the bulk [3, 12]. SS-PM-PA FTIR has been demonstrated as a suitable technique for the study of the degradation chemistry of coil coatings for near-surface analysis with the advantages including non-destructive sampling and controlled probing depth [10, 11]. As a supplementary technique to FTIR, CRM shows great applicability at the surface compositional distribution studies of clear PU coatings [85]. In terms of data interpretation, it is important to consider the different sampling volume between CRM and SS-PM-PA FTIR. The expected volumetric resolution of a single Raman beam is approximately 1 μm³ for CRM method, whereas the sampling volume of lateral 10 μm in diameter by 6 μm in depth is expected for FTIR method. Theoretically, CRM investigates the surface chemistry more closely and is more specific to the film-air interface than SS-PM-PA FTIR.

2.4.2. **The infrared (IR) spectroscopy**

2.4.2.1. **The IR Theory**

As with most other spectroscopic techniques IR spectroscopy involves the interaction of light with the atoms and molecules of the sample under investigation. The incident IR light can be absorbed by the oscillation arising from the vibration and rotation of molecules. The energy needed to excite most of the vibrational modes in organic molecules falls in the IR spectral wavenumber region 4000 cm⁻¹ – 250 cm⁻¹. In IR spectroscopy, wavenumbers are usually plotted from higher wavenumbers to lower wavenumbers and the plot is called an IR absorption spectrum. [86, 87]
The incident IR light is absorbed by various parts of molecules, which are vibrating with a particular frequency at room temperature. The absorption of this energy increases the frequency of vibration. In terms of quantum theory, the vibrational quantum number \( v \) is increased from 0 to 1, which is from ground state to the first excited state. The energy of the light must correspond exactly to the energy difference between the two states otherwise no absorption occurs. Additionally, IR absorption occurs only when a certain vibration changes the electric dipole moment. The molecule process this type of vibration is called infrared active.

Individual groups vibrate at different frequencies depending upon the strength of the bond between the constituent atoms, their masses and the type of vibration occurring. High energy transitions are stimulated by high frequency (high wavenumber) photons and vice versa, hence it is possible to identify the groups present by measuring the frequencies of the light absorbed. Similar functional groups executing similar modes of vibration absorb in very similar regions of the spectrum. Hence it is not necessary to carry out extensive calculations for each individual case in order to identify the groups present, but simply consult previously constructed correlation tables [88]. The exact frequency absorbed is dependent upon the other groups attached and the surrounding chemical environment. For example, C=O groups of \(-C=\text{C}-\text{C}=\text{O}\) and \(-\text{CH}_2\text{-CH}_2\text{-C}=\text{O}\) give different frequencies, and a \(-\text{C}=\text{O}\) group and \(-\text{C}=\text{O} \ldots \text{H-}\text{O}-\) also yield different frequencies [89]. Hydrogen bonds formed in urethane and/or urea functional groups with NH “donor” groups H-bonded to C=O “acceptor” groups can be detected with IR spectroscopy [90, 91].

IR spectroscopy provides detailed information about vibrations of a molecule. The different modes of vibrations of AX\(_2\) type groups are considered in Figure 2.12. They include symmetric stretch, asymmetric stretch, in-plane deformations (scissoring and rocking) and out-of-plane deformations (twisting and wagging). Stretching vibrations
generally require the most energy to initiate a transition whereas the wagging and out
of plane deformations need least. Symmetric vibrations in which the dipole does not
change are not very infrared active whereas asymmetric vibrations are. In order to
study symmetric vibrations, the related Raman spectroscopic technique is required,
which will be discussed in Section 2.4.4.

Figure 2.12 Molecular vibration of AX₂ group: (1) symmetric stretching vibration, (2)
asymmetric stretching vibration, (3) scissoring vibration, (4) rocking vibration, (5)
wagging vibration, and (6) twisting vibration. [89]

The wide bands in the IR spectra occur because several rotational energy levels are
associated with each vibrational level, with the consequence that the frequencies of the
light absorbed are broadened around the very specific frequency associated with the
energy gaps between the two vibrational levels. The problem with wide bands is that
those which occur close together are difficult to resolve, particularly if one is large and
the other small. These problems also exacerbate the difficulties in obtaining accurate quantitative data.

2.4.2.2. **The theory of the step scan phase modulation photo-acoustic (SS-PM-PA)**

*Photo-acoustic (PA) effect*

For a solid sample, PA signal generation includes absorption of modulated optical illumination by the sample, followed by thermal diffusion from the bulk of the sample to adjacent medium (usually helium gas) and finally generation of the pressure oscillation in the helium gas. The pressure wave (sound) is then detected using a very sensitive microphone. This process is illustrated in Figure 2.13.
2. Background

Figure 2.13 Schematics of photo-acoustic signal generation and detection, which involve three major steps, absorption of modulated light by the sample, thermal energy diffusion in the medium and sound intensity detection by the microphone [92].

The one-dimensional thermal piston model proposed by Rosencwaig and Geršo for the PA effect in condensed-phase matter has been most widely referenced in literature [93, 94]. In this theory, photo-acoustic signal generated can be modelled using the heat equation and assuming a one-dimensional heat flow within the sample and adjacent gas atmosphere. The model is shown schematically in Figure 2.14.
2. Background

Figure 2.14 One-dimensional signal generation schematic showing the decay length, \( L \), for thermal-waves and the optical decay lengths for lower \((\alpha_1)\) and higher \((\alpha_2)\) values of absorption coefficient. As \( \alpha \) increases, more of the absorption occurs in the region near the sample’s surface that is active in signal generation [95].

The modulated incident IR beam is partially reflected \((RI_0)\) at the front face of the sample but this reflection is ignored in the simple model. The beam then decays exponentially with an absorption coefficient, \( \alpha(\tilde{\nu}) \), as it propagates within the sample. The wavenumber of the infrared radiation is denoted by \( \tilde{\nu} \). In most cases all of the absorbed radiation is converted into heat, causing the temperature of each absorbing layer to oscillate at the beam modulation frequency with amplitude proportional to the amount of light absorbed in it. Each of these layers becomes a source for inducing propagating temperature oscillations called thermal waves.

Thermal waves have a short decay length called the thermal diffusion depth or thermal wave decay length, \( L \), given by Equation 2.1:
where $D$ and $f$ denote the sample’s thermal diffusivity and the infrared beam modulation frequency, respectively. Thermal waves decay to 37% (i.e. $1/e$) of their original amplitude over a distance of $L$.

After the thermal waves are induced, those that propagate to the front face of the sample contribute to the PA signal, but most of their amplitude is not detected because they are reflected back into the sample and decay. The small thermal-wave amplitude that does transmit into the gas results in thermal expansion and a pressure oscillation in the gas, which increases with $\alpha(\bar{v})$, and that is detected as an acoustic signal containing both phase and magnitude information by a sensitive microphone. The phase of the PA signal is equal to the phase lag between the signal and the waveform of the IR beam that excites it. The lag is caused by the finite propagation time of thermal waves during signal generation. It results in the phase angle being a measure of the depth from which the signal evolves within the sample.

*Step scan and continuous scan*

The step scan (SS) is produced by dithering the fixed mirror along the retardation direction at a constant frequency. The term *phase modulation* (PM) comes from the fact that the optical path difference (OPD) modulation, or dithering, actually modulates the phase of the IR intensity. The PM interferogram is antisymmetric with respect to ZPD, when a digital signal processor (DSP) is used for demodulating the detector signal. Conversely, the moving mirror velocity is kept constant and the fixed mirror is still in the continuous scan experiment.

For heterogeneous or layered samples, the variation in sampling depth across the entire spectral region makes the interpretation of a continuous scan PA spectrum ambiguous,
because the spectral features in different regions could come from different layers. Since
the modulation frequency (MF) varies with wavenumber in continuous scan, the probing
depth varies across the entire spectrum. According to Equation 2.2, the probing depth at
400 cm\(^{-1}\) is about three times deeper than that at 4000\(^{-1}\) in a continuous scan PA FTIR
spectrum:

\[
(f_{4000}/f_{400})^{1/2} = (4000/400)^{1/2} = 3.16 \quad \text{Equation 2.2}
\]

Also, at a constant velocity of the moving mirror, the PA signal becomes weaker at
higher wavenumbers (shorter wavelengths) because of the proportional dependency of
Fourier frequency on the wavenumber of the light. The limitation of continuous scan PA
can be overcome by coupling the photo-acoustic cell with a SS-PM FTIR spectrometer.
As already mentioned above, a single-frequency PM applied to the fixed mirror is
therefore used to modulate all wavelengths of the radiation to generate the PA signal,
resulting in a uniform probing depth across the entire spectrum.

The use of a discrete phase modulation frequency offers the convenience of using DSP
techniques to demodulate the PA signal and extract the signal phase from the
simultaneously generated in-phase, \(I(\sigma)\), and quadrature (out-of-phase), \(Q(\sigma)\),
components of the signal. Thus, the calculation of the PA signal phase \(\Phi(\sigma)\), and
magnitude, \(M(\sigma)\), spectra can be made, as illustrated by Equation 2.3 and 2.4.

\[
\Phi(\sigma) = \tan^{-1}[Q(\sigma)/I(\sigma)] \quad \text{Equation 2.3 [95]}
\]
\[
M(\sigma) = [I(\sigma)^2 + Q(\sigma)^2]^{1/2} \quad \text{Equation 2.4 [95]}
\]

2.4.3. FTIR peak fitting

2.4.3.1. The theory of FTIR peak fitting

The basic theory behind the origin of line shape is applicable to peak fitting [96, 97]. In
quantum theory, molecules possess well defined energy levels. Transitions between these levels, caused when molecules absorb or emit energy, therefore occurs in well defined intervals (quanta), which gives rise to the vibrational spectrum. Most vibrating molecules exist in a bath of surrounding molecules (the environment), with which they interact. Each molecule interacts with its environment in a dynamic way, and thus vibrates at a slightly different frequency. The observed line shape is the sum of these individual molecules vibrating.

The majority of molecules in the experiment initially are in the ground state, which called equilibrium. When the light beam strikes the sample, some of the molecules transition to the excited state. The resulting spectrum represents the signal seen by the instrument. Excited state molecules rapidly return to the ground state – for vibrations, this occurs after a few picoseconds ($10^{-12}$ sec). This relaxation is called the lifetime (or amplitude correlation time) $\tau_a$. Initially, all of the excited molecules are vibrating together (coherently) but motion and slight differences in vibrational frequencies randomises this over time. The spectrometer can only detect the molecules while they are both excited and coherently vibrating. As the coherence fades (with coherence lifetime $\tau_c$), the random components interfere, and effectively cancel one another (dephasing). In this situation, the sum of incoherence is zero.

The effective lifetime $\tau$ is a combination of these two components, the coherence lifetime $\tau_c$ and the amplitude correlation time $\tau_a$. When $\tau_c >> \tau_a$, the excited molecule relaxes before incoherence becomes severe. This is the case for solids, because the environment is not in motion. The various molecules of the solid experience a statistical distribution of environments and the line shape takes on the bell curve or Gaussian profile. This profile has the well-known shape from statistics, with a curving centre and wings that fall away relatively quickly. In the second case, where $\tau_c << \tau_a$, the incoherence sets in rapidly, so dephasing is the dominant energy loss channel. This occurs in gases or liquid where rotation and collisions happen quickly. The resulting line
shape is Lorentzian, which is sharp in the centre, but has long wings. The Voigt profile is similar to the G-L, except that the line width $\Delta x$ of the Gaussian and Lorentzian parts are allowed to vary independently.

The location of a peak (wavenumber) is controlled first by the natural vibrational frequency of the isolated molecule. However, the actual peak location also depends upon interactions with the environment. For instance, if the molecule is hydrogen bound to neighbours, this effectively lowers the bond energy (spreads the bonding energy over more space), and the peak will shift to lower energy.

The height of a peak depends upon the number of molecules present (concentration) and the strength of the absorption (absorptivity). On the other hand, as there may be peak broadening or shifting, the area of the peak is a better indicator of concentration. Peak fitting allows area to be used.

Line widths are normally reported as full width at half height (FWHH). There are many theories explaining the influence of various environments on line width [98]. At a simple level, the line width is inversely proportional to the effective lifetime $\tau$. Rapid loss of the excitation (short $\tau$) results in broad peaks, and a long lifetime (long $\tau$) leads to narrow peaks. This explains the enormously broad O-H peaks of water, as the tight hydrogen bonding network allows the molecules to relax extremely rapidly. Collisions between molecules can also enhance energy loss rates, and may broaden peaks.

2.4.3.2. The purpose of FTIR peak fitting

SS-PM-PA FTIR has been demonstrated as a suitable technique for the degradation chemistry study of PU coatings. However, the relative low resolution caused by the overlapping nature of IR band has been claimed to add difficulties for spectral interpretation and quantitative analysis [20]. In purpose of gaining more insight spectroscopic information, peak fitting procedure has been recognised as of great utility
2. Background

Previous work on the subject of biological materials has demonstrated the application of peak fitting procedure on the interpretation of complex IR bands, such as amide groups [21], carbonyl groups [6, 22], and hydrogen bonding [5, 23]. Quantitative evaluation of other polymer materials was also discussed in a few literatures by using peak fitting method. The main regions of interest are the NH region, with characteristic IR absorption bands at 3320 cm\(^{-1}\) and 3420 cm\(^{-1}\) corresponding to H-bonded and free NH group stretching, and the carbonyl region which is defined by three carbonyl stretching vibrations including the non H-bonded C=O (1732 cm\(^{-1}\)) and two stretching vibrations associated with disordered (1712 cm\(^{-1}\)) and ordered (1700 cm\(^{-1}\)) H-bonded C=O. Hydrogen bonds in PMMA and PVPh blends was investigated and the calculation of absorption coefficient of free hydrogen bond of such system was carried out [99]. More work using ATR/FTIR and peak fitting technique was concentrating on the influence of hydrogen bonding on the molecular structure of a polyamide in water [100]. Nevertheless, the application of FTIR peak fitting on the degradation evaluation of PU coatings has not been fully discussed.

2.4.4. Raman spectroscopy

The inelastic scattering of photons of light is named the Raman effect after its experimental discoverer [86]. The Raman effect (or Raman scattering) is a fundamental form of molecular spectroscopy [101]. Together with IR, Raman scattering is used to obtain information about the structure and properties of molecules from their vibrational transitions [102].

As introduced in Section 2.4.2.1, IR absorption arises from a direct resonance between the frequency of the IR radiation and the vibrational frequency of a particular mode of vibration. The property of the molecule involved in the resonant interaction is the change in the dipole moment of the molecule with respect to its vibrational motion. IR
absorption is a single-photon event. The IR photon encounters the molecule, the photon disappears and the chemical entity is elevated in vibrational energy correspondingly to the energy of the photon at the frequency of vibrational resonance. By contrast, Raman scattering is a two-photon event. In this case, the property involved is the change in the polarizability of the molecule with respect to its vibrational motion. The incoming radiation creates an induced dipole moment in the polarisable molecule, and the radiation emitted by this induced dipole moment contains the observed Raman scattering.

The light scattered by the induced dipole of the molecule consists of both Rayleigh scattering and Raman scattering. Rayleigh scattering corresponds to the light scattered at the frequency of the incident radiation, whereas the Raman radiation is shifted in frequency, and hence energy, from the frequency of the incident radiation by the vibrational energy that is gained or lost in the molecule. As illustrated in the simplified energy level diagram (Figure 2.15), a molecule at rest resides in the ground vibrational and electronic states. The electric field of the laser beam raises the energy of the system for an instant by inducing a polarization in the chemical species. The polarized condition is not a true energy state and is referred to as a ‘virtual energy level’. Relaxation from the virtual energy level occurs almost instantaneously and is predominantly to the initial ground state. This process results in Rayleigh scatter, in which the scattered light is of the same wavelength as the excitation laser. Relaxation to the first excited vibrational level results in a Stokes-Raman shift. In the Stokes-Raman shift, scattered light is of lower energy (longer wavelength) than that of the laser light. In addition, most systems have at least a small population of molecules that are initially in an excited vibrational state. When the Raman process initiates from the excited vibrational level, relaxation to the ground state is possible, producing scatter of higher energy (shorter wavelength) than that of the laser light. This type of scatter is called anti-Stokes Raman scattering [13].
2. Background

2.4.5. Scanning electron microscopy (SEM)

2.4.5.1. The theory of SEM

An SEM uses a rastered electron beam to produce an image. The resolution of a microscope employing electrons in place of visible photons is tremendously increased. A typical source used for generating the electron beam is by accelerating electrons emitted via the photoelectric effect from a lanthanum hexaboride cathode. The resolution can approach less than 5 nm with this electron source. A high vacuum is required for the electron sources in order to increase their life. The accelerating voltage is normally varied between 15 kV and 25 kV. The beam is focused by a series of electromagnetic lenses on to a sample and is scanned across it.

The sample is mounted on a stage which can be manipulated either manually or by software. A polymer sample is commonly sputter coated by carbon or gold to facilitate the surface charge. When the primary beam of electrons interacts with the sample several different kinds of event can occur.

Figure 2.15 The different possibilities of visual light scattering: Rayleigh scattering (no Raman effect), Stokes scattering (molecule absorbs energy) and anti-Stokes scattering (molecule loses energy). The latter two are reduced Raman scattering events.
Elastic collisions

The electrons are deflected from the incident path but with little loss of energy. If they are reflected back out of the sample, they are termed back scattered electrons. Their number increases with the atomic weight of the elements in the sample. They can be detected and information used to construct a grey scale map, which is an image of atomic number contrast.

Inelastic collisions

These absorb some of the energy from the primary electrons and dispose of it in several ways. Firstly, atoms can be ionised with the production of secondary electrons, which are emitted from the surface in all directions. The secondary electrons are detected and the signals used to form the typical SEM topographical image. Polymer coating samples are normally vacuum sputtered at the surface with a very thin layer of gold or carbon to facilitate the charging. Secondly, the holes left in the shells of atoms by the emission of secondary electrons can be filled with electrons from the outer shells. This leads to energy build up within the atom which needs to be released. One common mechanism is the emission of an x-ray which can be measured to give the information of the surface composition of a sample. Thirdly, an atom can lose energy by ejecting an electron from the outer shells termed Auger electron. Fourthly, when electrons recombine with holes some materials can radiate ultraviolet, visible or infrared radiation. Finally, if a nucleus of an atom in the sample scatters electrons and absorbs energy, it re-emits Bremsstrahlung radiation which forms part of the background of the entire radiation.

2.4.5.2. The purpose of SEM

It was recognised that the degradation of PU coating occurs initially near the film-air interface and presents a localised feature [11]. The degraded PU coating surface presents
topographic variation along with the degradation [16, 103]. SEM was employed to study the topographic features of degraded PU coatings [104, 105]. Supportive information to the FTIR spectroscopic results can be obtained by SEM images to demonstrate visualised physico-chemical changes as a result of degradation.

2.4.6. Other techniques

The spectroscopic methods which are available to measure the deterioration of a photo-oxidised or weathered polymer are many and varied. Some of them are found of more appropriate means of assessing the degraded polymeric coating materials than others. Ultraviolet-visible spectroscopy can be used to monitor the absorption curve broadening of the polymer caused by photo-oxidation [64]. Photo-luminescence spectroscopy have been related to polymer chain length and used to follow molecular weight changes [106]. Electron spin resonance (ESR) spectroscopy has been extensively used to follow radical processes in the radiation of polymers [5]. X-ray photo-electron spectroscopy (XPS) provides information on elemental, oxidation state and functional group composition, often in studies of adhesion failure of polymer coating systems [107]. Secondary ion mass spectrometry (SIMS) has been successfully applied in characterisation of coating system surfaces and interfaces obtained through delamination or sectioning techniques [108].

2.4.7. Summary

Degradation characterisation techniques such as those described herein allow designers of coating systems to take an intimate look at chemical composition and/or distribution. The studies discussed are aimed at determining correlations between chemistry and physical performance, which tend to be early indicators of impending appearance changes.
3. Methodology

Following to the background knowledge discussed in Chapter 2, this chapter describes the methods of the coil coating making, exposure and spectroscopic analysis used in this study. Firstly, the sample preparation technique for the spectroscopic analysis is given in Section 3.1. The details of the weathering protocols used for exposure tests are described in Section 3.2. Section 3.3 describes the instrumentations, software packages and experimental setting of the spectroscopic technique used.

3.1. Sample preparation

The model coil coating samples were prepared at Becker Industrial Coatings, Ltd (Liverpool, UK) using a conventional laboratory method which stimulates an industrial coating line. The liquid paint was pre-mixed with a spin mixer then applied onto a steel panel already coated with standard polyester-melamine primer coating. The primer coating contained TiO₂ and other pigments, and was approximately 5 μm in thickness. A wire wound draw down bar (0.15 mm wire diameter) was used to apply the paint onto the pre-primed substrate. The total dry film thickness (topcoat plus primer) of approximately 25 μm was measured. The panel was cured in an electric-heated oven for 30 seconds to reach a peak metal temperature of 232°C. The cured panels were then quenched with cool water and dried by an air knife. Coupons of diameter 8 mm were punched out on both exposed and unexposed samples and analysed with the spectroscopic methods discussed in Section 2.4.

The cross-section samples were prepared and polished using a standard method. Firstly, a strip was cut off the panel and mounted vertically in a mould. The position was maintained by an appropriate right angle bend so as to keep the strip standing vertically. Secondly, the mould was filled with a polyester based casting resin and allowed to solidify. Finally, the sample blocks were demoulded and polished using a Struer Labopol
5 grinding machine with the final fitness of a fine silk polishing cloth and associated diamond abrasive liquid (with the diamond particle size of approximately 3 μm).

3.2. Weathering protocols

The weathering protocols used in this study include:

(i) The weathering protocol used in this study was QUV A accelerated ageing, which consisted of placing samples in Q-Panel™ (Q-Panel Laboratory Products, Ohio) accelerated weathering chambers conforming to ASTM G-53 requirements. UV-340 fluorescent lamps emitting a spectral irradiance of 0.77 W m⁻² (measured at 340 nm) were used in conjunction with a daylight filter to closely approximate the spectral power distribution of noon summer sunlight in the range of approximately 295–450 nm. A temperature of 60°C was maintained inside the chambers for the 8 hours duration of the UV cycle and the prescribed 4 hours condensation cycle maintained at 50°C. Samples were subjected to alternative UV and water condensation exposure for a total duration of 4098 hours. Samples with exposure intervals of 0 hours (unexposed), 1200 hours and 4098 hours were then punched out as round coupons with 8 mm in diameter and analysed using spectroscopic methods discussed.

(ii) 12 month natural exposure test in Speke, Liverpool, UK (LIV). The weather is wet, urban and moderate.

(iii) 12 month natural exposure test in Vereeniging, South Africa (SA). The weather is warm and moderate.

(iv) 12 month natural exposure test in Kuala Lumpur, Malaysia (KL). The weather is hot, humid, high UV and high dirt.
The climate data of natural exposure sites were collected from the climate website [109] and the Meteonorm 6.0 software as summarised in Table 3.1.

Table 3.1 Climate data of natural exposure sites Speke, Liverpool, UK (LIV), Vereeniging, South Africa (SA) and Kuala Lumpur, Malaysia (KL) in the year of 2010.

<table>
<thead>
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<th>Natural exposure site</th>
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Gr - global radiation (kW/m²)
T - Average temperature (° C)
TM - annual mean maximum temperature (° C)
Tm - annual mean minimum temperature (° C)
PP - total annual precipitation of rain and / or snowmelt (mm)
V - mean annual wind speed (km / h)
RA - Total days it rained during
SN - Total days it snowed during
TS - Total days with thunderstorm during
FG - Total foggy days during the year
TN - Total days with tornado or funnel cloud during
3.3. Characterisation techniques

3.3.1. Fourier transform infrared (FTIR) analysis

3.3.1.1. The instrumentation of FTIR technique

Michelson interferometer

The heart of the most modern FTIR spectrometers is the two-beam Michelson interferometer. It consists of a source of infrared light, a fixed mirror, a moving mirror and a beam splitter, as illustrated in Figure 3.1. The collimated IR beam from the source (S) is partially transmitted to the moving mirror and partially reflected to the fixed mirror by the beam-splitter. The two IR beams are then reflected back by their respective mirrors to the beam-splitter. The light beams then leave the interferometer to interact with the sample and strike the detector (D). The detector then sees the transmitted beam from the fixed mirror and reflected beam from the moving mirror simultaneously. The two combined beams interfere constructively or destructively depending on the wavelength of the light and the optical path difference introduced by the moving mirror.

Figure 3.1 Optical diagram of a classic Michelson interferometer, which consists of three major components: a fixed mirror, a moving mirror and a beam-splitter.
If the moving mirror and fixed mirror are the same distance from the beam splitter, the distance travelled by the light beams that reflect off these mirrors is the same. This condition is known as zero path difference (ZPD). In a Michelson interferometer an optical path difference (OPD) is introduced between the two combination light beams by translating the moving mirror away from the beam splitter. The OPD is then defined by the difference of the travel distances of the two light beams reflected from the mixed mirror and the moving mirror, respectively.

The interferogram is a plot of the light intensity variation along the OPD, or optical retardation (δ). The interferogram is a simple sinusoidal wave when a monochromatic source is in use, as shown in Figure 3.2. In this case, when the beams that have reflected off the fixed and moving mirrors recombine at the beam-splitter, they will be in-phase. Their crests and troughs will overlap. Because the beam amplitudes are additive, the two reflected beams add to give a light beam whose amplitude is greater than the amplitude of each of the individual beams. This phenomenon is known as constructive interference. This also takes place when the OPD is equal to multiples of the wavelength.

When the monochromatic light source in the interferometer is replaced with a broadband infrared source, the source gives off light at a continuum of wavelengths, each one of which gives rise to a different cosine wave interferogram. The total interferogram measured by the detector is the summation of the interferograms from all the different infrared wavelengths. In this case, the interferogram is a superposition of sinusoidal waves for IR light at all wavenumbers. At ZPD, all the sinusoidal waves are totally constructive, producing a centerburst on the interferogram (Figure 3.2). As OPD is increased, sinusoidal waves of different frequency get out of phase with each other and destructively interfere. As a result, the intensity of interferogram drops off rapidly as the mirror moves away from ZPD and into the wings.
Figure 3.2 Sinusoidal and centre-burst interferograms for monochromatic and continuum light sources, respectively.

*Fourier transformation*

A Fourier transform is performed on the light spectrum as it passes through the interferometer. As illustrated in Figure 3.3, the generated interferogram must be Fourier transformed to get the spectrum back [110].

In mathematics, the Fourier transform is an operation that transforms one complex-valued function of a real variable into another. In such applications as signal processing, the domain of the original function is typically time (retardation) and is accordingly called the time domain. That of the new function is frequency, and so the Fourier transform is often called the frequency domain representation of the original function. It describes which frequencies are present in the original function. In other words, Fourier transform is to convert an interferogram (data in the time domain) to a single-beam spectrum (data in the frequency domain) to reveal the response at all frequencies within the spectral range.
The interferogram intensity of the IR source is mathematically described as:

\[
I(\delta) = \int_{-\infty}^{+\infty} B(\sigma) \cos(2\pi \sigma \delta) d\sigma
\]

where \( \delta \) is OPD (cm), or retardation, \( B(\sigma) \) is the spectral intensity as wavenumber \( \sigma \) (cm\(^{-1}\)). Thus, an interferogram is a plot of detector response versus OPD. Fourier transformation of \( I(\delta) \) gives the single-beam IR spectrum expressed as:

\[
B(\sigma) = \int_{-\infty}^{+\infty} I(\delta) \cos(2\pi \sigma \delta) d\delta
\]

When an interferogram is Fourier transformed, a single beam spectrum is obtained as a plot of raw detector response versus wavenumber. The Fourier transformed spectra are commonly acquired for spectroscopic techniques including FTIR for further qualitative and quantitative analysis.
3. Methodology

Figure 3.3 An illustration of how an interferogram is Fourier transformed to generate a single beam infrared spectrum. [110]

The following illustration (Figure 3.4) identifies some major components visible on the outside of the Nicolet™ 8700 Research FTIR Spectrometer.

*Nicolet™ 8700 Research FTIR Spectrometer*
There are two important parameters associated with SS-PM experiments: modulation frequency and amplitude. The frequency determines probing depth, and the amplitude defines modulation efficiency and affects the energy profile over the entire spectrum due to the Bessel function effect [111]. The distance of the mirror oscillation is usually expressed in terms of $\lambda_{\text{HeNe}}$. One of the principal advantages of the Nicolet 8700 FTIR spectrometer is that PM is actuated on the fixed mirror of the Vectra-Piezo interferometer by piezoelectric transducers [92]. This design allows PM frequencies and amplitudes to be varied over the wide range that is typically needed for SSPM experiments in both near-IR and mid-IR regions.

- PM Frequency: 5 – 1,000 Hz
- PM Amplitude: 0.5 – 3.5 $\lambda_{\text{HeNe}}$

KBr beam-splitter is used to facilitate the PA detector and data acquisition in Mid-IR region (400 – 4000 cm$^{-1}$). The aperture parameter setting of 100 is used throughout the experiment, which gives a nominal aperture diameter of 8 mm and an approximate IR
radiating area of 0.5 cm². Helium purging of the sample and microphone is used to enhance sensitivity, allow higher frequency operation and remove moisture and carbon dioxide.

3.3.1.2. **OMNIC™ SST software package**

The SST menu in OMNIC gives one access to the SS-PM experiments. A typical OMNIC SST setup screen for a SS-PM experiment is shown in Figure 3.5. The Start button allows a short setup scan using the setup parameters and displays the results in this window. The phase angle calibration button is located on the bottom right corner and must be pressed when the carbon black reference is placed in the PA cell. The phase angle calibration is used to maximise PA signals in the in-phase (I) channel and subsequently the quadrature (Q) channel is minimised. After this phase angle calibration is completed, the PM phase setting will remain unchanged for running samples under the same modulation frequency. The resulting in-phase spectrum of the sample will therefore enhance the surface absorption features and the quadrature spectrum will enhance those from the substrate for deeper part of the sample. When all the parameters are setup properly, the instrument is ready for spectra collection.
3. Methodology

3.3.1.3. Experimental settings

SS-PM-PA FTIR spectra were collected using a Nicolet 8700 FTIR spectrometer (Madison, USA) with a MTEC Model 200 PA cell (Ames, USA) throughout the experiments of this study. The PA cell was purged with dry helium gas at a rate of 30 cm$^3$ s$^{-1}$ for 5 minutes before spectra acquisition. Three spectra were collected for each sample at different positions, and the averaged spectra were employed for analysis. The spectra error of approximately 1% was expected based on the previous work by monitoring the peak area ratio of two strong peaks from the multiple spectra collected with the same sample. MF of 800 Hz and 500 Hz and amplitude of 3.5 $\lambda_{\text{HeNe}}$ were used to ensure constant sampling depth of approximately 5.6 µm and IR irradiation efficiency throughout the collecting region. Spectra were collected in the mid-IR (4000 cm$^{-1}$ – 400 cm$^{-1}$).
3. Methodology

The region with a spectral resolution of 8 cm\(^{-1}\) was used for background calibration. OMNIC software package was used for data acquisition and analysis.

3.3.2. OMNIC™ peak resolve operation

The goal of spectral peak fitting is to mathematically create individual peaks from a spectrum that, when added together, match the original data. Convergence is the process used to make this happen. The algorithm converges rapidly when started with satisfactory parameters.

Peak fitting involves three major steps including choice of initial profiles (line shapes and baseline handling), choice of initial parameters (width, height, location), and minimisation. Figure 3.6 demonstrates an example of the OMNIC™ peak resolve operation window. The first parameter in the Find Peaks box defines the peak type. The choices are Gaussian (good start for solids), Lorentzian (good start for gases) and mixed Gaussian/Lorentzian or Voigt (both good starts for liquids). The Sensitivity parameter determines the polynomial order used in calculating the derivative of the algorithm. The specified FWHH is used in defining the number of smooth points in the derivative calculation. Find Peaks button is to be pressed to automatically define a set of peaks based on the current sensitivity and FWHH settings. Noise Target to describe how much noise is in the spectrum. The type of baseline component in the fit operation Baseline drop-down list is to be selected, which includes None, Constant, Linear, Quadratic or Cubic types of baseline shape. When all the parameters are setup properly, Fit Peaks button is to be pressed to initiate the process of automatically adjusting the peak centre, height and width to produce a composite spectrum that matches the original. During the fit operation, a Fit Progress dialogue box indicates the number of iterations that have been performed and how closely the composite spectrum matches the original.
There are further considerations in making a peak fitting scientifically efficient and meaningful. First, fitting routines converge more effectively with the better the initial parameters. Further, the final fit values will “stay home” better if the initial estimates are close. Second, a fitting algorithm, given enough peaks and varying parameters, can fit any spectrum. A certain amount of scientific insight is needed to make the peak fitting procedure more meaningful. Third, the whole point of a fitting routine is to converge to a local minimum of the residual. Occasionally, fit routines can “move” peaks a substantial distance to a place in the spectrum where they make no physical sense, but where the convergence is slightly better. To solve this, the step of locking certain parameters should be carried out, which can keep peaks from drifting away from their original location.
3.3.3. Confocal Raman analysis

3.3.3.1. The instrumentation of Raman analysis

Four major components make up the commercially available Raman spectrometer. These consist of the following:

1. Excitation source, which is generally a continuous-wave laser
2. Sample illumination and collection system
3. Wavelength selector
4. Detection and computer control/processing systems

Lasers are ideal excitation sources for Raman spectroscopy due to the characteristics of the laser beam including highly monochromatic and easily focusing. Since the Raman scattering is inherently weak, the laser beam must be focused properly onto the sample and the scattered radiation collected efficiently. The focusing of the laser onto the sample can be readily achieved because of the small diameter of the laser beam (~ 1 mm). Excitation and collection from the sample can be accomplished by using several optical configurations. Wavelength selectors are used to select desired wavelengths produced by laser beams. The laser beam with selected wavelength passes prism or grating monochromators and spectrographs to generate Raman signal, which is then recorded by the detectors to produce Raman spectra. Charge-coupled device (CCD) has been increasingly used in Raman spectroscopy. A typical CCD is a silicon based semiconductor arranged as an array of photosensitive element, each one of which generates photo-electrons and stores them as a small charge. Charges are stored on each individual pixel as a function of the number of photons striking that pixel and read by an analogue-to-digital converter [13, 86].

Confocal Raman Microscope
The significant improvement for reducing the influence of scattered light for Raman microscopy was based on the hypothesis that all the scattered light could be avoided by preventing it from entering the microscope objective in the first instance. This was achieved by setting a pinhole aperture in front of the light source. In this case the small pinhole aperture refocused by the microscope objective illuminates only a single point on a sample, which reduced the total amount of scattered light by a few orders of magnitude without affecting the focal brightness. The second pinhole aperture placed between the microscope objective and the image plane rejects the residual scattered rays originated from any out-of-focus points on the sample and functions as a spatial filter (Figure 3.7). Such an optical design offers a few distinctive benefits. The first pinhole aperture greatly reduces scattered (stray) light and immensely improves the image quality while the second aperture eliminates any image degrading out-of-focus information, allows for controllable depth of field and gives the ability to collect series of optical sections from bulk specimens.

Figure 3.7 (a) Simplified scheme of the reflective confocal microscope with two pinhole apertures. (b) Spatial filtering with the second pinhole aperture of the
3. Methodology

horizontal and (c) out-of-focus rays.

**CRM**

CRM combines confocal Raman spectroscopy with digital imaging technology in order to visualise material chemical composition and molecular structure. Raman chemical imaging techniques have recently achieved a degree of technological maturity that allows the collection of high-resolution data [13].

The simplest mapping technique characterises flat samples by mapping a thin 2D layer on the sample surface which is called a single optical X-Y section (Surface Scan, Figure 3.8 (a)). A 2D cross-section information can be obtained non-destructively by scanning optical X-Z direction on a sample (Depth Profiling, Figure 3.8 (b)). In principle the 3D structure of a bulk sample can be revealed by combining surface scan and depth profile techniques. The resulting information is transferred into software to reconstruct the detailed 3D image (X-Y-Z scan, Figure 3.8 (c)). If obtaining a surface profile is of interest, one can use an auto-focusing technique which is faster than reconstructing a 3D surface of a sample from the X-Y-Z scan. While scanning the sample surface the focal point microscope objective is moved up and down to focus precisely on the sample surface (Auto-focusing, Figure 3.8 (d)). The technique resembles a profilometer in function but the confocal surface profiling can reveal not only morphological but also detailed chemical information about the sample.
3. Methodology

Figure 3.8 2D mapping with single X-Y (a) and X-Z (b) optical sections, 3D mapping with multiple X-Y-Z optical sections (c) and a single X-Y-Z profile (d) obtained in auto-focus mode.

Nicolet™ Almega® Visible Raman Spectrometer

The main components of Almega spectrometer are illustrated in Figure 3.9. The microscope allows one to position and focus on a microscopic area of a sample and collects data from that area. The sample can be moved by the motorised stage in the X, Y and Z directions by using a joystick controller. The sample can be positioned and focused while monitoring the live signal with the microscope doors closed.

The spectrograph of the instrument consists of an entrance slit or pinhole aperture, diffraction gratings, a CCD camera and optic. The amount of light from the sample that enters the spectrograph is controlled by the aperture in the spectrograph. Candidate apertures include several sizes of entrance slits and pinholes. The optimum selection of the aperture depends on the consideration of the spectral resolution and the intensity of the Raman signal. The diffraction grating is used to disperse the incident light into a spectrum of its composite wavelengths. The light with selected wavelength strikes the CCD camera. The CCD is a two-dimensional array of pixels, each of which responds as
an independent detector. The light from the grating is dispersed over the area of the array, each wavelength falling on a different column of pixel. Pixels in each horizontal row measure different spectral wavelengths. Pixels in each vertical column provide redundant signal at the same wavelength. By reading the signal from the entire array, the system constructs the sample spectrum.

Figure 3.9 Nicolet™ Almega® Visible Raman Spectrometer

The Raman Spectrometer used in this work is equipped with two laser sources with the wavelength of 785 nm and 532 nm, respectively. By changing the software parameters, the power of the corresponding laser can be turned on, a mirror is moved to direct its light into the beam path, and moves the appropriate filters and gratings into place.
3.3.3.2. Experimental settings

Confocal Raman spectra were collected using a Nicolet™ Almega® Visible Raman Spectrometer (Madison, USA) and a ×100 magnitude dry objective (Olympus) throughout the experiment of this study. 785 nm wavelength laser excitation with 100% laser power and 100 % pinhole size were setup to reach a volumetric resolution of approximately 1 μm³. The laser beam is directed through the objective, and back-scattered radiation is collected with the same objective. The collected radiation is directed through a notch filter that removes the Rayleigh photons, then through a confocal hole and the entrance slit onto a grating monochromator (950 groove/mm) that disperses the light before it reaches the CCD detector. All spectra were obtained at multiple spectrograph positions providing a spectral range of 400 – 4000 cm⁻¹ and 4 cm⁻¹ resolution. OMNIC™ software was used for data acquisition and analysis.

CRM results were established with OMNIC™ Atlys™ software package. The laser beam was focused on clear-coat surface throughout the entire collecting process. A 10 × 10 μm mapping area was selected in the x-y surface direction with a sample translation step size of 1 μm. Each sampling point was scanned 256 times with each scanning run taking 1 second, resulting in a total laser exposure of 256 seconds.

3.3.4. SEM analysis

SEM (Inspect F, FEI, USA) was used to examine topography of the PU coating film in this study. An SEM accelerating voltage of 20 kV and a secondary electron beam spot size of 3.5 μm were used throughout the studies. Samples were sputter coated with carbon prior to insertion in the SEM to facilitate charge compensation. The sample stage was 75° tilted for coupon samples to give better topographic images.
4. The applicability of step scan phase modulation photo-acoustic FTIR to the depth profiling of TiO\textsubscript{2} pigmented coil coatings

4.1. Introduction

As described in Section 2.4.2, step scan phase modulation photo-acoustic (SS-PM-PA) FTIR has gained significant importance for the investigation of polymer materials over the decades. The step scan function of the technique can be applied to review the depth profiling of certain components with the coating. There has been extensive work regarding the depth profiling of polymer laminates [112] and hybrids [113, 114] by using SS-PM-PA.

The durability of the coating can be significantly affected by the depth distribution of the pigment used, because of the stability variation of the pigment and polymer phases [115, 116]. TiO\textsubscript{2} pigment has been extensively used in polymer coatings to give hiding power, adjust the colour, and increase the UV stability of the coating. It has been reported that the TiO\textsubscript{2} pigmented coating is more durable towards the degradation compared with the non-pigmented due to the photo-stabilisation effect of the treated TiO\textsubscript{2} [117, 118]. Therefore, it is important to clarify the depth distribution of the TiO\textsubscript{2} pigment within the coating to evaluate the durability of the coil coating.

Apart from the durability, the investigation on the depth profiling of the pigment in the coating system is also attractive for coating formulators seeking for application method improvement of the liquid paint [119, 120]. By varying the particle size and the surface pretreatment methods to the pigment, the stratifying paints could be designed aiming to apply the multi-layered coating system in a single step [120]. It was believed that the
pigment distribution in a polymer coating can be affected by the mobility of the pigment particle, molecular weight of the polymer, the additives and the compatibility differences between the pigment and the polymer phases [119].

This study aims to examine the applicability of SS-PM-PA FTIR technique on the depth profiling study of a TiO$_2$ pigment of PU coil coatings. The depth distribution of the TiO$_2$ pigment (KRONOS® 2310) within a PU coil coating is investigated. This TiO$_2$ pigment product was surface treated with alumina, silica and zirconia and used as received. Coil coatings with varied TiO$_2$ pigment content were prepared. The modulation frequency (MF) settings of the SS-PM-PA FTIR were varied to record the depth distribution of the pigment within the coating. The contribution of the PA signal originated from the TiO$_2$ pigment and the primer layer in addition to the PU binder within the coating is examined. SEM cross-section imaging technique is used to verify the TiO$_2$ depth distribution deduced by SS-PM-PA FTIR technique. This work is expected to be an important step towards the further application of the technique on the degradation study of the pigmented PU coatings.

4.1.1. The theory of PA-FTIR

Photo-acoustic (PA) IR has developed dramatically since its emergence about 30 years ago [121]. Within the same period, PA-FTIR has gained more utility due to its enhanced capability [122, 123]. The ability to analyse solid samples at selected depths is generally recognised to be one of the most important attributes of PA-FTIR spectroscopy. The thickness of the sampling depth approximately equals to the thermal diffusion length $L$ of the sample [95]. This dimension is given by the expression:

$$L = (D/\pi f)^{1/2} \quad \text{Equation 4.1 [95]}$$

where $D$ denotes thermal diffusivity and $f$ is the modulation frequency (MF) of the
4. The applicability of step scan phase modulation photo-acoustic FTIR to the depth profiling of TiO₂ pigmented coil coatings

SS-PM-PA FTIR. Thus, at a specific D, L varies as f is changed and different layer thicknesses within sample are analysed.

In continuous scan PA-FTIR experiments using a Michelson interferometer, where the moving mirror velocity is constant, f is determined by the infrared frequency. Therefore, the sampling depth examined by continuous scan PA-FTIR varies considerably across the mid-infrared range. Obviously, this wavenumber dependent sampling depth influences the interpretation of IR spectra where composition varies on depth. The development of modern step scan (SS) FTIR instrumentation improves depth profiling analysis by using a discrete mirror movement in the SS spectrometer, rather than continuous mirror movement used in continuous scan PA-FTIR. In SS spectroscopy, the IR signal is typically produced by dithering the fixed mirror at a constant frequency referred to as phase modulation (PM). Therefore, a single-frequency PM applied to the fixed mirror is used to modulate all wavelengths of the radiation to generate the PA signal, resulting in a uniform probing depth across the entire spectrum.

Due to the significant benefit of the SS-PM-PA FTIR technique, the associated PA magnitude and phase spectra have gained applications in a number of research works where depth profiling analysis of polymeric coatings is required [10, 124, 125]. The PA magnitude and phase spectra can be established for data analysis by using demodulated PA signals [95]. The magnitude of the PA signal varies linearly with increasing absorptivity, concentration or sampling depth, whereas the phase corresponds to the time delay associated with heat transfer within the sample [95, 126].

4.1.2. Thermal diffusivity determined SS-PM-PA FTIR sampling depth

According to Equation 4.1, L is affected by the thermal diffusivity, D, which is expressed as:
Equation 4.2 \[ D = \frac{k}{\rho C} \]

where \( k \) is the thermal conductivity, \( \rho \) is the density, and \( C \) denotes the heat capacity at constant pressure of the material under study. For most organic polymeric materials, the thermal diffusivity value \( D \) is constant \((10^{-3}\text{cm}^2\text{s}^{-1})\), thus the sampling depth at different PM frequencies can be calculated using the following simplified equation:

Equation 4.3 \[ L = \frac{180}{(f/2)} \]

Equation 4.3 is relatively simple and has been employed to estimate the sampling depth in many studies on clear polymer films using SS-PM-PA FTIR method [10, 124, 125].

In comparison to clear polymeric coating samples, the thermal properties of pigmented coatings are potentially affected by inclusions of inorganic pigments, such as TiO\(_2\). The thermal diffusivity of a solid TiO\(_2\) sample is significantly higher than polymers [128]. Previous work suggested that the thermal diffusivity of TiO\(_2\) nanofibre film presented a descending profile along with the density increasing, and with a value scale of approximately 10 times higher than that of polymers, as shown in Figure 4.1 [129]. Therefore, the corresponding sampling depth for a solid TiO\(_2\) sample is approximately 3 – 6 times higher than that for a clear polymer sample under certain MF in an SS-PM-PA FTIR experiment, according to Equation 4.1 and values in Figure 4.1. Additionally, the thermal diffusivity of solid TiO\(_2\) shows a decreasing trend along with the increasing of the density (Figure 4.1). Therefore, the real L value of a TiO\(_2\) pigmented PU coating is expected to be higher than the L value of the PU binder and lower than the L value of the solid pigment.
4. The applicability of step scan phase modulation photo-acoustic FTIR to the depth profiling of TiO$_2$ pigmented coil coatings

4.1.3. Aim of the study

As introduced in Section 4.1.2, the sampling depth of the SS-PM-PA FTIR technique for a pigmented coating is determined by the thermal diffusivity of the coating as well as the MF applied. Previous work demonstrated that single beam and phase spectra of SS-PM-PA FTIR technique could be used for depth profiling on pigmented polymer compounds [127, 130]. However, to the best of our knowledge, no work has been reported that examines the SS-PM-PA FTIR sampling depth of pigmented coil coatings. While the aim of this study is not to determine the thermal properties of the pigmented coatings, the applicability of SS-PM-PA FTIR technique to depth profiling studies of pigmented PU coatings is of major interest. In this work, we investigated the influence of TiO$_2$ pigment content on the sampling depth of the SS-PM-PA FTIR technique by evaluating the TiO$_2$ depth distribution of a series of pigmented PU coil coatings. This study aims to provide supporting information for the further investigation on the degradation of pigmented PU coil coatings using SS-PM-PA FTIR technique.
4.2. Experimental

The TiO₂ particle size in the liquid paints was 0.1-0.25 μm approximately, measured by using a Hegman gauge before being applied. Five TiO₂ pigmented PU coil coating samples were studied and labelled as T00, T20, T30, T40 and T50, where T denotes TiO₂ and the two digits after T denotes the corresponding pigment content (wt%) in the dry film. A PU binder was used as binder for the pigmented coatings. The pigment volume concentration (PVC) values are commonly referred in coil coating industry, which can be calculated using Equation 4.4, by knowing the specific gravity of the TiO₂ pigment is 4.

Simplified paint formulations and calculated PVC values for T00 – T50 samples are listed in Table 4.1. The TiO₂ powder and the pre-primed substrate samples were tested as-received. For commercial confidentiality, other formulation components are omitted here.

\[
PVC = \frac{\text{volume of pigment}}{\text{volume total solids}} = \frac{V_p}{(V_p + V_b)} \quad \text{Equation 4.4}
\]
Table 4.1 Simplified paint formulations for TiO\textsubscript{2} pigmented PU coil coating samples T00 – T50 and corresponding pigment content in the dry film and Pigment Volume Concentration (PVC).

<table>
<thead>
<tr>
<th>Samples</th>
<th>TiO\textsubscript{2} in liquid paint / gram</th>
<th>Total other components in liquid paint / gram</th>
<th>pigment content in dry film / wt%</th>
<th>PVC / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>T00</td>
<td>0</td>
<td>200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T20</td>
<td>62</td>
<td>391</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>T30</td>
<td>72</td>
<td>286</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>T40</td>
<td>72</td>
<td>205</td>
<td>40</td>
<td>14</td>
</tr>
<tr>
<td>T50</td>
<td>72</td>
<td>128</td>
<td>50</td>
<td>20</td>
</tr>
</tbody>
</table>

The coil coating coupon and cross-section samples were prepared with the method as discussed in Section 3.1. The coupon samples were used for SS-PM-PA FTIR experiments. Based on the extensive experiment carried out in this laboratory, the error of less than 1% for the spectra collected with the same sample is expected. Therefore, single spectrum was collected for representing the sample. The cross-section samples were used for SEM imaging experiments. The SS-PM-PA FTIR and SEM analysis were carried out with the method as discussed in Section 3.3.1 and Section 3.3.4, respectively.

4.3. Results and discussion

4.3.1. IR magnitude spectra interpretation and band assignments

Figure 4.2 shows the SS-PM-PA FTIR magnitude spectra of the TiO\textsubscript{2} powder, the primer only (pre-primed metal substrate as-received) and T00 – T50 coating samples. As shown in Figure 4.2 (a), TiO\textsubscript{2} powder spectrum gives a broad IR band across the 3800 cm\textsuperscript{-1} – 3250 cm\textsuperscript{-1} region denoted as free and H-bonded OH groups due to the Si-OH treated surface (Section 2.2.3). A strong IR band with maxima at 1240 cm\textsuperscript{-1} and a weak IR band with maxima at 1637 cm\textsuperscript{-1} are assigned to H-O-H bending and carbonates [131] of the
The applicability of step scan phase modulation photo-acoustic FTIR to the depth profiling of TiO$_2$ pigmented coil coatings.

TiO$_2$ powder. The Si-O group included in the TiO$_2$ pigment powder is characterised by the strong IR band with maxima at 1076 cm$^{-1}$ [132]. A very strong and broad TiO$_2$ characteristic band in the 1000 cm$^{-1}$ – 780 cm$^{-1}$ region can be observed. The primer only spectrum gives a strong IR band with maxima at 1730 cm$^{-1}$ and hence significantly larger peak area ratio of 1730 cm$^{-1}$ : 1090 cm$^{-1}$ when compared to both of the T00 (PU binder only) and TiO$_2$ powder spectra. The PU binder can be characterised by the strong IR bands with maxima at 1690 cm$^{-1}$ and 1540 cm$^{-1}$ in the T00 spectrum, assigned to amide I and amide II groups, respectively [17]. The tentative band assignments are summarised in Table 4.2.

Table 4.2 IR band assignments for PU binder (T00), primer only and TiO$_2$ powder. [17, 131, 132]

<table>
<thead>
<tr>
<th>Wavenumber / cm$^{-1}$</th>
<th>T00</th>
<th>Primer only</th>
<th>TiO$_2$ powder pigment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3800 – 3250</td>
<td>OH, NH</td>
<td>OH</td>
<td></td>
</tr>
<tr>
<td>2952 – 2896</td>
<td>CH</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>1730</td>
<td>amide I</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>1690</td>
<td>amide I</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>1637</td>
<td>n.a.</td>
<td>H-O-H and carbonates</td>
<td></td>
</tr>
<tr>
<td>1540</td>
<td>amide II</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>1378</td>
<td>CH</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>1240</td>
<td>n.a.</td>
<td>H-O-H and carbonates</td>
<td></td>
</tr>
<tr>
<td>1076</td>
<td>n.a.</td>
<td>Si-O</td>
<td></td>
</tr>
<tr>
<td>1000 – 780</td>
<td>n.a.</td>
<td>TiO$_2$</td>
<td></td>
</tr>
</tbody>
</table>

n.a. – not available

In Figure 4.2 (b), the upper and lower spectra sets correspond to MF = 800 Hz and MF = 500 Hz. All spectra are normalised to the peak height of the reference peak with maxima at 1378 cm$^{-1}$ (CH bending). The normalisation was performed with the assumption that...
the PA signal intensity originating from the methylene groups in the PU binder is constant across the entire sampling path. The influence of the pigment on the spectral alteration is expected to be maximised using this normalisation method. Further discussion with regards to the IR spectra normalisation are made in Section 6.3.1.2 and Section 6.3.4.2.

As shown in Figure 4.2 (b), for both MF = 800 Hz and MF = 500 Hz spectra sets, the PA signal intensity shows increases along with the coating sample order T00 – T50 particularly in the 3800 cm$^{-1}$ – 3250 cm$^{-1}$ region and the 1240 cm$^{-1}$ – 780 cm$^{-1}$ region. The PA signal intensity increasing implies that the extent of the chemical groups characterised by these two wavenumber regions is related to the PVC value of the pigmented PU coating. This argument is obvious correct when considering the TiO$_2$ pigment characterised by the 1000 cm$^{-1}$ – 780 cm$^{-1}$ region (Table 4.2). However, neither the 3800 cm$^{-1}$ – 3250 cm$^{-1}$ region nor the 1240 cm$^{-1}$ – 1000 cm$^{-1}$ region characterises any PU coating components including PU binder, primer and TiO$_2$ pigment, due to the overlapping nature of the IR bands. The PA signal intensity is contributed by both PU binder and primer in the 3800 cm$^{-1}$ – 3250 cm$^{-1}$ region, whereas by both TiO$_2$ and primer in the 1240 cm$^{-1}$ – 1000 cm$^{-1}$ region (Table 4.2). Therefore, the PA signal intensity increasing in the 3800 cm$^{-1}$ – 3250 cm$^{-1}$ region and the 1240 cm$^{-1}$ – 1000 cm$^{-1}$ region implies the significant contribution of the TiO$_2$ pigment to the total intensity of the IR band.

Conversely, in the 3800 cm$^{-1}$ – 3250 cm$^{-1}$ region and the 1240 cm$^{-1}$ – 780 cm$^{-1}$ region, the spectra set of MF = 800 Hz gives the PA signal intensity increasing profile incomparable to MF = 500 Hz spectra set (Figure 4.2 (b)), which implies the heterogeneous distribution of the TiO$_2$ pigment on depth if assuming the sampling depth is constant with certain fixed MF value. A noticeable difference between MF = 800 Hz and MF = 500 Hz spectra sets can be found by examining the PA signal intensity of T40 spectrum.
Specifically, the T40 spectrum is similar to T50 spectrum when MF = 500 Hz but becomes comparable to T30 spectrum when MF = 800 Hz. In other works, marked PA signal intensity increases from T40 spectrum to T50 spectrum can be found when MF = 800 Hz, and from T30 spectrum to spectrum T40 when MF = 500 Hz. This PA signal intensity increase indicates an interface and/or an aggregation region of TiO₂ pigment formed within the PU coating. The possible interface and aggregated region includes the topcoat-primer interface and a TiO₂ pigment aggregated region, respectively.

Figure 4.2 (b) insert shows an amplified version of the 1600 cm⁻¹ – 1800 cm⁻¹ region. The lower PA signal intensity at 1690 cm⁻¹ is observed for T40 and T50 spectra, but is absent for T20 and T30 spectra. The IR band at 1690 cm⁻¹ characterises the PU binder (Table 4.2). It is obvious correct that the lower extent of PU binder corresponds to the higher PVC value of the TiO₂ pigmented PU coating. Therefore, IR band at 1690 cm⁻¹ can be employed to characterise the compositional alteration induced by the varied PVC values of the TiO₂ pigmented PU coating in addition to TiO₂ characteristic IR bands, as will be further discussed in Section 4.3.2.
Figure 4.2 The SS-PM-PA FTIR magnitude spectra of (a) the TiO$_2$ pigment powder and primer only (pre-primed metal substrate as-received), and (b) T00 – T50 PU coating samples with varied PVC values of 0 %, 6 %, 10 %, 14 %, 16 % and 20% along with the sample order. In Figure (b), the MF used for upper set spectra is 800 Hz, and the MF used for lower set spectra is 500 Hz. All spectra are normalised to the reference peak at 1378 cm$^{-1}$ (CH bending). The spectra error is less than 1% for the spectra collected with the same sample.

4.3.2. TiO$_2$ depth distribution revealed by SS-PM-PA FTIR phase spectra

The presence of an aggregation region of TiO$_2$ pigment within the PU coating was
indicated by using the SS-PM-PA FTIR magnitude spectra as discussed in Section 4.3.1. The relative depth position of this TiO$_2$ aggregation region can be more precisely identified by using the SS-PM-PA FTIR phase spectra. The phase angle values given by the SS-PM-PA FTIR phase spectra correspond to the time delay associated with heat transfer within the sample, as introduced in Section 2.4.2.2. Briefly, the larger phase angle value indicates a deeper sampling depth.

Figure 4.3 shows the phase angle spectra of S1 – S4. The sample and modulation frequency combinations (sample label, MF) of individual spectrum are marked as S1 (T20, 500 Hz), S2 (T20, 800 Hz), S3 (T50, 500 Hz) and S4 (T50, 800 Hz). The relative phase angle values in the $1000\ cm^{-1} – 780\ cm^{-1}$ region show the order of S2 > S1 > S4 > S3, which is indicative of the relative depth position of the TiO$_2$ aggregated region detected by individual (sample label, MF). Firstly, the fixed PVC value (T20, PVC = 6% or T50, PVC = 20%) results in S2 > S1 and S4 > S3, correspondingly, i.e., 800 Hz MF results in higher phase angle value compared to 500 Hz. According to Equation 4.1, a higher MF value corresponds to a shallower sampling depth within the bulk of the coating and vice versa. Therefore, the higher phase angle value given by 800 Hz MF indicates that the TiO$_2$ aggregated region is further away from the topcoat-air interface (or topcoat surface), and hence closer to the topcoat-primer interface. Secondly, the fixed MF value (800 Hz or 500 Hz) results in S1 > S3 and S2 > S4, correspondingly, i.e., PVC = 6% results in higher phase angle value compared to PVC = 20%. Considering the TiO$_2$ aggregated region is closer to the topcoat-primer interface, it can be deduced that the TiO$_2$ aggregated region is more close to the topcoat-primer interface when PVC value is relatively low.

The contribution of the primer signal to the total PA signal can be examined by using the SS-PM-PA FTIR phase spectra, in addition to the TiO$_2$ aggregated region as mentioned above. As shown in Figure 4.3, the relative phase angle values in the $1160\ cm^{-1} – 1020$
cm\(^{-1}\) region shows the order of S3 > S4, which is contrary to the order in the 3620 cm\(^{-1}\) – 3000 cm\(^{-1}\) region and the 1000 cm\(^{-1}\) – 780 cm\(^{-1}\) region. Conversely, the consistent order of S1 < S2 can be found in all above regions. The unique order of S3 > S4 indicates the additional contribution to the PA signal acquired with S3 (T50, 500 Hz) in the 1160 cm\(^{-1}\) – 1020 cm\(^{-1}\) region. As shown in Figure 4.2 (a), the primer only spectrum gives the strong and broad band in the 1160 cm\(^{-1}\) – 1020 cm\(^{-1}\) region, which characterises the primer layer. Therefore, the additional contribution to the PA signal acquired with the S3 (T50, 500 Hz) in the 1160 cm\(^{-1}\) – 1020 cm\(^{-1}\) region can be related to the primer originated signal. In other words, the primer signal significantly contributes the total PA signal intensity when MF = 500 Hz and PVC = 20%.

Figure 4.3 The phase angle spectra of S1 – S4. The sample and modulation frequency combinations (sample label, MF) of individual spectrum are marked as S1 (T20, 500 Hz), S2 (T20, 800 Hz), S3 (T50, 500 Hz) and S4 (T50, 800 Hz). T20 and T50 samples correspond to PVC value of 6 % and 20 %, respectively. The 3620 cm\(^{-1}\) – 3000 cm\(^{-1}\) region and the 1000 cm\(^{-1}\) – 780 cm\(^{-1}\) region are marked with faint lines. The spectra error is less than 1% for the spectra collected with the same sample.

The discussion above indicates that the primer originated signal, when PVC is high MF is low, contributes most significantly to the PA signal of the TiO\(_2\) pigmented PU coating. Further evidence on the primer contribution to the PA signal of the PU coating can be
found by examining the IR band at 1690 cm$^{-1}$, as introduced in Section 4.3.1. As shown in Figure 4.2 (a), the lower IR band intensity at 1690 cm$^{-1}$ (PU binder band, Table 4.2) can be observed in the T40 and T50 spectra in most cases but is absent in the T20 and T30 spectra. The presence of the lower IR band intensity at 1690 cm$^{-1}$ in the T40 and T50 spectra reflects the reduced influence of the PU binder when PVC value is relatively high. As shown in Figure 4.2 (a), the primer only spectrum gives a significantly lower peak intensity ratio of 1690 cm$^{-1}$ : 1730 cm$^{-1}$ compared to the PU binder (T00 spectrum) and the TiO$_2$ pigment. This lower peak intensity at 1690 cm$^{-1}$ characterises the primer signal in the PU coating spectra. Therefore, the lower IR band intensity at 1690 cm$^{-1}$ indicates the more significant contribution of the primer originated signal to the total PA signal intensity when the PVC value of the TiO$_2$ pigmented PU coating is relatively high.

4.3.3. SEM cross-section imaging

The TiO$_2$ depth profile was studied by using SS-PM-PA FTIR technique. In this section, the deduction made by the non-destructive FTIR technique is verified by destructive SEM cross-section imaging technique. Figure 4.4 shows the SEM cross-section imaging results of T20 – T50 coating samples with $\times$ 5,000 magnification. For individual samples, layered cross-section structures consist of the TiO$_2$ pigmented topcoat, the primer and the metal substrate can be clearly observed. The TiO$_2$ within the topcoat presents a relatively sparsely dispersed section near the topcoat surface and a comparatively more condensed section near the topcoat-primer interface. The heterogeneous depth distribution of TiO$_2$ observed by SEM cross-section imaging is in good agreement with the deduction made by SS-PM-PA FTIR (Section 4.3.2). In Figure 4.4, a relatively discrete TiO$_2$ aggregated region near the topcoat-primer interface can be observed for lower PVC value samples (T20 and T30) with a thickness of approximately 5 $\mu$m. However, a TiO$_2$ aggregated region is not observed for higher PVC value samples (T40 and T50). The more distinguishable TiO$_2$ aggregated region for lower PVC value
samples can be also correlated to the deductions made by SS-PM-PA FTIR (Section 4.3.2), where the TiO$_2$ aggregated region can be detected in a deeper position in lower PVC value samples compared to higher PVC value samples. In summary, the TiO$_2$ depth profile visualised by SEM cross-section imaging method shows a strong correlation with the TiO$_2$ depth distribution deduced using the SS-PM-PA FTIR method.
Figure 4.4 The SEM cross-section imaging results of T20 – T50. For individual samples, layered cross-section structures consisting of the TiO₂ pigmented topcoat, the primer and the metal substrate can be clearly observed. The TiO₂ within the topcoat presents a relatively dispersed section near the topcoat surface and a comparatively more condensed section near the topcoat-primer interface. A relatively distinguishable TiO₂ aggregated region near the topcoat-primer interface can be observed for lower PVC value samples (T20 and T30) with a thickness of approximately 5 μm, as opposed to higher PVC value samples (T40 and T50).
4.4. Conclusions

The SS-PM-PA FTIR signal intensity shows considerable contributions from the TiO$_2$ pigment as well as the PU binder for the TiO$_2$ pigmented PU coil coatings. The depth profile of the TiO$_2$ pigment in the topcoat varies along with the increasing of the TiO$_2$ pigment content, as observed by the SS-PM-PA FTIR technique. Furthermore, a TiO$_2$ aggregated region within the topcoat is found close to the topcoat-primer interface and further away from the topcoat surface. This TiO$_2$ aggregated region in lower TiO$_2$ pigment content topcoats is deeper within the coating compared to higher TiO$_2$ pigment content topcoats, as revealed by SS-PM-PA FTIR.

SEM cross-section imaging results show a strong correlation with the TiO$_2$ depth profile postulated using the SS-PM-PA FTIR method, which confirms the applicability of the SS-PM-PA FTIR technique to the depth profiling study of TiO$_2$ pigmented coil coatings.

The actual sampling depth of the SS-PM-PA FTIR technique is found significantly influenced by the PVC value of TiO$_2$ pigmented PU coatings, revealing the deficiency of taking the constant thermal diffusivity values for the sampling depth calculation.
5. The confocal Raman mapping (CRM) study of the cyclic trimer (CT) core in clear PU coil coatings

5.1. Introduction

Hexamethylene diisocyanate (HDI) is normally converted to polyisocyanates with CT core structures to be used for typical PU coil coating formulations (Section 2.2.2.1). HDI-CT has been extensively used to cross-link PU based coil coatings with benefits for enhanced resistance to the degradation comparing with other derivatives such as HDI biuret (HDI-BI) [42, 133]. Previous efforts have been made to evaluate the content of CT core by using non-imaging vibrational spectroscopy such FTIR [34, 134]. Visualised mapping results can be obtained by using analytical instruments coupled with digital imaging and chemometric functions [13, 135]. Raman spectroscopy provides information on coating system materials that is similar, but often complimentary, to that obtained from IR spectroscopy. The two techniques provide a high level of information on molecular structure (Section 2.4.1).

The current study aims to verify the applicability of the CRM chemometric method on the evaluation of CT core content and distribution at the surface of clear PU coil coatings. CRM chemometric method is used to study the CT core content and distribution at the surface of clear PU coil coatings cross-linked with HDI-CT. The CT core content in PU coatings is varied to test the correlation of the CRM imaging results. The correlation between the CRM imaging results and the original coating formulations with regards to the surface content of the CT core is examined. The distribution manner of the CT core at the surface of HDI-CT cross-linked PU clear-coats is investigated. This work is expected to provide supportive information towards the further degradation study of PU coatings using CRM technique.
5.1.1. Chemometric imaging

According to the International Chemometrics Society (ICS), chemometrics is the science of relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods [136]. Chemometrics has become an essential tool in modern vibrational spectroscopy-based instruments, allowing the treatment of large amounts of information on sample-component concentrations to be analysed in a relatively short time [137]. The chemometric imaging method couples a vibrational spectrometric technique, such as Confocal Raman, with appropriate optics, enabling the acquisition of visualised images of the samples containing chemical information [135].

The use of confocal Raman spectroscopy has grown enormously in physical and chemical characterisation due to the benefit of high sensitivity, high spatial resolution and non-destructive sampling [138]. CRM combines Confocal Raman spectroscopy with chemometric imaging technology in order to visualise the distribution of chemical composition and molecular structure [13]. The measurement procedure of the CRM permits scanning the sample without any pretreatment or destruction. The individual confocal Raman spectra acquired by the multiple scanned sampling points contain information about the identity, the distribution and the total concentration of the molecular structure present in the point scanned [38]. A data set consists of numerous individual confocal Raman spectrum can be acquired by moving the sample relative to the focus point of the microscope objective [139]. The data set is then imaged into a spectrograph and diffracted across the face of a CCD detector to construct the CRM imaging result.

5.1.2. CRM surface scan on pre-primed clear coil coatings

A CRM surface scan can be acquired by collecting the data set on the clear coating sample surface. A thin, flat 2D surface layer with the depth of approximately 1 – 2 μm is
characterised by using this method. This surface layer is of major interests for degradation studies of the clear coatings, since it is this surface which is exposed to the environmental stresses rather than the bulk coating. Therefore, the applicability of CRM method for this surface layer is of necessity to be verified.

Theoretically, the CRM image obtained by surface scan on a typical PU clear coil coating system reveals the chemometric distribution of the clear-coat-air interface with the expected spatial resolution of 1 μm³. In practice, the Raman spectra collected at clear-coat-air interface will also consist of other components in the coating system. A typical clear coil coating system is composed of a 5 μm pigmented primer layer with 18μm – 20μm clear-coat on the top. The common pigment used in a standard polyester primer layer includes TiO₂ and strontium chromate (SrCrO₄). Both TiO₂ and SrCrO₄ pigments are highly sensitive to the Raman laser beam and give very strong Raman signal. Therefore, in practice it has been found that these primer components strongly contribute to the Raman spectra collected at the clear-coat-air interface, as discussed in reference [4].

Apart from the influence of the primer layer, the clear-coat-air interface can distort the confocal properties of the microscope resulting in a misinterpretation of data, as an issue that has been addressed elsewhere [140, 141]. Conversely, other workers showed that the refractive distortion is not sufficient to disturb the laser focusing by using the mathematical modelling [142]. Many authors have used more rigorous mathematics to model the refractive distortion of the confocal laser beam [143, 144]. However, no simple model has been developed to correct the refractive distortion of the radiating laser beam when probing the clear-coat-air interface of the clear polymer coatings.

5.1.3. Aim of the study

The primer signal contribution together with the refractive distortion of the radiating laser beam on the clear-coat-air interface brings uncertainty to the CRM analysis at the
surface content and distribution of chemical structures. In this study, we aim to verify the applicability of CRM chemometric method on the evaluation of CT core content and distribution at the surface of clear PU coil coatings. This work is expected to provide supportive information towards the further degradation study of PU coatings using CRM technique.

5.2. Experimental

Simplified paint formulations for F1 – F5 samples are listed in Table 5.1. Five samples were studied and labelled as F1, F2, F3, F4 and F5. The main coating components include the cycloaliphatic polyester (Beckers, UK) and two isocyanate cross-linkers (Capro blocked HDI-CT and DMP blocked HDI-BI, Bayer, UK). The weight ratio of the HDI-CT to the polyester in liquid paint is varied and gives the values of 0.34, 0.35, 0.24 and 0.17 for F1, F3, F4 and F5, respectively. Other formulation components remain unchanged and are omitted here due to commercial confidentiality. A standard pre-primed substrate (Beckers, UK) with approximately 5 μm in primer thickness was used as-received.
5.3. Results and discussion

5.3.1. Raman band assignment

The characteristic Raman peaks are assigned by referring to the references [145, 146] and comparing with the related Raman spectra. Figure 5.1 shows the Raman spectra of polyester, HDI-CT and HDI-BI, F1 and F2 topcoat on primer (TOP) and F1 and F2 clear-coat only (CC). The HDI-CT spectrum gives a strong peak at 1760 cm\(^{-1}\), which is absent on the HDI-BI spectrum, thus 1760 cm\(^{-1}\) peak is denoted as C=O stretching on the
The HDI-BI spectrum gives a strong peak at 1620 cm\(^{-1}\) comparing to the HDI-CT spectrum, which can be assigned to C=O stretching on the BI structure. The polyester spectrum gives a C=O stretching peak at 1725 cm\(^{-1}\) and the vibration of cyclohexane ring (cyc) peak at 810 cm\(^{-1}\). The strong peak at 1452 cm\(^{-1}\) and multiple peaks in the 1305 cm\(^{-1}\) – 1050 cm\(^{-1}\) region are assigned to C-C and C-H vibrations. The primer-only spectrum gives very strong TiO\(_2\) peaks at 448 cm\(^{-1}\) and 610 cm\(^{-1}\), SrCrO\(_4\) peaks at 870 cm\(^{-1}\) and 900 cm\(^{-1}\) and benzene ring peak at 1000 cm\(^{-1}\). The primer-only spectrum gives a medium peak at 1620 cm\(^{-1}\) and significantly lower peak intensity ratio of 1452 cm\(^{-1}\) : 1725 cm\(^{-1}\) comparing to F1 and F2 TOP, and F1 and F2 CC spectra. 1620 cm\(^{-1}\) peak on primer-only spectrum is assigned to C=C stretching originated from phthalate type resin as the binder of the primer. Comparing to F2 TOP spectrum, F1 TOP spectrum gives a shoulder peak at 1760 cm\(^{-1}\) due to the presence of C=O stretching on the CT core structure. The Raman peak assignment is summarised in Table 5.2.

It is noticeable that both F1 TOP and F2 TOP spectra show full set of characteristic peaks of the primer, as well as other topcoat components including polyester, HDI-CT and/or HDI-BI, F1 CC and F2 CC (Figure 5.1). The presence of the full set of primer characteristic peaks on F1 and F2 TOP spectra demonstrates the strong contribution of the primer originated signal towards F1 and F2 clear-coat surface, as discussed in Section 5.1.2.
Figure 5.1 Confocal Raman spectra of polyester, HDI-CT and HDI-BI, F1 and F2 topcoat on primer (TOP), F1 and F2 clear-coat only (CC) and primer-only
Table 5.2 Raman peak assignment of HDI-CT and HDI-BI, polyester, F1 and F2 topcoat on primer (TOP), F1 and F2 clear-coat only (CC) and primer-only [145, 146]

<table>
<thead>
<tr>
<th>Raman shift (cm⁻¹)</th>
<th>CT core</th>
<th>BI core</th>
<th>polyester</th>
<th>F1 TOP</th>
<th>F2 TOP</th>
<th>F1 CC</th>
<th>F2 CC</th>
<th>primer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1760</td>
<td>CT core</td>
<td></td>
<td>polyester</td>
<td>CT core</td>
<td>CT core</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td></td>
<td></td>
<td>C=O</td>
<td>C=O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1725</td>
<td></td>
<td></td>
<td>polyester</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1620</td>
<td>bi. C=O</td>
<td></td>
<td>C=C</td>
<td></td>
<td>C=C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1452</td>
<td></td>
<td></td>
<td>CH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1305 - 1050</td>
<td></td>
<td></td>
<td>C-C and C-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td></td>
<td>Benzene ring</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900, 870</td>
<td></td>
<td></td>
<td>SrCrO₄</td>
<td></td>
<td>SrCrO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>810</td>
<td></td>
<td></td>
<td>cyclohexane ring</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>610, 448</td>
<td></td>
<td></td>
<td>TiO₂</td>
<td></td>
<td>TiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 5.3.2. CRM study

As discussed in Section 5.2, the Raman peak at 1760 cm⁻¹ and 810 cm⁻¹ characterise the CT core within the cross-linker and the cyclohexane ring within the polyester, respectively. A chemometric profiling strategy can be setup by mapping the peak area ratio of the Raman peaks with the maxima at 1760 cm⁻¹ and 810 cm⁻¹, which will reveal the content and distribution of CT core at the surface of the PU coatings. This chemometric profiling strategy is based on the assumption that the Raman peak intensity of the polyester is constant over the entire mapping area. The variation of CT core peak intensity is expected to be best highlighted by using this profiling strategy. The peak area selection is as demonstrated in Figure 5.2.
5. The confocal Raman mapping (CRM) study of the cyclic trimer (CT) core in clear PU coil coatings

Figure 5.2 The chemometric profiling strategy ‘peak area ratio of two peaks’ for constructing CRM images. The peak area of CT core characteristic peak at 1760 cm$^{-1}$ and cyclohexane ring peak at 810 cm$^{-1}$ were selected using ‘peak area measurement’ tool, as highlighted. The CT core and cyc peak areas represent the CT type isocyanate cross-linker and cycloaliphatic polyester, respectively. The higher value of the ratio of these two peaks indicates the more enriched CT core moiety content. (cyc – cyclohexane ring)

Figure 5.3 shows the CRM results of F1 – F5. The characteristic peak area ratio of the CT core to the polyester was used as the imaging data. The peak area ratios were measured as demonstrated in Figure 5.2. The data were selected with the method introduced in Section 3.3.3. The colour range for displaying the individual image is set between 0 and 0.4, represented by the blue to red colour bar. The colour value from 0 to 0.4 indicates the content of CT core from low to high. As shown in Figure 5.3, the green colour region on all F1, F3 F4 and F5 images displays a dispersed pattern, indicating the distribution of CT core is relatively even and free of significantly aggregated region. Additionally, the dispersed green colour region on all F1, F3 F4 and F5 images shows a similar pattern, indicating the consistency of the evenly distributed CT core on all F1, F3 F4 and F5 clear-coat surface. This is consistent with the results of previous studies that have demonstrated the evenness of the CT core distribution can be found in ref [147-149].
As shown in Figure 5.3, F1 image shows an obvious higher coverage density of the green coloured region compared to the F2 image which shows none, confirming the absence of CT core at the surface of F2 clear-coat (Table 5.1). Additionally, the coverage density of green colour region on F3 image is comparable to F1 image, confirming the similarity of CT core content and distribution on F1 and F3 clear-coat surface and the reproducibility of the CRM technique. The similarity of CT core content on F1 and F3 clear-coat surface represented by CRM images is as expected due to the close value of HDI-CT : polyester ratio for F1 and F3 coating formulation, as given in Table 5.1. F3, F4 and F5 images show a descending order in term of the coverage density of the green colour region, confirming the reduction of the CT core content in the formulations F3 to F5. The decrease of the CT core content represented by F3 to F5 images shows strong correlation with the ratio of HDI-CT : polyester values in original coating formulation, as given in Table 5.1.

In summary, all HDI-CT cross-linked PU clear-coat surfaces show relatively even CT core distribution and are free of significantly aggregated regions. CRM imaging results can be correlated to the original PU coating formulations in terms of the surface content of the CT core structure, by comparing the coverage density of the green colour region on the CRM images.
5. The confocal Raman mapping (CRM) study of the cyclic trimer (CT) core in clear PU coil coatings

Figure 5.3 CRM imaging results of F1 – F5 samples. The characteristic peak area ratio of the CT core to the polyester was used as the imaging data (Figure 5.2). The blue to red colour bar shows the colour range of 0 to 0.4 for displaying the image. The colour value from 0 to 0.4 indicates the content of CT core from low to high.

5.4. Conclusions

The consistency of the CRM imaging results has been evaluated by varying the CT core
content in the clear PU coil coating samples. The results show that HDI-CT cross-linked PU clear-coats consistently give relatively even surface CT core distribution. Additionally, CRM imaging results show strong correlation with the original coating formulations with regards to the content of the CT core at the surface of PU clear coatings. The consistent and well correlated CRM imaging results verify the applicability of CRM chemometric method on the evaluation of the CT core content and distribution at the surface of clear PU coil coatings.
6. The impact of isocyanate structures on the degradation of PU coil coatings

6.1. Introduction

Commercial PU coil coatings have been used widely for outdoor systems for many years. They are generally known to exhibit good weathering performance but there is little understanding of the impact of the differences of the polyisocyanate chemistry on durability. Thus, it is important to develop a better understanding of the chemical changes for specific PU systems to improve the durability of coil coating products submitted to various environmental stresses. This chapter addresses the impact of isocyanate structures on the degradation chemistry of PU coil coatings by using SS-PM-PA FTIR and CRM techniques.

In this study, the cross-linking and the degradation products build-up at the surface of degraded PU coating is investigated with varied isocyanate branch (IPDI and HDI) and core (CT and BI) structures. The schematic molecular structures of the isocyanate cross-linkers (a) HDI-CT, (b) HDI-BI and (c) IPDI-CT are illustrated in Figure 6.1. In addition to the degradation of urethane linkage as the predominant linkage within PU coatings, this study also elucidates the degradation chemistry involving primary amide and urea entities which are generated during the side reactions of PU coating formation.
6. The impact of isocyanate structures on the degradation of PU coil coatings

Figure 6.1 Schematic molecular structures of blocked isocyanate cross-linkers. (a) HDI-CT, (b) HDI-BI, and (c) IPDI-CT

6.2. Experimental

Clear-coat formulation samples F3, F2, and F4 were used as summarised in Table 6.1. Three blocked isocyanates were investigated including of (a) HDI-CT, (b) HDI-BI and (c) IPDI-CT in combination with the sample polyester to form a cross-linked PU network. Methyl ethyl ketoxime (MEKO) was used as the blocking agent for F3 and F4 samples, whereas 3,5 Dimethyl Pyrazole (DMP) blocking agent is used for F2 sample.
The polyester used was cycloaliphatic saturated polyester whose degradation is known to be negligible within PU systems under study compared to urethane linkage related degradation. For each formulation, the molar ratio of NCO/OH was maintained constant as 1.74. Other components of the coating formulations remain unchanged. For reasons of commercial confidentiality, their trade names are omitted here.

Table 6.1 Simplified formulations of PU clear coating samples F3, F2 and F4

<table>
<thead>
<tr>
<th>Component in liquid paint (grams)</th>
<th>Description</th>
<th>F3</th>
<th>F2</th>
<th>F4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td>Cycloaliphatic saturated polyester</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isocyanates</td>
<td>(a) HDI-CT</td>
<td></td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) HDI-BI</td>
<td></td>
<td>34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(c) IPDI-CT</td>
<td></td>
<td></td>
<td>41</td>
</tr>
</tbody>
</table>

The model coil coating samples were prepared with the method as discussed in Section 3.1. The weathering protocol used in this study was QUV A accelerated ageing with 1200 hours exposure time, with the technical details as stated in Section 3.2. The coupon samples were used for SS-PM-PA FTIR and CRM experiments. The SS-PM-PA FTIR analysis was carried out with the method as discussed in Section 3.3.1. In CRM experiment, the profile ‘peak area ratio of two peaks’ was employed as a mapping strategy with the method as discussed in Section 5.3.2.

6.3. Results and discussion

6.3.1. IR spectra interpretation and band assignments

A full understanding of the degradation chemistry of the PU system necessitates systematic interpretation and assignment of absorption bands in the IR spectra. IR bands are assigned by reference to published literature and comparison of IR spectra of PU coatings, as a common methodology for IR band assignment. In this work, the
6. The impact of isocyanate structures on the degradation of PU coil coatings

SS-PM-PA FTIR 800 Hz magnitude spectra of PU coatings with various isocyanate cross-linkers including HDI-CT, HDI-BI and IPDI-CT cross-linkers are shown in Figure 6.2 - Figure 6.5. An assumption is made that the degradation is not significantly influenced by the differences in blocking groups but is more attributed to the structural variation of isocyanates (CT or BI, HDI or IPDI). This assumption is based on the fact that the curing temperature applied is significantly higher than the deblocking temperature of both MEKO and DMP used in this study [23]. The completed deblocking is expected with the curing temperature of 232°C (Section 3.1), and so it is assumed that the blocked isocyanate groups is only a fraction of unblocked isocyanate groups remaining in the PU coatings in this study.

### 6.3.1.1. The 3720 cm⁻¹ - 2170 cm⁻¹ region

Figure 6.2 shows the IR spectra in the 3720 cm⁻¹ - 2170 cm⁻¹ region. All spectra are normalised to the PA signal intensity at 2935 cm⁻¹ (asymmetric CH stretching), in common with published work [12, 63]. The F3, F2, and F4 unexposed spectra give a broad IR band with maxima at 3385 cm⁻¹, assigned to H-bonded NH stretching [11, 17, 40, 150]. The F2-unexposed spectrum shows a higher PA signal intensity at 3385 cm⁻¹ than both F3-unexposed and F4-unexposed spectra. The BI core structure differs in F2 from both F3 and F4 which contain CT core structure. Therefore, the higher PA signal intensity at 3385 cm⁻¹ in F2-unexposed spectrum indicates the higher content of H-bonded NH groups in HDI-BI cross-linked PU coating due to the presence of additional NH groups in BI core compared to HDI-CT. The F2-unexposed spectrum shows a shoulder IR band near 3294 cm⁻¹ (H-bonded NH stretching) which is less intense in F3-unexposed and F5-unexposed spectra, revealing the noticeably high content of H-bonded urea groups in the BI core structure compared to the CT core structure. A weak broad IR band in the 3669 cm⁻¹ - 3488 cm⁻¹ region can be found on all F3, F2, and F4 unexposed spectra (OH stretching [151]). The F4-unexposed spectrum shows a marked IR band at 2258 cm⁻¹ (unblocked isocyanate –N=C=O, [151, 152]), indicating the remaining unblocked and unreacted isocyanate –N=C=O group in the IPDI cross-linked PU coating. The formation of free isocyanate groups in
unexposed IPDI cross-linked PU coatings may be proposed based on published work [14, 15, 44, 153]. Firstly, the blocking group deblocks via elimination-addition route and generate free –N=C=O group [15, 44]. Secondly, the IPDI branch structure deters the further nucleophilic reaction between -N=C=O and -OH due to the steric hindrance effect of IPDI [14, 153]. Consequently, a noticeable amount of unreacted –N=C=O group remains within unexposed IPDI cross-linked PU coatings. The chemical scheme of the reactions is as demonstrated in Figure 2.8 (a).

The spectral alteration revealed by the comparison of exposed and unexposed IR spectra is indicative of the chemical changes as well as the degradation rate of PU coatings. As shown in Figure 6.2 (a) and (b), both F3 and F2 exposed spectra show the IR band intensifying and broadening when compared with the corresponding unexposed spectrum. The IR band intensifying can be found particularly in the 3700 cm\(^{-1}\) - 3000 cm\(^{-1}\) region (NH, OH stretching) and the 2860 cm\(^{-1}\) - 2340 cm\(^{-1}\) region (H-bonded COOH [154]). However, in Figure 6.2 (c), F4-exposed spectrum does not show similar IR band increases in these two regions when compared to F4-unexposed spectrum, but shows the removal of the unblocked isocyanate peak at 2258 cm\(^{-1}\). The IR band increases in the 3700 cm\(^{-1}\) - 3000 cm\(^{-1}\) region and the 2860 cm\(^{-1}\) - 2340 cm\(^{-1}\) region are normally ascribed to the build-up of PU degradation products including alcohols, carboxylic acids, peresters, primary urethanes, acetylurethanes, and primary amides [16, 17, 155]. The IR band increase for F2 is close, if not slightly higher than that in F3 in these two regions, indicating the comparable amount of degradation products built up at the surface of two HDI cross-linked PU coatings. Conversely, the spectra of F4 do not show any of the same increases in IR band intensity in the 3700 cm\(^{-1}\) - 3000 cm\(^{-1}\) region and the 2860 cm\(^{-1}\) - 2340 cm\(^{-1}\) region. This indicates a significantly lower level of degradation build-up at the surface of IPDI cross-linked PU coating comparing to HDI cross-linked PU coatings. The degradation of IPDI cross-linked PU coating can be seen to be primarily the degradation of the unblocked isocyanate groups. This is further discussed in Section 6.3.4.3.
6. The impact of isocyanate structures on the degradation of PU coil coatings

(a) IR spectra of MEKO blocked HDI-CT before and after exposure
6. The impact of isocyanate structures on the degradation of PU coil coatings

(b) IR spectra of DMP blocked HDI-BI before and after exposure
6. The impact of isocyanate structures on the degradation of PU coil coatings

Figure 6.2 SS-PM-PA FTIR 800 Hz magnitude spectra of F3, F2 and F4 samples in the 3720 cm\(^{-1}\) – 2170 cm\(^{-1}\) region. Unexposed spectra are marked with solid line. Exposed spectra are marked with dotted line. ‘-exposed’ denotes 1200 hours QUV A exposure time. Spectra are normalised to the PA signal intensity at 2935 cm\(^{-1}\).

6.3.1.2. The 1950 cm\(^{-1}\) - 1330 cm\(^{-1}\) region

Figure 6.3 shows the IR spectra in the 1950 cm\(^{-1}\) - 1330 cm\(^{-1}\) region. All spectra are normalised to the PA signal intensity of the IR band with maxima near 1385 cm\(^{-1}\) - 1378 cm\(^{-1}\) (CH bending). The normalisation is based on the deduction that the PA signal intensity of this IR band with maxima near 1385 cm\(^{-1}\) - 1378 cm\(^{-1}\) is relatively stable towards the degradation. As shown in Figure 6.3, F3 and F2 spectra give IR band with maxima at 1378 cm\(^{-1}\), whereas this maxima shifts to 1385 cm\(^{-1}\) in F4 spectra. The shifted maxima indicate the chemical environment variation of the backbone CH group.
between HDI and IPDI. Therefore, the IR band with maxima near 1385 cm\(^{-1}\) and 1378 cm\(^{-1}\) can be ascribed to the in-chain CH bending in IPDI and HDI, respectively. The in-chain CH group is expected to be relatively stable towards the degradation and therefore can be used preferably as the reference IR band for spectral normalisation. (Another supportive point with regards to the high stability of the in-chain CH group is made in Section 6.3.4.2.) The spectral alteration caused by degradation is expected to be clarified after this normalisation.

As shown in Figure 6.3, all F3, F2 and F4 unexposed spectra give IR band with maxima at 1735 cm\(^{-1}\), 1690 cm\(^{-1}\), 1640 cm\(^{-1}\) (all related to amide I) and 1523 cm\(^{-1}\) (amide II). The strong band at 1735 cm\(^{-1}\) (amide I) is assigned to free C=O stretching [11, 17, 40, 150]. F3-unexposed and F4-unexposed spectra give higher PA signal intensity at 1690 cm\(^{-1}\) (amide I) than the F2-unexposed spectra, indicating the higher content of the amide I band in HDI-CT cross-linked PU coatings compared to HDI-BI. The molecular structure of CT core and BI core (Figure 2.5 and Figure 2.6) shows different content of urea groups (-N-(C=O)-N-). Therefore, the IR band with maxima at 1690 cm\(^{-1}\) can be assigned to the urea group (-N-(C=O)-N-) in the BI and CT core. The F2-unexposed spectrum gives a strong IR band with maxima at 1640 cm\(^{-1}\) (amide I). This IR band is present as a weak shoulder in F3-unexposed and F4-unexposed spectra. The molecular structure of BI core gives the urea entity (-NH-(C=O)-N-) compared to CT core (Figure 2.5 and Figure 2.6). Therefore, the IR band with maxima at 1640 cm\(^{-1}\) can be assigned to the urea entity (-NH-(C=O)-N-) in BI core structure. IR band with maxima at 1523 cm\(^{-1}\) (amide II) is assigned to cross-linked urethane amide group (-(C=O)-NH-) in many previous studies [11, 17, 40, 150]. Here, the F2-unexposed spectrum gives a higher PA signal intensity at 1523 cm\(^{-1}\) than both F3-unexposed and F4-unexposed spectra, revealing the higher content of amide II group (-(C=O)-NH-) in HDI-BI cross-linked PU coating compared to HDI-CT. Therefore, the IR band with maxima at 1523 cm\(^{-1}\) can be ascribed to an overlapped amide II band with the chemical entity originated from both urethane linkage and BI core when the BI isocyanate is present in the PU coating.
Again, the chemical changes as well as the degradation rate of PU coatings can be revealed by comparing exposed to unexposed IR spectra. As shown in Figure 6.3, the PA signal intensity reduction that can be seen at 1735 cm\(^{-1}\), 1690 cm\(^{-1}\), 1640 cm\(^{-1}\) and 1523 cm\(^{-1}\) for F3 and F2 indicates the decomposition of amide type linkages for HDI cross-linked PU coatings. F2 shows greater change in the PA signal reduction than F3 especially at 1640 cm\(^{-1}\) and 1523 cm\(^{-1}\), indicating the greater decomposition rates of urea entity (-NH-(C=O)-N-) and urethane amide group ((C=O)-NH-) in HDI-BI cross-linked PU coating compared to HDI-CT. Therefore, we may deduce that BI core structure is more inclined to degrade or break down than CT core structure during the exposure. Conversely, F4 shows much less change in the PA signal intensity reduction compared to F3 and F2, indicating the higher stability of amide type linkages in IPDI cross-linked PU coating compared to HDI. In contrast to F3 and F2, F4 shows very slight increases in the PA signal intensity near 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\), indicating that the degradation products of IPDI cross-linked PU coating are of a different composition compared to HDI cross-linked PU coating, which will be further discussed in Section 6.3.4.3. The PA signal intensity reduction can be found at 1465 cm\(^{-1}\) for all F3, F2 and F4, indicating the variation of chemical environment of CH group induced by the amide type linkage decomposition. Therefore, IR band with maxima near 1465 cm\(^{-1}\) can be assigned to end-chain CH bending in the backbone of HDI or IPDI molecular structure. PA signal intensity increases can also been seen at 1760 cm\(^{-1}\) (perester, acid, anhydride [16, 150]), 1710 cm\(^{-1}\) (H-bonded -COOH [16, 105]) in all F3, F2 and F4 spectra. This can be attributed to the build-up of degradation products as mentioned. The changes in the PA signal intensity for F2 is close, if not slightly higher than F3 at 1760 cm\(^{-1}\) and 1710 cm\(^{-1}\), indicating the comparable extent of the surface degradation and photo product build-up at the surface for the two HDI cross-linked PU coatings. Conversely, F4 gives significantly smaller changes in PA signal intensity at 1760 cm\(^{-1}\) and 1710 cm\(^{-1}\) compared to F3 and F2, indicating the less degradation and photo products build-up at the surface of IPDI cross-linked PU coating comparing to HDI cross-linked PU coatings.
6. The impact of isocyanate structures on the degradation of PU coil coatings

(a) IR spectra of MEKO blocked HDI-CT before and after exposure
(b) IR spectra of DMP blocked HDI-BI before and after exposure
The impact of isocyanate structures on the degradation of PU coil coatings

6.3.1.3. The 1350 cm⁻¹ - 720 cm⁻¹ region

Figure 6.4 shows the IR spectra in the 1350 cm⁻¹ - 720 cm⁻¹ region. All spectra are normalised to the PA signal intensity of the IR band with maxima near 1385 cm⁻¹ - 1378 cm⁻¹ (CH bending), for the same reason mentioned previously. All F3, F2 and F4 spectra give strong IR bands with maxima at 1240 cm⁻¹ and 1170 cm⁻¹ (-COO-). The IR band at 765 cm⁻¹ can be found for F3 and F4 and absent for F2, therefore assigned to the CT core. The F2-exposed spectrum shows a significant PA signal intensity reduction at 1240 cm⁻¹ and 1170 cm⁻¹ comparing with the F2-unexposed spectrum. This reduction in PA signal intensity is seen to be less significant for F3 and F4. The
significant PA signal intensity reduction for F2 reveals the high sensitivity of HDI-BI cross-linked PU coating towards degradation compared to HDI-CT. The PA signal intensity reduction at 1240 cm\(^{-1}\) and 1170 cm\(^{-1}\) may be ascribed to the overall film erosion effect [79]. F4 shows the least PA signal intensity reduction at 1240 cm\(^{-1}\) and 1170 cm\(^{-1}\), indicating the relatively high stability of IPDI cross-linked PU coating.

Increases in the PA signal intensity can be found at 1089 cm\(^{-1}\) and 1069 cm\(^{-1}\) in F2-exposed spectrum compared to F2-retain due to the formation of degradation products.

(a) IR spectra of MEKO blocked HDI-CT before and after exposure
6. The impact of isocyanate structures on the degradation of PU coil coatings

(b) IR spectra of DMP blocked HDI-BI before and after exposure

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F2-exposed
F2-unexposed

F4-exposed
F4-unexposed

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Wavenumbers (cm⁻¹)
6. The impact of isocyanate structures on the degradation of PU coil coatings

(c) IR spectra of MEKO blocked IPDI-CT before and after exposure

Figure 6.4 SS-PM-PA FTIR 800 Hz magnitude spectra of F3, F2 and F4 samples in the 1350 cm⁻¹ – 720 cm⁻¹ region. Unexposed spectra are marked with solid line. Exposed spectra are marked with dotted line. ‘-exposed’ denotes 1200 hours QUV A exposure time. Spectra are normalised to the PA signal intensity at 1378 cm⁻¹.

6.3.1.4. Summary

The IR band assignments can be summarised as shown in Table 6.2 according to the above discussion and previously published work.
Table 6.2 IR band assignments [11, 16, 17, 21, 40, 74, 105, 150, 151, 156, 157]

<table>
<thead>
<tr>
<th>IR band position (cm⁻¹)</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3700 - 3000</td>
<td>NH, OH stretching</td>
</tr>
<tr>
<td>3669 - 3488</td>
<td>OH stretching</td>
</tr>
<tr>
<td>3385</td>
<td>H-bonded NH stretching, urethane, BI core</td>
</tr>
<tr>
<td>3294</td>
<td>H-bonded urea NH stretching, BI core</td>
</tr>
<tr>
<td>2935</td>
<td>asymmetric CH stretching</td>
</tr>
<tr>
<td>2858</td>
<td>symmetric CH stretching</td>
</tr>
<tr>
<td>2860 - 2340</td>
<td>H-bonded COOH</td>
</tr>
<tr>
<td>2258</td>
<td>unblocked isocyanate –N=C=O</td>
</tr>
<tr>
<td>1760</td>
<td>perester, acid, anhydride</td>
</tr>
<tr>
<td>1735</td>
<td>amide I, C=O stretching, urethane and ester</td>
</tr>
<tr>
<td>1710</td>
<td>H-bonded COOH</td>
</tr>
<tr>
<td>1690</td>
<td>amide I, -N-(C=O)-N-, isocyanate core, urea</td>
</tr>
<tr>
<td>1640</td>
<td>amide I, -NH-(C=O)-N-, urea, BI core</td>
</tr>
<tr>
<td>1523</td>
<td>amide II, -(C=O)-NH-, urethane, BI core,</td>
</tr>
<tr>
<td>1385 - 1378</td>
<td>isocyanate in-chain CH bending</td>
</tr>
<tr>
<td>1240 - 1170</td>
<td>-COO-</td>
</tr>
<tr>
<td>1089 - 1069</td>
<td>degradation products</td>
</tr>
<tr>
<td>765</td>
<td>CT core</td>
</tr>
</tbody>
</table>

Based on the knowledge of IR band assignment and spectra interpretation as discussed above, the impact of different isocyanate branch (HDI and IPDI) and core (CT and BI) structure to the PU coating formation and degradation is further elaborated in Section 6.3.2 and Section 6.3.3.

**6.3.2. The comparison of HDI and IPDI branch structures**

Unexposed HDI and IPDI cross-linked PU clear coatings can be distinguished by comparing the IR spectra of F3-unexposed and F2-unexposed to F4-unexposed, as
shown in Figure 6.2 – Figure 6.4. The IR bands with maxima at 2952 cm\(^{-1}\), 2896 cm\(^{-1}\), 2258 cm\(^{-1}\) and 1385 cm\(^{-1}\) on the F4-unexposed spectra characterise the IPDI cross-linked PU coating compared to HDI. The IR bands with maxima at 1450 cm\(^{-1}\) and 1385 cm\(^{-1}\) in both F3-unexposed and F2-unexposed spectra characterise the HDI cross-linked PU coating compared to IPDI. The F4-unexposed spectra gives lower PA signal intensity at 1690 cm\(^{-1}\), 1640 cm\(^{-1}\) and 1523 cm\(^{-1}\) (all amide IR bands) compared to the F3-unexposed spectra, which can be ascribed to the lower cross-linking rate of IPDI cross-linked PU coating compared to HDI. The IPDI induced lower cross-linking rate of the PU coating may be attributed to the steric hindrance effect of IPDI (Section 2.2.2.1), which may obstruct the nucleophilic reaction between –N=C=O and –OH (Figure 2.8).

IR subtraction spectra have been adopted by many authors to demonstrate degradation related chemical changes, on which positive IR bands are attributed to the gaining of degradation products and negative bands are related to the loss of the original PU coating system [158, 159]. Figure 6.5 shows the subtraction results of individual PU coating systems, labelled as F3-sub, F2-sub and F4-sub. F4-sub gives strong negative peak at 2258 cm\(^{-1}\) and multiple weak positive peaks across the 1852 cm\(^{-1}\) - 1490 cm\(^{-1}\) region with the maxima at 1760 cm\(^{-1}\), 1710 cm\(^{-1}\), 1670 cm\(^{-1}\), 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\). In general, F4-sub shows much less significant spectral alteration than both F3-sub and F2-sub, if not taking the marked removal of –N=C=O peak (2285 cm\(^{-1}\)) in to account, which reflects the significantly higher stability of IPDI cross-linked PU coating compared to HDI. The IPDI induced high stability of the PU coating may also result from the steric hindrance effect of IPDI, in addition to the lower cross-linking rate as mentioned above. The bulky structure of IPDI may largely prevent the free radical attack towards the liable hydrogen on IPDI end-chain α-CH\(_2\), and consequently deter the overall degradation process (Figure 2.9).

### 6.3.3. The comparison of CT and BI core structures

Unexposed CT and BI isocyanates cross-linked PU clear coatings can be distinguished by comparing the IR spectra of both F3-unexposed and F4-unexposed to F2-unexposed
The impact of isocyanate structures on the degradation of PU coil coatings (Figure 6.2 – Figure 6.4). The broad IR band with maxima near 3294 cm\(^{-1}\) characterises BI isocyanate cross-linked PU coating compared to CT. The 3294 cm\(^{-1}\) band in F2-unexposed spectra is ascribed to the higher density of H-bond urea NH group (Table 6.2). Therefore, the higher PA signal intensity of IR band with maxima near 3294 cm\(^{-1}\) given by F2-unexposed spectra may be ascribed to the presence of the additional extent of NH groups (-NH-(C=O)-N-(C=O)-NH-) in BI core compared to CT core. The F2-unexposed spectrum gives the peak height ratio of approximately 3:2 for IR bands with maxima at 1690 cm\(^{-1}\) and 1640 cm\(^{-1}\). The lower ratio of approximately 4:1 of the peak height ratio of these two IR bands can be observed in both F3-unexposed and F4-unexposed spectra. This reflects the relatively lower extent of -N-(C=O)-N- group and higher extent of -NH-C=O-N- presented in BI core compared to CT core. As shown in Figure 6.5, F3-sub shows a lower spectral alteration than F2-sub, implying the CT core induced higher stability of PU coating compared to BI core. The discussion on the degradation mechanism of BI core is made in Section 6.3.4.3.

6.3.4. Side reactions involved degradation

6.3.4.1. Unblocked Isocyanate (–N=C=O) group in IPDI-CT

Based on the discussion made in Section 6.2, the unexposed IPDI cross-linked PU coating has been shown to contain more unblocked and unreacted isocyanate –N=C=O groups compared to HDI. According to Scheme 2.2, the remaining active –N=C=O can react with ambient water and produce CO\(_2\), primary amide and urea, allophanate and to a less extent BI. The conversion of urethane to allophanate and urea to BI was kinetically less favourable compared to the conversion of isocyanate to urethane and urea (Section 2.2.2.1). However, the excess of –N=C=O may lead the reaction to the generation of allophanate and BI as the minor side reactions. In this section, the isocyanate (–N=C=O) group involved degradation is studied. The chemical changes related to the remaining –N=C=O involved degradation is revealed by the subtraction spectra as introduced in Section 6.3.1.
As shown in Figure 6.5, F4-sub gives strong negative peak at 2258 cm\(^{-1}\) and multiple weak positive peaks across the 1852 cm\(^{-1}\) - 1490 cm\(^{-1}\) region with the maxima at 1760 cm\(^{-1}\), 1710 cm\(^{-1}\), 1670 cm\(^{-1}\), 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\). These peaks characterise the unblocked isocyanate –N=C=O group involved degradation of the IPDI-CT cross-linked PU coating. Firstly, the positive peaks in F4-sub at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\) are presented as strong negative peaks in F3-sub and F2-sub. IR bands with maxima at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\) are uniquely positive in F4-sub compared to both F3-sub and F2-sub and therefore can be largely attributed to the generation of primary amide (-NH\(_2\)) and the urea entities. The 1560 cm\(^{-1}\) IR band attributed to amide II and could be -NH-(C=O)-N- contained in urea, allophanate and to a less extent BI core. The strong negative peaks in F3-sub and F2-sub imply the loss of the primary amide (-NH\(_2\)) and the urea entity (-NH-(C=O)-N-), which is further discussed in Section 6.3.4.3. These two IR bands with maxima at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\) can be used as representative indicators for monitoring the degradation of the primary amide (-NH\(_2\)) and the urea entity (-NH-(C=O)-N-) related chemical changes, which is further discussed in Section 6.3.4.2. Secondly, the positive peaks at 1760 cm\(^{-1}\), 1710 cm\(^{-1}\) and 1670 cm\(^{-1}\) are seen in F3-sub, F2-sub and to a much less extent F4-sub, and therefore can be ascribed to the urethane linkage degradation products.
6.3.4.2. The proven of the surface top-film rich of primary amide and urea entity

The residual unblocked isocyanate –N=C=O group at the surface of IPDI-CT may react with ambient water to form primary amide (-NH$_2$) and the urea entity (-NH-(C=O)-N-), according to Scheme 2.2. These reactions are more likely to occur at the PU coating surface than in the bulk (Section 2.4.1.3) and can be monitored by using characteristic IR bands with maxima at 1640 cm$^{-1}$ and 1560 cm$^{-1}$ (Section 6.3.4.1). Therefore, the presence of a top-film rich in primary amide (-NH$_2$) and the urea entity (-NH-(C=O)-N-)
is expected at the surface of IPDI-CT cross-linked PU coating. This hypothesis can be proven by analysing SS-PM-PA FTIR phase spectra and CRM images. The applicability of SS-PM-PA FTIR CRM techniques are verified in Chapter 4 and Chapter 5, respectively.

Figure 6.6 shows the SS-PM-PA FTIR 800 Hz MF phase spectra of unexposed F3, F2 and F4 coating samples. The spectra are presented as common scale. The phase angle value can be viewed as a measure of the depth from which the signal evolves within the sample (Section 2.4.2.2). The phase angle spectra of F3-unexposed, F2-unexposed and F4-unexposed give the close phase angle value of approximately 0.24 radians at 1378 cm\(^{-1}\), indicating the consistency of the depth profile of the in-chain CH group (Table 6.2) in the clear PU coatings cross-linked with HDI-CT and IPDI-CT. The consistency of the depth profile supports the deduction made in Section 6.3.1.2 with regards to the high stability of the in-chain CH group towards the degradation.

As shown in Figure 6.6, the F4-unexposed phase angle spectrum gives the phase angle value of approximately 0.07 radians at 1600 cm\(^{-1}\), which is considerably lower than the phase angle value of 0.24 given by both F3-unexposed, F2-unexposed phase angle spectra at 1378 cm\(^{-1}\). In addition, F3-unexposed and F2-unexposed phase angle spectra give the phase angle values of approximately 0.23 and 0.34 respectively, which are considerably high compared to phase angle value of 0.07 given by F4-unexposed phase angle spectrum at the same wavenumber of 1600 cm\(^{-1}\). The relatively low phase angle value given by F4-unexposed spectrum at 1600 cm\(^{-1}\) implies the lower depth (more close to the film-air interface) of the chemical groups represented by the negative peak with maxima at 1600 cm\(^{-1}\) compared to 1378 cm\(^{-1}\) (in-chain CH group). Therefore, the negative peak with maxima at 1600 cm\(^{-1}\) in the 1520 cm\(^{-1}\) – 1680 cm\(^{-1}\) region in F4-unexposed spectrum proves the presence of primary amide (-NH\(_2\)) and the urea entity (-NH-(C=O)-N-) at the surface of IPDI-CT cross-linked PU coating with the characteristic IR bands with maxima at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\).
The impact of isocyanate structures on the degradation of PU coil coatings

Figure 6.6 SS-PM-PA FTIR 800 Hz MF phase spectra of unexposed F3 (MEKO blocked HDI-CT), F2 (DMP blocked HDI-BI) and F4 (MEKO blocked IPDI-CT) coating samples. The spectra are presented as common scale.

Figure 6.7 shows the CRM results collected at the surface of unexposed F3, F2 and F4 samples. The peak area ratio value of CT core : cyc (Figure 5.2) is represented by the gradient blue to red colour bar with scale 0 – 0.55. The transition from blue to red shows the CT core content from low to high. As shown in Figure 6.7, the F2-unexposed image shows a deeper blue colour, revealing the significantly less extent of CT core structure at the surface of HDI-BI cross-linked PU coating compared to F3-unexposed and F4-unexposed images. The colour variation present on F2-unexposed image shows the erroneous effect of the CRM method. The F4-unexposed image demonstrates brighter blue colour than the F2-unexposed image on average, representing a higher content of CT core at the surface of IPDI-CT cross-linked PU coating compared to HDI-BI. Compared to the F3-unexposed image, the F4-unexposed image shows darker blue colour on average, revealing the lower CT core content at the surface of IPDI-CT cross-linked PU coating compared to HDI-CT. As described in Section 6.2, the comparable CT core content shall be expected at the surface of IPDI-CT and HDI-CT.
cross-linked PU coatings under study, by considering the controlled addition of the polyester and isocyanate cross-linker components in the coating formulations. However, CRM results demonstrate the variation of the CT core contents at the surface of IPDI-CT and HDI-CT cross-linked PU coatings, which is in contrast to this expectation. Therefore, the higher top-film thickness at the surface of IPDI-CT cross-linked PU coating compared to HDI-CT may be deduced. The top-film can act as the barrier and reduce the transmittance of the CT core signal buried underneath. The CT core signal approach the CRM detector is expected to be inversely dependent to the thickness of the top-film, according to the well-known Beer–Lambert law. Therefore, the darker blue colour on average presented by F4-unexposed image than F3-unexposed image indicates the higher top-film thickness at the surface of IPDI-CT cross-linked PU coating compared to HDI-CT.

![Figure 6.7 CRM results of F3-unexposed, F2-unexposed and F4-unexposed samples (F3](image)

Figure 6.7 CRM results of F3-unexposed, F2-unexposed and F4-unexposed samples (F3
6. The impact of isocyanate structures on the degradation of PU coil coatings

– MEKO blocked HDI-CT, F2 – DMP blocked HDI-BI, F4 – MEKO blocked IPDI-CT). The characteristic peak area ratio of the CT core to the polyester was used as the imaging data (Figure 5.2). The content of CT core is represented by the gradient blue – red colour bar with scale 0 – 0.55. The transition from blue to red shows the CT core content from low to high.

6.3.4.3. The degradation of the top-film

The degradation of the top-film layer is discussed in this section, based on the knowledge of the presence and composite of this top-film as discussed in Section 6.3.4.2. The IR bands with maxima at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\) are used as the indicators to characterise the degradation of the top-film.

As shown in Figure 6.5, F2-sub gives strong negative band at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\), indicating the loss of the BI core structure.

The negative 3294 cm\(^{-1}\) peak in F2-sub also implies the loss of BI core, as discussed in Section 6.3.3. Unlike CT core with adjacent \(\alpha\)-CH\(_2\) groups linked to a tertiary amide group (\(-\text{CH}_2\text{-N(C=O)\_2}\)), BI core presents two \(\alpha\)-CH\(_2\) group linked to a secondary amide group (\(-\text{CH}_2\text{-NH(C=O)-N}\)). The degradation mechanism of BI core is demonstrated in Scheme 6.1, based on the previous work reported [11]. As shown in Scheme 6.1, the BI core may go through a homolytic chain scission to generate two free radicals, which will then form urea linkage and carbamic acid. The carbamic acid is likely to decompose rapidly to form primary amide and CO\(_2\), and/or undergo an esterification reaction with the residual polyester-OH to form a urethane linkage. It is noticeable that a weak band at 3450 cm\(^{-1}\) (free urethane linkage and/or orderly H-bonded urea [21, 160]) appeared in F3-exposed spectrum comparing to F3-unexposed spectrum (Figure 6.2), which may be an indication of the formation of urea and/or urethane as the products of the BI core decomposition.
6. The impact of isocyanate structures on the degradation of PU coil coatings

Scheme 6.1 Proposed BI core decomposition mechanism [11]

Based on the same principle of BI core decomposition, the degradation mechanism of allophanate linkage may be deduced as shown in Scheme 6.2. The allophanate may also go through a homolytic chain scission to generate two free radicals. These free radicals will then form urethane linkage and carbamic acid. The carbamic acid may decompose rapidly to form primary amide and CO$_2$, and/or undergo esterification reaction with residual polyester-OH to form urethane linkage.

Scheme 6.2 Proposed allophanate decomposition mechanism

As shown in Figure 6.5, a strong negative band at 1640 cm$^{-1}$ and 1560 cm$^{-1}$ can be found in F3-sub, indicating the decomposition of allophanate linkage in HDI-CT cross-linked PU coating, which is further discussed in Chapter 7.
6.4. Conclusions

The IPDI cross-linked PU coating gives lower cross-linking rate and higher stability compared to HDI, which can be attributed to the steric hindrance effect of IPDI. The bulky structure of IPDI may obstruct the nucleophilic reaction between \(-\text{N}=\text{C}=\text{O}\) and \(-\text{OH}\), as well as prevent the free radical attack towards the liable hydrogen adjacent to IPDI, and consequently deter the overall degradation process. CT core structure brings higher stability of PU coating compared to BI core.

The degradation of IPDI-CT cross-linked PU coating includes the top-film enrichment with primary amide and urea entities, to a greater extent than is indicated at the surface of HDI-CT cross-linked PU coatings. This top-film degrades in preference to the cross-linked PU film beneath with chemical changes monitored by IR bands at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\), which are attributed to the formation of primary amides, urethanes resulted from the homolytic chain scission of BIs and allophanates.
7. The impact of isocyanate blocking agents on the degradation of PU coil coatings

7.1. Introduction

In Chapter 6, we discussed the impact of isocyanate structures on the degradation of PU coil coatings. In addition to isocyanate structures, the blocking agents of the isocyanate cross-linkers also play vital roles in the film formation and degradation of PU coil coatings [15, 23, 42, 45]. The curing reaction mechanism of blocked isocyanate with polyester is discussed in Section 2.2.2.1. The structure of the blocking group has a major effect on deblocking temperature \( T_d \) and consequent cure rate of the PU coating. In the coil coating industry, three commonly used blocking agents are Capro, MEKO, and DMP (Figure 7.1). Capro has a relatively high \( T_d \) (about 157°C) due to a great steric effect of seven-member ring. \( T_d \) of MEKO is lower than Capro (about 130°C) and can react with isocyanates rapidly even without catalyst. DMP has an even lower \( T_d \) due to the high basicity of the pyrazole. [23]

![Schematic molecular structure of blocking agents. (a) Capro, (b) MEKO, (c) DMP](image)

In this chapter, the impact of isocyanate blocking agents, Capro, MEKO, and DMP, on the degradation chemistry of PU coil coatings is investigated. The cross-linking density and the top-film composition of unexposed PU coatings are examined. The chemical changes and degradation rate of the PU coating are investigated. Spectroscopic
The impact of isocyanate blocking agents on the degradation of PU coil coatings

Techniques of SS-PM-PA FTIR and CRM are employed for monitoring near-surface chemical changes within the PU coatings. The applicability of these two techniques has been verified as discussed in Chapter 4 and Chapter 5. SEM is used to study the topography change caused by degradation. This study is a part of ongoing work aiming to investigate the degradation pathway of PU coil coatings using advanced spectroscopy methods.

7.2. Experimental

Clear-coat formulations F1, F3, and F5 were used as summarised in Table 7.1. HDI-CT blocked with three blocking agents (a) Capro (b) MEKO and (c) DMP were used to as cross-linkers of PU network. The polyester used was cycloaliphatic polyester whose degradation is assumed to be negligible within PU systems under study compared to urethane linkage related degradation. For each formulation, the molar ratio of NCO : OH was maintained constant as 1.74. Other components of the coating formulations remain unchanged. For commercial confidentiality, trade names of the component products and other agents are omitted here.

Table 7.1 Simplified formulations of PU clear coating samples F1, F3 and F5

<table>
<thead>
<tr>
<th>Component in liquid paint (grams)</th>
<th>Description</th>
<th>F1</th>
<th>F3</th>
<th>F5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td>Cycloaliphatic saturated polyester</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Isocyanate blocking agents</td>
<td>(a) Capro</td>
<td>34</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) MEKO</td>
<td></td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(c) DMP</td>
<td></td>
<td></td>
<td>34</td>
</tr>
</tbody>
</table>

The model coil coating samples were prepared by the method as discussed in Section 3.1. The weathering protocol used in this study was QUV A accelerated ageing, the technical details of which were given in Section 3.2. The coupon samples were used for SS-PM-PA FTIR, CRM and SEM experiments. The SS-PM-PA FTIR and SEM analysis
were carried out with the method discussed in Section 3.3.1 and Section 3.3.4, respectively. In the CRM experiment, the profile ‘peak area ratio of two peaks’ was employed as a mapping strategy with the method discussed in Section 5.3.2.

7.3. Results and discussion

7.3.1. SS-PM-PA FTIR study

Figure 7.2 (a), (b) and (c) shows the SS-PM-PA FTIR 800 Hz magnitude spectra in the 3720 cm\(^{-1}\) – 2200 cm\(^{-1}\) region for F1, F3 and F5 samples, respectively. For individual F1, F3 and F5 samples, unexposed spectra (denoted as -unexposed) are marked with solid lines and 1200 hours exposed spectra (denoted as -1200) are marked with dotted lines. The symmetric CH stretching peak at 2935 cm\(^{-1}\) is used as the reference peak for spectra normalisation. This normalisation method is commonly used in previous work on the degradation study of PU coil coatings using FTIR technique [3, 161-163].

As shown in Figure 7.2, all spectra give a broad band with maxima at 3385 cm\(^{-1}\), assigned to H-bonded urethane NH stretching [11, 17, 40, 150]. The 3385 cm\(^{-1}\) peak can be viewed as the characteristic absorption peak of the urethane linkage. Therefore, the PA signal intensity at 3385 cm\(^{-1}\) is an indication of the content of urethane linkage. The PA signal intensity at 3385 cm\(^{-1}\) gives an order of F1-unexposed < F3-unexposed < F5-unexposed when comparing individual unexposed spectra in Figure 7.2 (a), (b) and (c). This order can be related to the urethane linkage content, hence the cross-linking density of coating samples. Higher PA signal intensity at 3385 cm\(^{-1}\) given by F5-unexposed than by F3-unexposed and F1-unexposed indicates the higher cross-linking density of the PU coating cross-linked with DMP blocked isocyanate (DMP-PU) comparing to MEKO blocked isocyanate (MEKO-PU) and Capro blocked isocyanate (Capro-PU). Additionally, the PA signal intensity increasing at 3385 cm\(^{-1}\) can be observed on exposed spectra compared to unexposed spectra for individual F1, F3 and F5 samples as shown in Figure 7.2 (a), (b) and (c). This PA signal intensity increasing indicates the formation of urethane linkage after exposure for all PU coating
systems with varied isocyanate cross-linkers. The PA signal intensity increasing rate at 3385 cm$^{-1}$ gives an order of F1 > F3 > F5, suggesting that more of the urethane linkage formed at the surface of exposed Capro-PU compared to MEKO-PU and DMP-PU.

In addition to urethane linkages, the formation of other types of chemical bonds may be indicated by the emergence of new peaks when comparing exposed to unexposed spectra for individual F1, F3 and F5 samples. As shown in Figure 7.2 (a), F1-1200 spectra shows two weak peaks with maxima at 3450 cm$^{-1}$ and 3294 cm$^{-1}$ compared to F1-unexposed. These two peaks are less obvious on F3-1200 (Figure 7.2 (b)) and F5-1200 (Figure 7.2 (c)). The 3450 cm$^{-1}$ and 3294 cm$^{-1}$ peaks can be assigned to urethane and/or orderly H-bonded urea [40, 151, 157]. Therefore, the emergence of two weak peaks at 3450 cm$^{-1}$ and 3294 cm$^{-1}$ on F1-1200 spectra comparing to F1-unexposed spectra indicates that a considerably higher amount of free and H-bonded urethane and/or orderly H-bonded urea formed at the surface of exposed Capro-PU compared to MEKO-PU and DMP-PU.

Apart from 3385 cm$^{-1}$ peak discussed above, the PA signal intensity increase can be observed in the 3700 cm$^{-1}$ – 3000 cm$^{-1}$ region and the 2860 cm$^{-1}$ – 2340 cm$^{-1}$ region on exposed spectra compared to unexposed spectra for individual F1, F3 and F5 samples as shown in Figure 7.2 (a), (b) and (c). The PA signal intensity increase rate in these two regions is in the order of F1 > F3 > F5. The broad IR bands in these two regions can be assigned to the PU degradation products including carboxylic acids, perester, primary urethane, acetylurethane and primary amide [16, 17, 74, 75]. Therefore, the PA signal intensity increasing rate in the 3700 cm$^{-1}$ – 3000 cm$^{-1}$ region and the 2860 cm$^{-1}$ – 2340 cm$^{-1}$ region indicates the build-up rate of the degradation products hence the degradation rate of the PU coatings. Consequently, the degradation rate order can be deduced to be Capro-PU > MEKO-PU > DMP-PU.
7. The impact of isocyanate blocking agents on the degradation of PU coil coatings

(a)

(b)
Figure 7.2 SS-PM-PA FTIR 800 Hz magnitude spectra of (a) F1, (b) F3 and (c) F5 samples in the 3720 cm\(^{-1}\) – 2200 cm\(^{-1}\) region. Unexposed sample spectra (denoted as -unexposed) are marked in solid line and 1200 hours exposed sample spectra (denoted as -1200) are marked in dotted line. The symmetric CH stretching peak at 2935 cm\(^{-1}\) are used as the reference peak for spectra normalisation.

Figure 7.3 (a), (b) and (c) shows the SS-PM-PA FTIR 800 Hz magnitude spectra in the 1950 cm\(^{-1}\) – 1330 cm\(^{-1}\) region for F1, F3 and F5 samples, respectively. For individual F1, F3 and F5 samples, unexposed spectra (denoted as -unexposed) are marked with a solid line and 1200 hours exposed spectra (denoted as -1200) are marked with a dotted line. All spectra are normalised to the PA signal intensity of the IR band with maxima at 1378 cm\(^{-1}\) (CH bending). The normalisation is based on the deduction that the PA signal intensity of this IR band at 1378 cm\(^{-1}\) is relatively stable towards the degradation, with for reasons discussed in Section 6.2.
The assignment of amide peaks of interest is carried out based on the published work [11, 17, 40, 150] and discussions made in Chapter 5. As shown in Figure 7.3, all spectra give amide peaks with maxima at 1735 cm\(^{-1}\), 1690 cm\(^{-1}\), 1640 cm\(^{-1}\) (amide I), 1560 cm\(^{-1}\) and 1523 cm\(^{-1}\) (amide II). The strong band at 1735 cm\(^{-1}\) (amide I) is assigned to free C=O stretching [11, 17, 40, 150]. The 1690 cm\(^{-1}\) peak can be assigned to the urea group (-N-(C=O)-N-) in CT core (-N-(C=O)-N-, Chapter 5, [40]). 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\) peak can be assigned to amide I and amide II, respectively, of the urea entity (-NH-(C=O)-N-, Chapter 5, [11]). 1523 cm\(^{-1}\) peak can be assigned to amide II of the urethane linkage (-(C=O)-NH-, [11, 17, 40, 150]).

The content of various amide type linkages at the surface of unexposed samples can be monitored by comparing the PA signal intensity of corresponding amide bands on F1-unexposed, F3-unexposed and F5-unexposed spectra as shown in Figure 7.3 (a), (b) and (c). Firstly, the PA signal intensity at 1735 cm\(^{-1}\) gives an order of F1-unexposed > F3-unexposed > F5-unexposed, indicating that the content of free C=O groups is in an order of Capro-PU > MEKO-PU > DMP-PU at the surface of unexposed samples. Secondly, the PA signal intensity ratio of 1690 cm\(^{-1}\) : 1735 cm\(^{-1}\) gives an order of F1-unexposed < F3-unexposed < F5-unexposed, indicating the concentration ratio of CT core to free C=O is relatively high at the surface of unexposed DMP-PU comparing to MEKO-PU and Capro-PU, which will be further discussed in Section 7.3.2. Thirdly, the PA signal intensity at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\) gives an order of F1-unexposed < F3-unexposed < F5-unexposed, indicating that the concentration order of the urea entity is Capro-PU < MEKO-PU < DMP-PU at the surface of unexposed samples. Fourthly, the PA signal intensity at 1532 cm\(^{-1}\) gives an order of F1-unexposed > F3-unexposed > F5-unexposed, indicating that the concentration of urethane linkage is in an order of Capro-PU > MEKO-PU > DMP-PU at the surface of unexposed samples. In summary, the content of free C=O groups and urethane linkage is in the order Capro-PU > MEKO-PU > DMP-PU at the surface of unexposed samples. This order can be inversely correlated to the content of CT core and urea entity.
The comparison of exposed and unexposed IR spectra is indicative of the chemical changes as well as the degradation rate of PU coatings. As shown in Figure 7.3 (a), (b) and (c), the PA signal intensity reduction at 1735 cm\(^{-1}\), 1690 cm\(^{-1}\), 1640 cm\(^{-1}\), 1560 cm\(^{-1}\) and 1523 cm\(^{-1}\) can be found when comparing exposed to unexposed spectra, indicating the decomposition of amide type linkages. The PA signal intensity reduction at 1465 cm\(^{-1}\) can be ascribed to the loss of \(\alpha\)-CH\(_2\) due the free radical recombination during the degradation process. The PA signal intensity increasing at 1790 cm\(^{-1}\) and 1710 cm\(^{-1}\) can be ascribed to the build-up of the degradation products including carboxylic acids, perester, primary urethane and primary amide [74, 164]. The PA signal intensity difference between exposed and unexposed spectra is of indication of the degradation rate for individual samples. The PA signal intensity difference between F1-1200 and F1-unexposed is relatively high compared to F3 and F5, indicating the higher degradation rate of Capro-PU compared to MEKO-PU and DMP-PU.
7. The impact of isocyanate blocking agents on the degradation of PU coil coatings
Based on the above discussion, we can summarise that the cross-linking density of unexposed PU coatings gives the order Capro-PU < MEKO-PU < DMP-PU. At the surface of unexposed samples, (i) the content of free C=O group and urethane linkage is in an order of Capro-PU > MEKO-PU > DMP-PU, and (ii) the content of CT core and urea entity is in an order of Capro-PU < MEKO-PU < DMP-PU. Varied blocking agents of isocyanate cross-linkers are likely to cause the content variation of different amide linkages at the surface of unexposed PU coatings. The unexposed PU coating with high content of free C=O group and urethane linkage and low content of CT core and urea entity are likely to lead to the high degradation rate of the PU coating subsequently.

The cross-linking density of unexposed PU coatings can be inversely correlated to the degradation rate of the exposed PU coatings. Therefore the degradation rate of Capro-PU > MEKO-PU > DMP-PU is expected. More of urethane and/or urea linkages formed at the surface of Capro-PU comparing to MEKO-PU and DMP-PU as a result of degradation.

### 7.3.2. CRM study

As mentioned in Section 7.3.1, the content of CT core is in an order of Capro-PU < MEKO-PU < DMP-PU. This result can be confirmed by CRM results as shown in Figure 7.4. The characteristic peak area ratio of the CT core to the polyester was used as the imaging data. The peak area ratios were measured as demonstrated in Figure 5.2. The data were selected with the method introduced in Section 3.3.3. The peak area ratio value of CT core : cyc is represented by the gradient blue to red colour bar, on which
0-blue represents the relative shortage of CT core and 0.55-red indicates richer content of CT core. The CRM results of unexposed (denoted as -unexposed) samples F1, F3 and F5 show different colour distribution, indicating the different surficial content of CT core. F5-unexposed shows a higher coverage of green colour followed by F3-unexposed and F1-unexposed, indicating the higher content of CT core at the surface of DMP-PU followed by MEKO-PU and Capro-PU.

Figure 7.4 CRM results of F1-unexposed, F3-unexposed and F5-unexposed samples. The characteristic peak area ratio of the CT core to the polyester was used as the imaging data (Figure 5.2). The content of CT core is represented by the gradient blue – red colour bar with scale 0 – 0.55. The transition from blue to red shows the CT core content from low to high.
7. The impact of isocyanate blocking agents on the degradation of PU coil coatings

7.3.3. SEM study

Figure 7.5 shows the SEM images of unexposed, F1-4098, F3-4098 and F5-4098 samples with \( \times 1,000 \) and \( \times 10,000 \) magnifications, correspondingly. All F1, F3 and F5 unexposed samples gives similar results and only one is presented here.

As shown in Figure 7.5, the unexposed sample presents a very smooth surface, whereas obvious topographic changes can be observed on all F1-4098, F3-4098 and F5-4098 images compared to the unexposed image. The topographic feature of exposed samples presents as remarkable surface sinking sites which are roughly round-shaped and with the diameter of approximately 15 \( \mu m \). These surface sinking sites may indicate that the degradation initiated and developed at the localised sites rather than evenly distributed at the surface of PU coating. The localised degradation site on the F5-4098 image seems less significant compared to F1-4098 and F3-4098 images, indicating that the durability of DMP-PU is relatively high compared to MEKO-PU and Capro-PU. Pinholes can be found inside the sinking sites on exposed samples with a diameter of approximately 1 – 2 \( \mu m \), which may be caused by the CO\(_2\) gas or other volatile degradation products emitting from the surface of the PU coating.
7.4. Conclusions

The cross-link density of unexposed PU coatings gives the order Capro-PU < MEKO-PU < DMP-PU. At the surface of unexposed samples, (i) the content of free C=O groups and urethane linkages is in the order Capro-PU > MEKO-PU > DMP-PU, and (ii) the content of CT core and urea entity is in an order of Capro-PU < MEKO-PU < DMP-PU. The order of CT core content can be confirmed by the CRM technique. Varied blocking agents of isocyanate cross-linkers are likely to cause the content variation of different amide linkages at the surface of unexposed PU coatings. The unexposed PU coating with high content of free C=O group and urethane linkage and low content of CT core and urea entity are likely to lead to the higher degradation rate of the PU coating subsequently.
The degradation rate of Capro-PU > MEKO-PU > DMP-PU is deduced by using SS-PM-PA FTIR technique. More of urethane and/or urea linkages formed at the surface of Capro-PU comparing to MEKO-PU and DMP-PU as a result of degradation. SEM technique confirms the high durability of DMP-PU compared to MEKO-PU and Capro-PU.
8. The degradation rate correlation of the PU coatings exposed in different weathering conditions

8.1. Introduction

The degradation rate of polymer materials can be quantitatively evaluated by using the degradation index plot method, as discussed in Section 2.3.2.2. FTIR technique has been commonly used to generate the degradation index data [19]. The disadvantage of this technique is thought to be the overlapping nature of the IR band, which adds difficulties for accurate quantitative analysis [20]. The accuracy of the FTIR quantitative analysis is expected to be improved by using peak fitting procedure (Section 2.4.3.2).

In this study, the FTIR peak fitting method is developed to establish degradation index plots. FTIR peak fitting method is developed to give high duplicability results, which is of necessity for accurate degradation rate evaluation. The degradation rate correlation of the PU coatings exposed in the QUV A test and natural exposure sites is investigated by using degradation index plots method. Three natural exposure sites under study are LIV, SA and KL, with the weathering conditions as described in Section 3.2. The formulation of PU coating is varied with regards to the isocyanate cross-linkers. The degradation chemistry of the PU coatings under study has been extensively discussed in Chapter 6 and Chapter 7. SEM is employed to provide supportive information in the form of topographic features of degraded PU coatings. This work aims to develop a method which can be used to monitor the degradation rate of PU coatings quantitatively and with improved accuracy. The quantitative degradation data are expected to be used for further degradation rate prediction of the PU coatings.

8.2. Experimental

Clear-coat formulations F1, F2, F3, F4 and F5 were as summarised as in Table 8.1. Five isocyanate cross-linkers of the PU coatings were (a) Capro blocked HDI branch with
The degradation rate correlation of the PU coatings exposed in different weathering conditions is discussed. The coating samples were prepared with the method as discussed in Section 3.1. The weathering protocol used in this study was QUV A accelerated ageing and natural exposure tests in three locations including LIV, SA and KL, with the technical details as introduced in Section 3.2. The coupon samples were used for SS-PM-PA FTIR experiment, with the method as discussed in Section 3.3.1.

The FTIR peak fitting procedure was carried out using OMNIC ‘peak resolve’ software programme. The 1880 cm\(^{-1}\) – 1430 cm\(^{-1}\) region and the 3700 cm\(^{-1}\) – 3000 cm\(^{-1}\) region of the spectra were fitted to determine the degradation rate correlation.

Table 8.1 The simplified formulations of PU coating samples F1 – F5.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (grams)</th>
<th>Description</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td></td>
<td>Cycloaliphatic saturated polyester</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Isocyanate</td>
<td></td>
<td>(a) Capro-HDI-CT</td>
<td>34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cross-linkers</td>
<td></td>
<td>(b) DMP-HDI-BI</td>
<td>34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c) MEKO-HDI-CT</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d) MEKO-IPDI-CT</td>
<td>41</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(e) DMP-HDI-CT</td>
<td>34</td>
<td></td>
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</tr>
</tbody>
</table>
the IR spectra were selected for peak fitting. Gaussian peak and constant baseline were used as deconvolution strategy. The full width at half height (FWHH) of two sharp peaks at 2858 cm\(^{-1}\) and 765 cm\(^{-1}\) was approximately 50 cm\(^{-1}\) and 25 cm\(^{-1}\), respectively, which were employed for setting up the FWHH values for the peak fitting procedure. FWHH was set up to 50 cm\(^{-1}\) in the 3700 cm\(^{-1}\) – 3000 cm\(^{-1}\) region, and 25 cm\(^{-1}\) in the 1880 cm\(^{-1}\) – 1430 cm\(^{-1}\) region. The sensitivity for finding peaks was setup as ‘high’. The programme was initiated to adjust the peak centre and height automatically with fixed FWHH to produce a composite spectrum that matches the original with a noise target value of 3.

8.3. Results and discussion

8.3.1. The weathering condition of the natural exposure sites

The weathering condition of the natural exposure sites were examined to obtain knowledge on the relative harshness. The harshness of the weathering condition at the natural exposure sites can be understood by comparing the SS-PM-PA FTIR magnitude spectra. Figure 8.1 – Figure 8.3 show F1 – F5 spectra exposed in natural sites of LIV, SA and KL together with the unexposed spectra. Unexposed spectra are shown with a black line, and exposed spectra are shown as grey lines. Spectra are normalised to the peak height of the IR band at 1378 cm\(^{-1}\) to maximise the spectra alteration for reasons discussed in Section 6.2. As shown in Figure 8.3, more significant spectral alteration can be found by comparing unexposed and exposed spectra of individual samples when compared to both Figure 8.1 and Figure 8.2. The more significant spectral alteration shown in Figure 8.3 suggests that the harshness of KL site is relatively high and causes more significant degradation compared to SA and LIV sites.
8. The degradation rate correlation of the PU coatings exposed in different weathering conditions

Figure 8.1 SS-PM-PA FTIR magnitude spectra of F1 – F5 unexposed and exposed samples in LIV natural exposure site. Unexposed spectra are shown in black line, and exposed spectra are shown in grey lines. Spectra are normalised to the peak height of the IR band at 1378 cm\(^{-1}\).
Figure 8.2 SS-PM-PA FTIR magnitude spectra of F1 – F5 unexposed and exposed samples in SA natural exposure site. Unexposed spectra are shown in black line, and exposed spectra are shown in grey lines. Spectra are normalised to the peak height of the IR band at 1378 cm$^{-1}$. 
8.3.2. The method of degradation index plots

8.3.2.1. FTIR peak fitting

Figure 8.4 and Figure 8.5 show the examples of FTIR peak fitting results performed at F3-unexposed and F3-4098 (-4098 denotes 4098 hours QUV A exposure test) spectra in the 3700 cm\(^{-1}\) – 3000 cm\(^{-1}\) region and the 1880 cm\(^{-1}\) – 1430 cm\(^{-1}\) region. Grey curves represent original IR spectra. Black curves are converged spectra with the peak fitting procedure. Individual deconvoluted Gaussian peaks are demonstrated with grey lines. The constant baseline is shown as the horizontal line under the IR band of the region. For each figure, three peak fitting results carried out separately are overlapped to
The degradation rate correlation of the PU coatings exposed in different weathering conditions demonstrate the high duplicability of the method. Deconvoluted peaks are grouped as A, B, C, D, E, F, G, H, M and N along with the increasing of the IR wavenumber. The band assignments of the groups A – N are marked according to the discussion made in Chapter 6 and Chapter 7.

Figure 8.4 Examples of FTIR peak fitting results performed with F3-unexposed and F3-4098 spectra in the 3700 cm$^{-1}$ – 3000 cm$^{-1}$ region. Grey curves represent original IR spectra. Black curves are converged spectra with peak fitting procedure. Individual deconvoluted Gaussian peaks are demonstrated with grey lines. The constant baseline is shown as the horizontal line under the IR band of the region. For each figure, three peak fitting results carried out separately are overlapped with one another to demonstrate the duplicability of the method. Deconvoluted peaks are grouped as A, B, C, D, E, F, G, H, M and N with band assignments along with the wavenumber increasing.
8.3.2.2. Normalised Peak Area (NPA) histograms

Peak area normalisation was carried out by modifying the peak area data of the
individual deconvoluted peaks. The Normalised Peak Area (NPA) data can be used for further quantitative analysis such as histogram and curve plots. The IR band with a maximum at 1378 cm\(^{-1}\) (CH bending) is used as the reference peak. The normalisation is based on the assumption that the PA signal intensity of the IR band at 1378 cm\(^{-1}\) is relatively stable towards the degradation for reason discussed in Section 6.2. The NPA of individual groups B – N can be calculated by normalizing the sum of the deconvoluted peak area of each group B – N to the reference group A.

Figure 8.6 and Figure 8.7 show the histogram plots of the NPA of deconvoluted groups B – N. The NPA of each set of histogram F1 – F5 are plotted against the QUV A exposure time intervals at 0 hours (unexposed), 1200 hours, and 4098 hours. The individual histogram sets F1 – F5 are marked with different patterns.

As shown in Figure 8.6, for group B, histogram set F2 shows higher unexposed NPA and significant NPA reduction along with the exposure time, indicating the significant BI core decomposing in DMP-HDI-BI cross-linked PU coating during the degradation. Comparatively, histogram sets F1, F3 and F5 show similar unexposed and reduction rate of NPA along with the exposure time, implying that the content of amide II type linkage is similar in the unexposed PU coatings cross-linked with Capro-HDI-CT, MEKO-HDI-CT and DMP-HDI-CT. Exceptionally, histogram set F4 shows the lowest unexposed NPA and different NPA variation pattern along with the exposure time compared to other histogram sets, which can be related to the lower density of amide II type linkage in the unexposed and unique chemical change process during the degradation of PU coating cross-linked with MEKO-IPDI-CT. The NPA alteration pattern of group C and D shows more complicate tendency, reflecting the complication of the amide group alteration during the exposure period. For group E, except histogram set F4, all histogram sets F1, F2, F3 and F5 show considerable decrease of NPA along with the exposure time, indicating the decomposition of carbonyl group associated chemical groups. For group F, except histogram set F4, all histogram sets F1, F2, F3 and F5 show marked NPA value increasing along with the exposure time, indicating the
The degradation rate correlation of the PU coatings exposed in different weathering conditions build-up of degradation products including acid, anhydride and perester. NPA for group C, D and E show less obvious trend compared to group B and F, reflecting the complication of the amide group alteration during the exposure period.

As shown in Figure 8.7, NPA for group G, H, M and N demonstrates various trends along with the exposure time. All histogram sets F1, F3, F4 and F5 show NPA increasing on group G, H and N along with the exposure time, indicating the similar build-up rate of degradation products at the surface of PU coatings cross-linked with Capro-HDI-CT, MEKO-HDI-CT, MEKO-IPDI-CT and DMP-HDI-CT. Histogram set F2 does not show the similar NPA increasing trend on group G, H and N, particularly at 1200 hours exposure time interval. For histogram set F2, NPA reduction of group N at 1200 hours exposure time interval may indicate the noticeable consumption of residual polyester-OH. For group M, both histogram sets F1 and F3 show increasing tendency of NPA along with the exposure time, whereas all histogram sets F2, F4 and F5 demonstrates different NPA trend particularly with the reduction at 1200 hours exposure time interval. The increasing tendency of NPA for both histogram sets F1 and F3 may indicate the higher urethane build-up effect occurred at the surface of Capro-HDI-CT and MEKO-HDI-CT cross-linked PU coatings.
8. The degradation rate correlation of the PU coatings exposed in different weathering conditions

Figure 8.6 The histogram plot of the Normalised Peak Area (NPA) of deconvoluted groups B – F. The NPA of each set of histogram F1 – F5 are plotted against the QUV A exposure time intervals at 0 hours (unexposed), 1200 hours, and 4098 hours. The individual histogram sets F1 – F5 are marked with different patterns.

Figure 8.7 The histogram plot of the Normalised Peak Area (NPA) of deconvoluted groups G – N. The NPA of each set of histogram F1 – F5 are plotted against the QUV A exposure time intervals at 0 hours (unexposed), 1200 hours, and 4098 hours. The
individual histogram sets F1 – F5 are marked with different patterns.

In summary, degradation monitored by using NPA histogram plots shows the characteristics including (i) the significant BI core decomposing in DMP-HDI-BI cross-linked PU coating, (ii) the similar content of amide II type linkages in the unexposed PU coatings cross-linked with HDI-CT isocyanates although with different blocking agents including Capro, MEKO and DMP, (iii) the lower content of amide II type linkages and unique chemical change process in IPDI-CT isocyanate cross-linked PU coating compared to HDI-CT, (iv) the complication of the amide group alteration, (v) the similar build-up rate of degradation products at the surface of PU coatings unless it is HDI-BI cross-linked, and (vi) the higher urethane build-up effect at the surface of Capro-HDI-CT and MEKO-HDI-CT cross-linked PU coatings. These degradation characters are consistent with the degradation chemistry of the PU coatings as discussed in Chapter 6 and Chapter 7.

8.3.2.3. Degradation Index plots

Degradation Index plots can be made by using modified NPA as well as the integrated peak area measurement to monitor the degradation rate of the PU coating, as shown in Figure 8.8 - Figure 8.12. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b). The degradation rate correlation of the PU coatings exposed in QUV A and natural exposure tests can be obtained by using degradation index plots method.

_Hydroxyl index plots_

Hydroxyl index plots of F1 – F5 samples made by peak area measurement data are shown in Figure 8.8. Peak areas are measured in the 3700 cm\(^{-1}\) – 2400 cm\(^{-1}\) region representing [NH, OH, COOH] groups and in the 3024 cm\(^{-1}\) – 2816 cm\(^{-1}\) region representing [CH] group, by using the method illustrated in Figure 2.11. In Figure 8.8 (a),
The degradation rate correlation of the PU coatings exposed in different weathering conditions except F1 curve, all F2, F3, F4 and F5 curves show decreasing trend in early exposure time (0 hour – 1200 hours QUV A exposure) with hydroxyl index values of approximately 1000 – 1300. All F1 – F5 curves show significant increasing with prolonged exposure time (1200 hours – 4098 hours QUV A exposure) with hydroxyl index values within a wide range of 1700 – 5400. The increasing rate of hydroxyl index value gives the order of $F_5 \approx F_3 > F_2 > F_4 > F_1$ with prolonged exposure time.

In Figure 8.8 (b), hydroxyl index values given by the natural exposure sites show the order of Unexposed $\approx$ LIV > SA > KL. It is interesting that this order is contradict to the conclusion made in Section 8, which suggests that the harshness of the KL site is relatively high. Hydroxyl index values given by all F1 – F5 histogram sets are in the range of 400 – 2000, reflecting that the degradation rate of natural exposed samples can be correlated to 0 hour – 1800 hours exposure time in QUV A test. LIV histogram set show hydroxyl index order of $F_2 \approx F_1 > F_3 \approx F_4 \approx F_5$, which is in agreement with the order of hydroxyl index values near 800 hours exposure in QUV A test. The SA histogram set show hydroxyl index order of $F_2 > F_1 \approx F_3 \approx F_5 > F_4$. This order can be correlated to the near 1200 hours exposure in QUV A test. However, SA histogram set show overall lowered hydroxyl index values compared to QUV A test. No QUV A exposure time can be found correlating to KL histogram set.

Figure 8.8 hydroxyl index curves of F1 – F5 samples plotted by peak area measurement data. Peak area is integrated in the 3700 cm$^{-1}$ – 2400 cm$^{-1}$ region representing [NH, OH,
The degradation rate correlation of the PU coatings exposed in different weathering conditions

COOH] groups and in the 3024 cm⁻¹ – 2816 cm⁻¹ region representing [CH] group. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).

**Index I plots**

The accuracy of the peak measurement method used for obtaining hydroxyl index is expected to be improved by peak fitting method, as introduced in Section 2.4.3.2. Therefore, more degradation index plots can be obtained by using NPA data as discussed in Section 8.3.2.2. Index I is calculated as the sum of NPA of group G, H, M and N, reflecting the build-up of degradation products containing NH and OH groups. Figure 8.9 demonstrates Index I plots of F1 – F5 samples. In Figure 8.9 (a), F2 curve shows a noticeable decreasing in early exposure time, then significant increasing in prolonged exposure time. The similar trend of F2 curve can be found in the hydroxyl index plots (Figure 8.8 (a)). F1, F3, F5 and F4 curves give close Index I values at 4098 hours exposure time, indicating that the degradation products containing OH, NH groups gradually reach a constant level in prolonged exposure time. The index I values given by F1, F3, F5 and F4 curves at 1200 hours exposure time show a descending order, which can be ascribed to the varied build-up rate of the degradation products containing OH and NH groups. Here, we may summarise that Index I plots demonstrate consistency compared to hydroxyl index plots (Figure 8.8) in early exposure time however diversity in prolonged exposure time. As mentioned, hydroxyl index monitors degradation products containing COOH group as well as NH, OH groups. Therefore, the diversity between Index I and hydroxyl index plots indicates that degradation products containing COOH group accumulated more rapidly in prolonged exposure time compared to NH and OH groups.

In Figure 8.9 (b), LIV, SA and KL histogram sets give Index I values in the range of 0.5 – 1.5. Some correlations can be found for the degradation rate of the PU coatings exposed in QUV A test and natural exposure sites. Firstly, F2 histogram gives the
highest Index I values at both LIV and SA sites. Secondly, F4 histogram gives the lowest Index I value at SA exposure site. Both of these points are in agreement with the Index I order throughout the entire QUV A exposure period given by all F1 – F5 curves shown in Figure 8.8 (a). However, no Index I order given by all F1 – F5 curves in QUV A test can be found correlating to KL histogram set.

Figure 8.9 Index I plots of F1 – F5 samples. Index I is calculated as the sum of NPA of group G, H, M and N, reflecting the build-up rate of degradation products containing NH and OH groups. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).

Index II plots

Index II equals the NPA of group B, representing the content of amide II type linkages within the PU coatings. Figure 8.10 demonstrates Index II plots of F1 – F5 samples. In Figure 8.10 (a), F2 curve shows significantly higher Index II value especially during early exposure time. All F1, F2, F3 and F5 curves present decreasing trend throughout the entire exposure time. The decreasing rate of the Index II values gives the order of F2 > F5 > F1 > F3. F4 curve gives a lower Index II value initially, which is increasing towards a maximum value of about 0.5 around 1200 hours exposure time, before the down turn in prolonged exposure time. All F1 – F5 curves gradually approach a relatively consistent
8. The degradation rate correlation of the PU coatings exposed in different weathering conditions

Index II value of approximately 0.35 – 0.45 at prolonged exposure time.

In Figure 8.10 (b), LIV histogram set gives the Index II value order of F2 > F5 > F3 > F1 > F4. The correlation can be found between LIV histogram set and QUV A exposure time of within 0 hours – 200 hour. SA histogram set gives the Index II value order of F2 > F5 > F1 > F3 > F4. The correlation can be found between SA histogram set and QUV A exposure time of around 700 hours exposure time. No correlation can be found between KL histogram set and QUV A exposure time.

![Index II plots of F1 – F5 samples.](a)

![Index II plots of F1 – F5 samples.](b)

Figure 8.10 Index II plots of F1 – F5 samples. Index II is calculated as the sum of NPA of group B, reflecting the variation rate of amide II type linkages. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).

**Index III plots**

Index III is calculated by NPA C/(C+D), representing the ratio of the branch urea entity and primary amide to the sum of the core and branch urea entities and primary amide within the PU coatings. Figure 8.11 demonstrates Index III plots of F1 – F5 samples. In Figure 8.11 (a), F1, F2 and F5 curves show slight decreasing within early exposure time and significant increasing in prolonged exposure time. F3 and F4 curves show
increasing throughout the entire exposure period. For all F1 – F5 curves, Index III values gradually approach a relatively consistent value in a range of 0.6 – 0.65, reflecting that the content of the branch urea entity and primary amide over the sum of the core and branch urea entities reaches a relatively stable amount at prolonged exposure time.

In Figure 8.11 (b), LIV histogram set gives the Index III value order of F2 > F5 > F4 > F1 > F3. The correlation can be found between LIV histogram set and QUV A exposure time of within 300 hours – 500 hours. SA histogram set gives the Index III value order of F2 > F4 > F5 > F1 > F3. The correlation can be found between SA histogram set and QUV A exposure time of within 400 hours – 500 hours exposure time. KL histogram set gives the Index III value order of F2 > F4 > F5 > F1 > F3. The correlation can be found between KL histogram set and QUV A exposure time of around 1000 hours exposure time.

Figure 8.11 Index III plots of F1 – F5 samples. Index III is calculated by NPA C/(C+D), reflecting the variation rate of the branch urea entity and primary amide within the sum of the core and branch urea entities. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).
Index IV plots

Index IV is calculated by NPA F/(E+F), reflecting the ratio of the amide I (C=O) group contained in acid, anhydride and perester to the sum of the amide I (C=O) group. Figure 8.12 demonstrates Index IV plots of F1 – F5 samples. In Figure 8.12 (a), F4 curve shows a significant decreasing after 1200 hours exposure time, reflecting the significant urethane linkage build-up effect within the prolonged exposure time. All F1, F2, F3 and F5 curves show consistent increasing along with the entire exposure time.

In Figure 8.12 (b), SA histogram set gives the Index IV value order of F4 > F2 > F1 > F3 > F5. The correlation can be found between SA histogram set and QUV A exposure time of around 500 hours. No correlation can be found between LIV and KL histogram sets and QUV A exposure time.

Figure 8.12 Index IV plots of F1 – F5 samples. Index IV is calculated by NPA F/(E+F), reflecting the ratio of the amide C=O group in acid, anhydride and perester to the sum of the amide I C=O groups. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).

8.4. Conclusions

FTIR peak fitting method developed in this study gives high duplicability results, which
is of necessity for accurate degradation rate evaluation. The Normalised Peak Area (NPA) histograms demonstrate quantitative IR information which is consistent with the known degradation chemistry. Degradation index plots are established by using modified NPA data as well as peak area measurements to monitor the time depending degradation rate. The degradation rate correlation of the PU coatings exposed in QUV A test and natural exposure sites including LIV, SA and KL are demonstrated.

Hydroxyl index values given by the natural exposure sites show the order of Unexposed ≈ LIV > SA > KL. The degradation rate of natural exposed samples can be correlated to 0 hour – 1800 hours exposure time in QUV A test according to hydroxyl index plots. Index I plots demonstrate consistency with hydroxyl index plots in early exposure time and diversity in prolonged exposure time. In most cases, the degradation plots made by Index II, III and IV approach a relatively consistent value gradually, indicating the degradation rate reaches a plateau at prolonged exposure time. An exception can be found for F4 curve at the ultimate exposure time in Index IV plot, due to the extraordinary stability of IPDI cross-linked PU coating. The degradation rate correlation made by degradation index plots method for the PU coatings F1 – F5 exposed in QUV A test and natural exposure sites including LIV, SA and KL are summarised in Table 8.2.

Table 8.2 The degradation rate correlation made by degradation index plots method for the PU coatings with varied isocyanate cross-linkers exposed in QUV A test and natural exposure sites including LIV, SA and KL.

<table>
<thead>
<tr>
<th>QUV A exposure time (hours)</th>
<th>Degradation index plots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hydroxyl index</td>
</tr>
<tr>
<td>LIV</td>
<td>800</td>
</tr>
<tr>
<td>SA</td>
<td>1200</td>
</tr>
<tr>
<td>KL</td>
<td>n.c.c</td>
</tr>
</tbody>
</table>

n.c.c – no consistent correlation
9. The impact of minor film formers, additives and NCO/OH to the degradation of PU coil coatings

9.1. Introduction

The physical and chemical characters of the components of PU paint formulation influence the polymerisation reaction, as well as final properties of the finished coating. In this chapter, the impact of minor film formers or additives (less than 5%) and NCO/OH of the coating formulation to the degradation of the PU coil coating is investigated, in addition to the isocyanate cross-linkers as the major component as discussed in Chapter 6 and Chapter 7. The PU coating formulation can be modified by adding minor film formers such as melamine and BI isocyanate, or additives such as HALS (Section 2.2.4) or varying the stoichiometry of isocyanate/hydroxyl (NCO/OH) (Section 2.2.5) to improve the property and durability of the coating [51, 56, 66]. The BI isocyanate is added into the PU formulation with the anticipation of improved curing speed, although the BI core showed relatively less stability towards the degradation compared to CT core, based on the discussion made in Chapter 6. The consequent degradation of the modified PU coatings can be varied significantly. In this study, the impact of the addition of melamine, BI isocyanate, HALS and the variation of NCO/OH to the degradation of the clear PU coil coatings is studied. The degradation chemistry is studied by SS-PM-PA FTIR technique. The degradation rate correlation of the PU coatings exposed in different weathering conditions including QUV A test and natural exposure sites is examined by degradation index plots method as discussed in Chapter 8. The topographic change of the PU coating due to the degradation is studied by SEM.

9.2. Experimental

Clear PU coating formulations F1, F1_A, F1_B, F12_A, F12_B and F12_C were as summarised in Table 9.1. Five isocyanate cross-linkers of the PU coatings were Capro blocked HDI-CT, DMP blocked HDI-BI, MEKO blocked HDI-CT, MEKO blocked IPDI-CT, and DMP blocked HDI-CT. Melamine is added in the formulations except
F1. HALS is added in the formulations except F1_B and F1. The DMP blocked HDI-BI is added and NCO/OH is varied for formulation F12_A, F12_B and F12_C. The polyester used was cycloaliphatic polyester whose degradation is assumed be negligible within PU systems under study compared to urethane linkage related degradation. For reasons of commercial confidentiality, trade names of the component products and other agents are omitted here.

Table 9.1 The simplified formulations of PU coating samples F1, F1_A, F1_B, F12_A, F12_B and F12_C.

<table>
<thead>
<tr>
<th>Component in paint (grams)</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F12_A</td>
</tr>
<tr>
<td>Polyester</td>
<td>95.5</td>
</tr>
<tr>
<td>Capro blocked HDI-CT</td>
<td>28.5</td>
</tr>
<tr>
<td>DMP blocked HDI-BI</td>
<td>4.0</td>
</tr>
<tr>
<td>HALS</td>
<td>0.9</td>
</tr>
<tr>
<td>Melamine</td>
<td>6.8</td>
</tr>
<tr>
<td>TOTAL</td>
<td>192.9</td>
</tr>
<tr>
<td>NCO/OH</td>
<td>1.74</td>
</tr>
</tbody>
</table>

The model coil coating samples were prepared with the method as discussed in Section 3.1. The weathering protocol used in this study was QUV A accelerated ageing and natural exposure test in three locations including LIV, SA and KL, with the technical details as introduced in Section 3.2. The coupon samples were used for SS-PM-PA FTIR and SEM experiments. The SS-PM-PA FTIR and SEM analysis were carried out with the method as discussed in Section 3.3.1 and Section 3.3.4. The FTIR peak fitting was carried out with the method as discussed in Section 8.2.
9.3. Results and discussion

9.3.1. The impact of melamine

The impact of melamine to the degradation of PU coatings are revealed by comparing the SS-PM-PA FTIR magnitude spectra of F1 and F1_B, unexposed, QUV A 1200 hours exposed and subtraction result spectra. As shown in Figure 9.1, all magnitude spectra are normalised to the peak height at 1378 cm\(^{-1}\) (CH bending). Subtraction result spectra are obtained by using exposed minus unexposed spectra for individual samples.

As shown in Figure 9.1, F1_B-unexposed gives the higher PA intensity at 1553 cm\(^{-1}\) compared to F1-unexposed at 1534 cm\(^{-1}\), indicating the higher content of amide II type linkages in the PU coatings containing melamine. The subtraction result spectrum F1_B gives relatively less significant spectra alteration throughout the entire spectra region comparing to F1, if not considering the negative band near 1550 cm\(^{-1}\). The significant spectra alteration given by the subtraction result spectrum F1_B suggests that the addition of melamine improves the durability of the PU coating. The lower negative amide II band given by the subtraction result spectrum F1_B indicates that melamine linkage is more sensitive to the degradation compared to urethane linkage. The subtraction result spectrum F1 gives a strong positive band at 1078 cm\(^{-1}\), which may be attributed to the decomposition of the ether group in the melamine linkage (ether linkage is of a major degradation products of urethane linkage decomposition). The subtraction result spectrum F1_B gives weak positive bands at 1872 cm\(^{-1}\) and 1820 cm\(^{-1}\) compared to F1, which may be denote to the degradation products of the decomposition of the melamine linkage.
9.3.2. The impact of HALS

The impact of HALS additive to the PU coatings can be revealed by comparing the subtraction result spectra of F1_A and F1_B, as shown in Figure 9.2. Each subtraction result spectrum is obtained by using exposed minus unexposed spectra of individual samples. The exposed samples are acquired with two QUV A exposure time intervals at 1200 hours and 4098 hours. All spectra are shown in common scale.

As shown in Figure 9.2, the overall spectral alteration of the subtraction result spectra shows the order F1_A-1200 minus F1_A-unexposed < F1_A-4098 minus F1_A-unexposed < F1_B-1200 minus F1_B-unexposed < F1_B-4098 minus
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F1_B-unexposed. The spectral alteration of F1_A-4098 minus F1_A-unexposed is comparable to F1_B-1200 minus F1_B-unexposed, reflecting that the durability of PU coating can be significantly improved by the addition of HALS. F1_A-1200 minus F1_A-unexposed shows negative bands with maxima at 1780 cm\(^{-1}\) and 1405 cm\(^{-1}\), indicating the unique chemical revolution due to the addition of HALS particularly at early exposure time in QUVA test (0 hours – 1200 hours QUVA exposure). F1_A-4098 minus F1_A-unexposed, F1_B-1200 minus F1_B-unexposed and F1_B-4098 minus F1_B-unexposed demonstrate similar spectral alteration feature, reflecting that HALS does not change the degradation mechanism of PU network during prolonged exposure time in QUVA test (1200 hours – 4098 hours QUVA exposure). A similar conclusion drawn by other authors can be found in reference [65].

Figure 9.2 subtraction result spectra of F1_A and F1_B, marked with different colours. Each subtraction result spectrum is obtained by using exposed minus unexposed spectra of individual samples. The exposed samples are acquired with two QUVA exposure time intervals at 1200 hours and 4098 hours. All spectra are shown in common scale.
9.3.3. The impact of NCO/OH

The impact of NCO/OH to the PU coatings can be revealed by comparing the SS-PM-PA FTIR magnitude spectra set F12_A, F12_B and F12_C. As shown in Figure 9.3, each spectra set consists of three spectra acquired with individual samples at unexposed, QUV A 1200 hours and 4098 hours exposure time. The NCO/OH value is marked behind individual sample labels. All spectra are normalised to the peak height at 1378 cm\(^{-1}\) (CH bending).

As shown in Figure 9.3 the F12_A spectra set shows more significant PA intensity increasing in the 3700 cm\(^{-1}\) – 3000 cm\(^{-1}\) region at 1200 hours exposure compared to the F12_B and F12_C spectra sets, indicating the more significant degradation products build-up rate of at the surface of PU coating with higher NCO/OH within the early exposure time. The F12_C spectra set shows more significant PA intensity increasing in the 3700 cm\(^{-1}\) – 3000 cm\(^{-1}\) region at 4098 hours exposure compared to the F12_B and F12_A spectra sets, indicating the more significant degradation products build-up rate of at the surface of PU coating with lower NCO/OH within the prolonged exposure time.

As shown in Figure 9.3, the F12_C spectra set shows more significant PA intensity decreasing at 1553 cm\(^{-1}\) compared to the F12_B and F12_A spectra sets along with the exposure time, indicating that higher NCO/OH can lead to the reduced amide II type linkage decomposition particularly during prolonged exposure time.
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9.3.4. The impact of BI isocyanate

The spectral alteration difference between spectra set F1_A and F12_A demonstrates the influence of the addition of BI type isocyanate to the degradation of the PU coatings, as shown in Figure 9.3. The F1_A spectra set show more significant PA intensity reduction near 1553 cm\(^{-1}\) (amide II band) at 4098 hours exposure, whereas the F12_A spectra set show marked PA intensity increasing in the 3700 cm\(^{-1}\) – 3000 cm\(^{-1}\) region (NH, OH, COOH band) at 1200 hours exposure. The different spectra alteration between F1_A and F12_A spectra sets reveals that the addition of BI isocyanate in the PU formulation can result in higher degradation products build-up rate during early exposure time and reduced amide II type linkage decomposition during prolonged exposure time in QUV A test.

Figure 9.3 SS-PM-PA FTIR magnitude spectra of F1_A, F12_A, F12_B and F12_C. The NCO/OH value \(r\) is marked behind the sample label. All spectra are normalised to the peak height at 1378 cm\(^{-1}\) (CH bending).
9.3.5. The weathering condition of the natural exposure sites

The weathering condition of the natural exposure sites are examined to obtain the knowledge on the relative harshness. The harshness of the weathering condition at the natural exposure sites can be understood by comparing the SS-PM-PA FTIR magnitude spectra. Figure 9.4 – Figure 9.6 show SS-PM-PA FTIR magnitude spectra of F1_A, F1_B, F12_A, F12_B and F12_C samples exposed in natural sites of LIV, SA and KL together with the unexposed spectra. Unexposed spectra are shown with black lines, and exposed spectra are shown with grey lines. Spectra are normalised to the peak height of the IR band at 1378 cm\(^{-1}\). As shown in Figure 9.6, significant spectral alteration can be found by comparing unexposed and exposed spectra of individual samples when comparing to both Figure 9.4 and Figure 9.5. The more significant spectral alteration shown in Figure 9.6 suggests that the harshness of KL site is relatively high and causes more significant degradation compared to SA and LIV sites. This is in agreement with the discussion made in Section 8.

As shown in Figure 9.6, the PA intensity reduction can be observed in the 3700 cm\(^{-1}\) – 1800 cm\(^{-1}\) region when comparing exposed to unexposed spectra of all F1_A, F1_B, F12_A, F12_B and F12_C samples. No such PA intensity reduction can be found in this region as shown Figure 9.4 and Figure 9.5. Therefore, the PA intensity reduction in the 3700 cm\(^{-1}\) – 1800 cm\(^{-1}\) region indicates the different degradation chemistry of the PU coatings exposed in KL site compared to LIV and SA sites. Additionally, the exposed spectra shows overall band reduction across the entire wavenumber region when compared to the unexposed spectra for individual samples, as shown in Figure 9.6, which may be related to the significant surface densification occurred at the surface of PU coatings exposed in KL site.
Figure 9.4 SS-PM-PA FTIR magnitude spectra of F1_A, F1_B, F12_A, F12_B and F12_C unexposed and exposed samples in LIV natural exposure site for 1 year. Unexposed spectra are shown in black line, and exposed spectra are shown in grey lines. Spectra are normalised to the peak height of the IR band at 1378 cm⁻¹.
Figure 9.5 SS-PM-PA FTIR magnitude spectra of F1_A, F1_B, F12_A, F12_B and F12_C unexposed and exposed samples in SA natural exposure site for 1 year. Unexposed spectra are shown in black line, and exposed spectra are shown in grey lines. Spectra are normalised to the peak height of the IR band at 1378 cm$^{-1}$. 

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Figure 9.6 SS-PM-PA FTIR magnitude spectra of F1_A, F1_B, F12_A, F12_B and F12_C unexposed and exposed samples in KL natural exposure site for 1 year. Unexposed spectra are shown in black line, and exposed spectra are shown in grey lines. Spectra are normalised to the peak height of the IR band at 1378 cm\(^{-1}\).

9.3.6. The degradation index plots method

The degradation rate correlation of the PU coatings F1_A, F1_B, F12_A, F12_B and F12_C exposed in QUV A test and natural exposure sites can be obtained by using degradation index plots method, based on the knowledge of the degradation chemistry of the PU coatings as discussed in Section 9. The degradation index plots method used here is similar as which is developed in Chapter 8 however with the different peak fitting recipe developed to best match the FTIR spectra of the PU coatings under study.

9.3.6.1. FTIR peak fitting

Figure 9.7 shows an example of FTIR peak fitting results performed with
F12_A-unexposed spectrum in the 1880 cm\(^{-1}\) – 1430 cm\(^{-1}\) region, with the method as introduced in Section 8.2. Grey curves represent original IR spectra. Black curves are converged spectra with peak fitting procedure. Individual deconvoluted Gaussian peaks are demonstrated with grey lines. The constant baseline is shown as the horizontal line under the IR band of the region. Here, three peak fitting results carried out separately are overlapped to demonstrate the high duplicability of the method. Deconvoluted peaks are grouped as A, B, C, D, E and F along with the increasing of the IR wavenumber. The band assignments of the groups A – F are marked according to the discussion made in Chapter 6 and Chapter 7.

Figure 9.7 An example of FTIR peak fitting results performed with F12_A-unexposed spectrum in the 1880 cm\(^{-1}\) – 1430 cm\(^{-1}\) region. Grey curves represent original IR spectra. Blue curves are converged spectra with peak fitting procedure. Individual deconvoluted Gaussian peaks are demonstrated with grey lines. The constant baseline is shown as the horizontal line under the IR band of the region. Here, three peak fitting results carried out separately are overlapped to demonstrate the high duplicability of the method. Deconvoluted peaks are grouped as A, B, C, D, E and F along with the increasing of the IR wavenumber. The band assignments of the groups A – F are marked according to the
9.3.6.2. **Degradation Index plots**

The degradation rate correlation of the PU coatings exposed in QUV A test and natural exposure sites are examined by using degradation index plots method. Degradation Index plots are established with the same method as discussed in Section 8.3.2. Figure 9.8 – Figure 9.11 shows the degradation index plots of hydroxyl index, Index II, III, and IV. Index I plots give similar result as the hydroxyl index plots and therefore omitted here. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).

*Hydroxyl index plots*

Hydroxyl index plots of F1_A, F1_B, F12_A, F12_B and F12_C samples are shown in Figure 9.8. Peak areas are measured in the 3700 cm\(^{-1}\) – 2400 cm\(^{-1}\) region representing [NH, OH, COOH] groups and in the 3024 cm\(^{-1}\) – 2816 cm\(^{-1}\) region representing [CH] group, by using the method illustrated in Figure 2.11. In Figure 9.8 (a), F12_A and F12_B curves show hydroxyl index value increasing along with the exposure time, indicating the significant degradation products build-up when the NCO/OH is relatively high. F1_B curve shows higher hydroxyl index value compared to F1_A curve particularly during prolonged exposure time, indicating the improved durability of F1_B sample due to the addition of HALS into the PU coating formulation.

In Figure 9.8 (b), both SA and KL histogram sets give the hydroxyl index value order F12_A > F12_B > F1_B > F1_A > F12_C. The same order can be found with hydroxyl index curves at 1700 hours – 4098 hours exposure time in QUV A test (Figure 9.8 (a)), however with higher hydroxyl index values for all F1_A, F1_B, F12_A, F12_B and F12_C samples. No correlation can be found between KL histogram set and QUV A exposure time.
Figure 9.8 Hydroxyl index plots of F1_A, F1_B, F12_A, F12_B and F12_C samples plotted by peak area measurement data. Peak area is integrated in the 3700 cm\(^{-1}\) – 2400 cm\(^{-1}\) region representing [NH, OH, COOH] groups and in the 3024 cm\(^{-1}\) – 2816 cm\(^{-1}\) region representing [CH] group. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).

**Index II plots**

Index II equals the NPA of group B, representing the amide II type linkages in the isocyanate molecular structure. Figure 9.9 demonstrates Index II plots of F1_A, F1_B, F12_A, F12_B and F12_C samples. In Figure 9.9 (a), F1_B curve shows an exceptional decreasing trend, reflecting the higher degradation rate of the PU coatings without the addition of HALS.

In Figure 9.9 (b), F12_B histograms give the highest value whereas F1_B histograms give the lowest value of Index II at both LIV and KL sites, which can be correlated to 1000 hours – 4098 hours exposure time in QUV A test. KL histogram set shows overall lower Index II value compared to LIV histogram set. Therefore, KL histogram set may be correlated to a later QUV A exposure time compared to LIV histogram set. No correlation can be found between KL histogram set and QUV A exposure time.
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Figure 9.9 Index II plots of F1_A, F1_B, F12_A, F12_B and F12_C samples. Index II is calculated as the sum of NPA of group B, reflecting the variation rate of amide II type linkages. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).

*Index III plots*

Index III is calculated by NPA C/(C+D), representing the ratio of the branch urea entity and primary amide to the sum of the core and branch urea entities and primary amide within the PU coatings. Figure 9.10 shows Index III plots for F1_A, F1_B, F12_A, F12_B and F12_C samples. In Figure 9.10 (a), F12_A, F12_B and F12_C curves show different trends, indicating the different chemical change pathway of the PU coating during the entire exposure period caused by the NCO/OH variation. F1_A curve shows lower Index III value compared to F1_B curve throughout the exposure period, which can be related to the improved durability of F1_A sample due to the addition of the HALS in the PU formulation.

In Figure 9.10 (b), F12_A histograms give the highest Index III value, whereas the F12_C histograms give the lowest Index III value at both LIV and SA sites, which can be correlated to 400 hours – 3700 hours exposure time in QUV A test. SA histogram set
gives an overall higher Index III value compared to LIV histogram set, indicating that SA site can be correlated to a later exposure time in QUV A test comparing to LIV site. LIV and SA histogram sets can be correlated to 400 hours – 2100 hours for the former and 2100 hours – 3700 hours for the later in QUV A test. KL histogram set shows close Index III values for all samples, which may be correlated to an even later exposure time (around 4098 hours) in QUV A test.

Figure 9.10 Index III plots of F1_A, F1_B, F12_A, F12_B and F12_C samples. Index III is calculated by NPA C/(C+D), reflecting the variation rate of the branch urea entity and primary amide within the sum of the core and branch urea entities. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).

**Index IV plots**

Index IV is calculated by NPA F/(E+F), reflecting the ratio of the amide C=O group in acid, anhydride and perester to the sum of the amide I C=O groups. Figure 9.11 shows the Index IV plots for F1_A, F1_B, F12_A, F12_B and F12_C samples. In Figure 9.11 (a), F1_A curve shows lower Index IV value compared to F1_B curve throughout the entire exposure period, indicating the improved durability of F1_A due to the addition of HALS in the PU formulation. All F12_A, F12_B and F12_C curves show the increasing trend especially during the prolonged exposure time, which may be related to the
addition of BI isocyanate in the PU coating formulation. F12_C curve shows less significant increasing rate compared to F12_A and F12_B curves, indicating the less significant of the degradation products build-up at the surface of PU coating with lower NCO/OH.

In Figure 9.11 (b), LIV and SA histogram sets show comparable order with the unexposed histogram set, indicating the similar chemical changes occurred at the surface of PU coatings exposed at LIV and SA sites. LIV histogram set is close to Unexposed histogram set, which can be correlated to near 0 hours exposure time in QUV A test. The correlation can be found between SA histogram set and around 1400 hours exposure time in QUV A test. KL histogram set demonstrate different Index III order compared to LIV and SA histogram sets, indicating the different chemical changes at the surface of PU coating exposed at KL site. No correlation can be found between KL histogram set and QUV A exposure time.

Figure 9.11 Index IV plots of F1_A, F1_B, F12_A, F12_B and F12_C samples. Index IV is calculated by NPA F/(E+F), reflecting the ratio of the amide C=O group in acid, anhydride and perester to the sum of the amide I C=O groups. The curves are plotted along with the exposure time intervals at 1200 hours and 4098 hours in QUV A test (a). The histograms are plotted for 12 month natural exposure sites including LIV, SA and KL (b).
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9.3.7. SEM imaging

Figure 9.12 – Figure 9.15 demonstrate SEM images of 1200 hours QUV A test and 12 month KL site exposure for F12_A, F12_B, F12_C, F1_A and F1_B samples with $\times$ 10,000 and $\times$ 1,000 magnifications, respectively. In Figure 9.12, F1_A-1200 image shows relatively smooth topography compared to F1_A-KL image, reflecting the higher degradation rate of F1_A exposed in KL site compared to 1200 hours QUV A test. The same conclusion can be drawn by comparing F1_B-1200 and F1_B-KL images as shown in Figure 9.13. The higher harshness of KL site compared to 1200 hours QUV A test is in agreement with the result as listed in Table 9.2, where the correlation between KL site 4098 hours exposure in QUV A test is indicated.

Figure 9.12 SEM images of 1200 hours QUV A test and 12 month KL site exposure for
9. The impact of minor film formers, additives and NCO/OH to the degradation of PU coil coatings

F1_A and F1_B samples.

Figure 9.13 SEM images of F1_B-1200 and F1_B-KL samples.

Figure 9.14 shows SEM images of 1200 hour QUV A test for F12_A, F12_B and F12_C samples with × 10,000 and × 1,000 magnifications, respectively. All F12_A-1200, F12_B-1200 and F12_C-1200 images show crater features with the outer diameter of approximately 20 – 80 μm distributed over the surface. Similar craters can be found for all F12_A-KL, F12_B-KL and F12_C-KL images as show in Figure 9.15. The craters can be related to the addition of BI isocyanate in the PU coating formulations. F12_A-KL, F12_B-KL and F12_C-KL images show the deeper and larger craters compared to F12_A-1200, F12_B-1200 and F12_C-1200, which may represent further degraded topographic features in F12_A-KL, F12_B-KL and F12_C-KL. F12_A-KL
images show holes with the outer diameter of approximately 20 – 80 μm at the surface, which may be the implication of the further developed craters along with the degradation. The localised craters may act as weak points and response more quickly towards the degradation than the background (non-crater) area.
Figure 9.14 SEM images of 1200 hours QUV A test for F12_A, F12_B and F12_C samples.
9.4. Conclusions

The PU coatings containing melamine as a minor film former give higher content of amide II type linkages. The durability of PU coating can be improved by the addition of...
The melamine linkage is more sensitive to the degradation compared to the urethane linkage. The durability of PU coating can be significantly improved by the addition of HALS. The addition of HALS in the PU coating formulations gives unique chemical changes particularly at early exposure time in QUV A test. HALS does not change the chemical changes of PU the coatings during prolonged exposure time in QUV A test. The addition of BI isocyanate in the PU formulation can result in more significant build-up of degradation products during early exposure time and reduced amide II type linkage decomposition during prolonged exposure time in QUV A test. The higher NCO/OH of the PU coating gives more significant degradation products build-up within the early exposure time in QUV A test. The lower NCO/OH of the PU coating gives more significant degradation products build-up within the prolonged exposure time in QUV A test. Higher NCO/OH in the PU coating can lead to the reduced amide II type linkage decomposition particularly during prolonged exposure time.

KL site gives more significant degradation and unique degradation chemistry of the PU coatings compared to both SA and LIV sites. This is in agreement with the discussion made in Chapter 8. The degradation rate correlation of the PU coatings exposed in QUV A test and natural exposure sites are demonstrated by using degradation index plots method.

The degradation rate correlation made by degradation index plots method for the PU coatings exposed in QUV A test and natural exposure sites including LIV, SA and KL are summarised in Table 9.2.
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Table 9.2 The degradation rate correlation made by degradation index plots method for the PU coatings with varied additives and NCO/OH ratio exposed in QUV A test and natural exposure sites including LIV, SA and KL.

<table>
<thead>
<tr>
<th>QUV A exposure time (hours)</th>
<th>Degradation index plot</th>
</tr>
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<tr>
<td></td>
<td>hydroxyl index</td>
</tr>
<tr>
<td>LIV</td>
<td>n.c.c.</td>
</tr>
<tr>
<td>SA</td>
<td>n.c.c.</td>
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<tr>
<td>KL</td>
<td>n.c.c.</td>
</tr>
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</table>

n.c.c.— no consistent correlation

SEM imaging results confirm the higher harshness of KL site compared to 1200 hours QUV A test. The craters of approximately 20 – 80 μm in diameter shown on the SEM imaging results confirms the adverse effect of the addition of BI isocyanate to the durability of PU coatings. The holes formed imply the further developed craters along with the degradation at the surface of KL exposed PU coatings.
10. Conclusions

The degradation of the new generation of polyurethane (PU) coil coatings has been comprehensively studied in this project. The advanced spectroscopic methods, such as step scan phase modulation photo-acoustic (SS-PM-PA) FTIR, peak fitting and confocal Raman mapping (CRM), as well as scanning electron microscopy (SEM), have been successfully developed to study the degradation chemistry and evaluate the degradation rate of a system of PU coatings with varied formulations. The degradation related PU chemistry, especially the reaction of the polyester with the isocyanate cross-linkers, the melamine additive as a secondary film former, and the ratio of the isocyanate to hydroxyl group has been extensively studied. Based on a solid knowledge of PU degradation chemistry and a novel quantitative analysis method, FTIR peak fitting has been developed to establish the degradation index plots. The strong and clear correlation between the accelerated and the natural weathering has been found by analysing the degradation index plots. The newly developed techniques in this study have been proved to be promising in the coating industry for the new product validation and the efficient lift time prediction, owing to the significantly improved accuracy and shortened time period than the traditional appearance based methods. The major findings can be summarised as follows.

Firstly, the applicability of SS-PM-PA FTIR technique on the depth profiling study of a TiO$_2$ pigment for PU coil coatings has been verified by examining the depth distribution of the TiO$_2$ pigment (KRONOS® 2310) within a PU coil coating. It was found the SS-PM-PA FTIR signal intensity to be significantly contributed by the TiO$_2$ pigment as well as the PU binder for the TiO$_2$ pigmented PU coil coatings. The depth profile of the TiO$_2$ pigment in the topcoat varies along with the increase of the TiO$_2$ pigment content, as observed by the SS-PM-PA FTIR technique. Furthermore, a TiO$_2$ aggregated region within the topcoat is found close to the topcoat-primer interface and further away from the topcoat surface. This TiO$_2$ aggregated region in lower TiO$_2$ pigment content topcoats is deeper within the coating compared to higher TiO$_2$ pigment content topcoats, as
revealed by SS-PM-PA FTIR. SEM cross-section imaging results show a strong correlation with the TiO$_2$ depth profile postulated using the SS-PM-PA FTIR method, which confirms the applicability of the SS-PM-PA FTIR technique to the depth profiling study of TiO$_2$ pigmented coil coatings. The actual sampling depth of the SS-PM-PA FTIR technique is found significantly influenced by the PVC value of TiO$_2$ pigmented PU coatings, revealing the deficiency of taking the constant thermal diffusivity values for the sampling depth calculation.

Secondly, the CRM chemometric method has been developed and verified to study the distribution of the cyclic trimer (CT) molecular structure in the clear PU coil coatings cross-linked with the hexamethylene diisocyanate (HDI). It was found that the HDI-CT cross-linked PU clear-coats consistently give relatively even CT core distribution at the surface. Additionally, CRM imaging results show strong correlation with the original coating formulations with regards to the content of the CT core at the surface of PU clear coatings. The consistent and well correlated CRM imaging results verify the applicability of CRM chemometric method on the evaluation of the CT core content and distribution at the surface of clear PU coil coatings.

Thirdly, the impact of the isocyanate structures on the degradation of PU coil coatings has been extensively discussed. The conclusion can be drawn that the isophorone diisocyanate (IPDI) cross-linked PU coating gives lower cross-linking rate and higher stability compared to the HDI, which can be attributed to the steric hindrance effect given by the molecular structure of IPDI. The bulky structure of IPDI moiety may obstruct the nucleophilic reaction between –N=C=O and –OH, as well as prevent the free radical attack towards the liable hydrogen adjacent to IPDI, and consequently deter the overall degradation process. CT core structure brings higher stability of PU coating compared to BI core. The degradation of IPDI-CT cross-linked PU coating includes the top-film enrichment with primary amide and urea entities, to a greater extent than is indicated at the surface of HDI-CT cross-linked PU coatings. This top-film degrades in preference to the cross-linked PU film beneath with chemical changes monitored by IR
bands at 1640 cm\(^{-1}\) and 1560 cm\(^{-1}\), which are attributed to the formation of primary amides, urethanes resulted from the homolytic chain scission of BIs and allophanates.

Fourthly, the impact of isocyanate blocking agents, including \(\varepsilon\)-caprolactam (Capro), methyl ethyl ketoxime (MEKO) and 3,5 dimethyl pyrazole (DMP) on the degradation of PU coil coatings has been studied. It was found that the cross-link density of unexposed PU coatings gives the order Capro-PU < MEKO-PU < DMP-PU. At the surface of unexposed samples, (i) the content of free C=O groups and urethane linkages is in the order Capro-PU > MEKO-PU > DMP-PU, and (ii) the content of CT core and urea entity is in an order of Capro-PU < MEKO-PU < DMP-PU. The order of CT core content can be confirmed by the CRM technique. Varied blocking agents of isocyanate cross-linkers are likely to cause the content variation of different amide linkages at the surface of unexposed PU coatings. The unexposed PU coating with high content of free C=O group and urethane linkage and low content of CT core and urea entity are likely to lead to the higher degradation rate of the PU coating subsequently. The degradation rate of Capro-PU > MEKO-PU > DMP-PU is deduced by using SS-PM-PA FTIR technique. More urethane and/or urea linkages formed at the surface of Capro-PU compared to MEKO-PU and DMP-PU as a result of degradation. SEM technique confirms the high durability of DMP-PU compared to MEKO-PU and Capro-PU.

Fifthly, the degradation rate of the PU coatings exposed in accelerated (QUV A) and natural weathering conditions has been correlated by comparing the degradation index plots. The FTIR peak fitting method developed in this study gives high duplicability results, which is of necessity for accurate degradation rate evaluation. The degradation rate correlation of the PU coatings exposed in QUV A test and natural exposure sites including Liverpool, UK (LIV), Vereeniging, South Africa (SA) and Kuala Lumpur, Malaysia (KL) is demonstrated. The degradation rate of natural exposed samples can be correlated to 0 hour – 1800 hours exposure time in QUV A test according to hydroxyl index plots. Index I plots demonstrate consistency with hydroxyl index plots in early exposure time and diversity in prolonged exposure time. In most cases, the degradation
plots made by Index II, III and IV approach a relatively consistent value gradually, indicating the degradation rate reaches a plateau at prolonged exposure time.

Finally, the impact of the melamine film formers, the additives and the NCO/OH to the degradation of PU coil coatings has been investigated. The PU coatings containing melamine as a secondary film former give higher content of amide II type linkages. The durability of PU coating can be improved by the addition of melamine. The melamine linkage is more sensitive to the degradation compared to the urethane linkage. The durability of PU coating can be significantly improved by the addition of HALS. The addition of HALS in the PU coating formulations gives unique chemical changes particularly at early exposure time in QUV A test. HALS does not change the chemical changes of PU the coatings during prolonged exposure time in QUV A test. The addition of BI isocyanate in the PU formulation can result in more significant build-up of degradation products during early exposure time and reduced amide II type linkage decomposition during prolonged exposure time in QUV A test. The higher NCO/OH of the PU coating gives more significant degradation products build-up within the early exposure time in QUV A test. The lower NCO/OH of the PU coating gives more significant degradation products build-up within the prolonged exposure time in QUV A test. Higher NCO/OH in the PU coating can lead to the reduced amide II type linkage decomposition particularly during prolonged exposure time.

KL site gives more significant degradation and unique degradation chemistry of the PU coatings compared to both SA and LIV sites, in agreement with the discussion made in the previous study when the isocyanate cross-linkers are varied. The degradation rate correlation of the PU coatings exposed in QUV A test and natural exposure sites are demonstrated by using degradation index plots method.

SEM imaging results confirm the higher harshness of KL site compared to 1200 hours QUV A test. The craters of approximately 20 – 80 μm in diameter shown on the SEM imaging results confirms the adverse effect of the addition of BI isocyanate to the
durability of PU coatings. The holes formed imply the further developed craters along with the degradation at the surface of KL exposed PU coatings.
11. The future work

This study successfully demonstrated the application of the spectroscopy techniques on the degradation of polyurethane based coil coating products, especially during the early stage degradation when the physical or appearance of the coating surface have not been detectable with traditional methods such as visible defects, colour change and gloss loss. The degradation evaluation system developed in this study opens expensive routes for future applications on other coil coating products, such as polyester-melamine, acrylic, epoxy, and bio-based organic coatings. Apart from coatings, the methods developed are with considerable application prospects on moulded and laminated polymer products in a wild of industries such as construction, transport, aircraft, medical device, textile, electronics, agriculture and civic engineering. The shortened time needed for the ageing tests and the significantly improved accuracy for the analysis can bring the considerable benefit for the characterisation and validation of the polymer products when limited time and lowered risk are of more importance in a rapidly and dynamically changing business environment.

The step scan (SS) photo-acoustic (PA) FTIR spectroscopy is of major advantages on the non-destructive sampling and controlled probing depth. These advantages and years of experiences provides opportunities for the upgrade of the research and development (R&D) laboratory in coating industry owning to the value added function by performing the depth profiling study, compared to the commonly used continuous FTIR based on transmittance and attenuate total reflection (ATR) techniques. Further work is on-going to bring the step scan photo-acoustic function to the commercially running FTIR instrument in the R&D lab in Becker Industrial Coatings, Ltd (Liverpool, UK). The potential applications include developing the stratifying coatings with the expectation that the pigmented layer and the top clear layer can be applied in the meantime. Another application is to monitor the depth profile and migration of the minor compounds with the considerations of reducing the health and safety issues.
The confocal Raman mapping (CRM) technique has the similar advantage of the FTIR regarding the don-destructive sampling method when applied to the samples with relatively low thermal conductivity. The probing depth control function of the CRM technique is debatable due to the significant light scattering effect given by the optical system. However, the near surface analysis of the CRM technique is promising for studying the lateral distribution of the individual components of interest. Future work will apply the CRM technique to study the pigment chalking effect of a series of pigmented coatings with varied film formers. The CRM results are expected to be quantified by using the digital imaging analysis function of the OMNIC Atlμs software.

The surface migration of the minor components or additives of the coating, such as isocyanate, melamine, UV stabiliser will be studied by using the CRM technique.

With the benefit of the controlled sampling depth, the SS-PA FTIR can reveal the degradation related polymer chemistry occurred at the surface of the polymer coatings to a comprehensive level. Furthermore, the high sensitivity of the technique towards the chemical changes during the very early stage of the exposure tests provides valuable methods for validating a variety of coating systems with modified formulations. Further work will apply the technique to study the polymer coating laminates used in the construction industry. The efficiency and accuracy of the product validation and characterisation are expected to be significantly improved.

The peak fitting method developed demonstrates considerable advantage regarding the accuracy improvement on the FTIR quantitative analysis for the polymer degradation study. The accelerated and natural weathering tests can be correlated by comparing the degradation index curves established using peak fitting data. With this method, the acceleration test methods can be further designed or modified with the parameters, such as radiation, temperature, PH and humidity, controlled to imitate the real natural weathering condition more closely. Furthermore, the mathematical models such as Arrhenius theory will be applied to quantify the individual parameters of the ageing tests. The on-going work involves the new design of an ageing oven with additional
weathering parameters than QUV A, such as ventilation and air force controls to imitate the real weathering conditions with stronger wind force.

In addition to the near surface degradation study of the topcoat of the polymer coatings, the interfacial failures, such as adhesion loss (between topcoat and primer), corrosion related defects (between metal substrate and coating) are interesting research avenues in the future work.
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