

The durability of clear polyurethane coil coatings studied by FTIR peak fitting

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ARTICLE INFO

Article history:

Received 6 August 2012

Received in revised form

18 November 2012

Accepted 4 December 2012

Available online 12 December 2012

Keywords:

Coil coating

Polyurethane

Isocyanate

Photo-acoustic

FTIR peak fitting

Durability

ABSTRACT

A step scan phase modulation photo-acoustic (SS-PM-PA) Fourier transform infrared (FTIR) peak fitting method has been developed and applied to study (i) the degradation of the polyurethane (PU) coatings crosslinked with different isocyanates, (ii) the harshness of the natural exposure sites, and (iii) the correlation between the accelerated and natural exposure sites in terms of the degradation. Methyl ethyl ketoxime (MEKO) blocked hexamethylene diisocyanate biuret (HDI-BI), MEKO blocked hexamethylene diisocyanate cyclic trimer (HDI-CT) and 3,5-dimethyl pyrazole (DMP) blocked isophorone diisocyanate cyclic trimer (IPDI-CT) were used as-received to crosslink a cycloaliphatic saturated polyester resin binder. It was found that HDI-CT crosslinked PU coating is more durable compared to the HDI-BI. IPDI-CT crosslinked PU coating gives higher durability than the HDI-CT and the HDI-BI. The areas of deconvoluted peaks with Centre X (cm^{-1}) = 1573, 1553 and 1535 (amide II, NH–CO) and Centre X (cm^{-1}) = 1832, 1813, 1792 and 1770 (acid, anhydride, peracid) are used for degradation index calculation, due to their consistent decreasing and increasing trends, respectively, along with the degradation. It has been found that the natural weathering site in Kuala Lumpur, Malaysia (KL) is harsher than that at Vereeniging, South Africa (SA). The harshness of one year SA and KL natural weathering is comparable to 300 h–900 h of the QUV A exposure test. FTIR peak fitting method outperformed the integration method by giving a better correlation between the accelerated and natural weathering tests in terms of the degradation.

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1. Introduction

1.1. Durability prediction of polymer coatings

The prediction of the long-term durability of the polymer coatings has been a high priority research and development avenue for both material academics and manufacturing industries to fulfil the demand of continually innovating and marketing advanced materials [1–4]. A reliable life-time prediction requires extensive information regarding the degradation behaviour of the products collected over a prolonged period of time [5]. To evaluate the durability, the polymer products are usually sent to a certain

location for natural exposure before validation. Years of exposure are required to monitor the degradation with indicators such as colour change, gloss retention, physical failure, chemical change and so on [6]. The local natural exposure period is normally planned based on the expected warranty to the product and likely to be limited by the availabilities including the space, labour, equipment, knowledge and budget. Accelerated weathering techniques such as weather-o-meters were designed to overcome the disadvantages of the time consuming natural weathering tests [7,8]. A number of accelerated weathering techniques have been used over the decades together with continuously upgraded industrial, national and international standards to evaluate the durability of the polymer materials [9]. The ideal accelerated weathering tests are expected to be comparable to the natural weathering conditions in terms of the degradation, however with significantly shortened exposure time when the validation efficiency of the products is of importance. Risks are inevitable when one predicts long-term outdoor durability based on accelerated weathering tests. In many cases, the correlation between the two tests could be arbitrary and sometimes contradictory, mainly because of the low accuracy when one attempts to imitate the dynamically changing

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climate conditions [2,10,11]. Extensive efforts have been made over the decades to mathematically model climate data to precisely control the parameters in the accelerated weathering tests [12,13]. However, these models could be complicated and many are still in the research phase, therefore with limited applications in the polymer coating industry [14].

In this work, a FTIR peak fitting method is developed and applied to quantitatively evaluate (i) the degradation of polyurethane (PU) coatings crosslinked with different isocyanates, (ii) the harshness of the natural exposure sites, and (iii) the correlation between the accelerated and natural exposure sites in terms of degradation. This work is expected to contribute to reliable life-time prediction methods and improve the efficiency of the characterisation and validation process for new coil coating products.

1.2. Polyurethane (PU) clear coil coatings

PU clear coil coatings can be chemically complex materials due to the versatility of isocyanate crosslinkers and the polyester resins and additives used in the formulations, and consequently their durability varies significantly [15]. Thus, it is important for the formulators to develop a better understanding of the chemical changes for specific PU systems submitted to various environmental stresses.

PU systems have attracted much interest in terms of their degradation and oxidation. In previous studies, it was found that irradiation with longer wavelength of UV light (>300 nm) provoked UV-induced oxidation on the methylene group in the α position to the N–H groups (α -CH₂) [16,17]. The oxidative reaction that follows was thought to lead to the formation of secondary peroxides and hydroperoxides, which would evolve further by reacting with water to form carboxylic acids [18]. The main photoproducts may include peracid, primary urethane, acetylurethane, and primary amine [19]. The degradation mechanism of the urethane linkage can be schematically summarised as shown in Fig. 1. It was also demonstrated that PU films are composed of urethane-rich and urea-rich surface domains with a dimension scale of around 50 μ m. When exposed to UV radiation at 340 nm and water vapour condensation, urea entities are converted to urethane entities over a prolonged period [20].

1.3. The polyester binder

Polyesters are polymers with more than one ester linkage per molecule prepared by esterification reactions. The polyester resin can account for between 70–90 wt% of the total clear coating. 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 [21].

Many years of development have shown certain types of polyester resins to demonstrate better outdoor long-term performance, including hydroxylated polyesters, acrylic or acrylic-polyesters. Recent development in the durability performance has led to the validation of so called ‘super durable’ polyester, which has been achieved by the use of cycloaliphatic monomers within the polyester. Naturally such an approach favours the use of cycloaliphatic polyisocyanates as cross-linking agents to maximise durability rather than the triazine based, melamine chemistry [22].

1.4. The isocyanate crosslinkers

The molecular structures of the isocyanate crosslinkers are vital towards the degradation of the polyurethane thermosets [23,24]. Many types of isocyanate crosslinkers with varied molecular structures are synthesised to give different film formability and durability of the polyurethane coil coating products, including the commonly used structures listed:

- Core structures – cyclic trimer (CT), biuret (BI)
- Branch structures – hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI)
- Blocking groups – methyl ethyl ketoxime (MEKO), 3,5 dimethyl pyrazole (DMP)

The introductions to the characteristics of the individual structures can be found in Refs. [25,26] and are omitted here.

1.5. Fourier transform infrared (FTIR) spectroscopy

The advanced spectroscopy techniques such as step scan phase modulation photo-acoustic (SS-PM-PA) Fourier transform infrared (FTIR) have been widely acknowledged to be suitable and are increasingly gaining industrial applications to qualify and quantify the degradation of the polymer products, especially during the very early exposure stage [27–29]. The high sensitivity towards the chemical changes and controlled probing depth of the technique are vital functionalities to capture the initial degradation characteristics at the polymer surface [30–32]. The degradation related chemical changes can be used as indicators for predicting the long-term performance of the material [33,34]. A system of information is obtained comprising of the degradation characteristics of a series of the polyurethane based coil coating samples exposed in a variety of exposure conditions. These informations can be organised and analysed logically to rank the harshness of the exposure conditions and predict the relative durability of the coating samples in certain natural weathering sites. The expected exposure time scales for the accelerated and natural exposure tests are less than 6 month and 1 year, respectively.

The degradation of polymer coatings is recognized as initially occurring near the PU film/air interface. This can be attributed to the enhanced interaction between polymer film and environment factors including, oxygen, water, and pollutants at the surface rather than at depth in the bulk if the coating [35,36]. Step scan phase modulation photo-acoustic (SS-PM-PA FTIR) has been demonstrated to be a suitable technique for study of the degradation chemistry of coil coatings for near-surface analysis with the advantages including non-destructive sampling and controlled probing depth [20,29,31,32].

1.6. Quantitative analysis by FTIR spectroscopy

FTIR spectroscopy has been well-acknowledged as a powerful tool to study polymer degradation quantitatively [10,37].

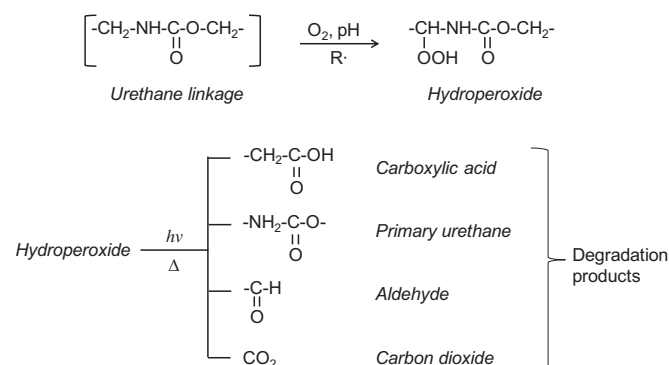


Fig. 1. The brief degradation mechanism of the urethane linkage [16–20].

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