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Photooxidation of polymers: Relating material properties to chemical changes

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ABSTRACT

This paper is devoted to a comprehensive study of the photo-oxidation of polymeric materials with the goal of correlating modifications of the polymer properties at the molecular and macroscopic levels. Several techniques were used to characterise the modifications of the chemical properties and mechanical behaviour over time under UV light. The methodology was developed on materials used as organic coatings; initially, a well-characterised phenoxy resin (PKHJ®) was chosen as a model and then the approach was applied to an acrylate-melamine thermoset currently used as a topcoat in the automotive industry. Analysis of degraded samples by IR spectroscopy allowed us to propose a photo-oxidation mechanism. This mechanism suggested that chain scission occurred under photo-oxidation. To entirely understand the degradation of the polymers, gel fraction, thermoporosimetry, DMA, AFM nanoindentation and micro-hardness determinations were performed. The results showed that crosslinking reactions occurred in competition with chain scission and explained for the first time why crosslinking reactions were quite prevalent. Based on the obtained results, quantitative correlations were made between the various criteria of degradation, thus relating the chemical structure changes to the mechanical property modifications.

1. Introduction

Organic polymeric coatings are widely used in engineering applications [1–3] and include several types of materials, including polyesters, polyurethanes, epoxies and acrylic-melamine composites, among others. Depending on the application, these materials are subjected to several environmental ageing factors, including UV light, temperature variations and oxygen. One of the most important properties that organic coatings must have is weathering resistance. The property changes due to ageing have to be monitored and quantified to determine the weatherability of materials. Keeping track of the material properties [4,5] (gloss, cracking, colourimetry, etc.) is too empirical and does not take into account the polymeric system. In this context, a more rational approach is based on recognition of the events at the molecular level that lead to changes in the morphology and macroscopic physical properties. Previous works have focused on investigations of the chemical mechanisms by infrared (IR) spectroscopy [6–8], which is a useful tool in characterising the degradation of the chemical structure and understanding the pathways of degradation.

In this work, we focus on degradation under UV light, O_2 and temperature variation without water to determine the impact of photo-oxidation on coating behaviour on both the microscopic and macroscopic levels. To achieve this goal, two different polymers were chosen. The objective was to develop an approach for the case of a two-dimensional polymer and apply the method to a three-dimensional thermoset. At first, the approach was developed for a well-defined and characterised polymer, a two-dimensional phenoxy resin (PR), denoted as PKHJ®, which is usually treated as part of epoxy resins. Epoxy networks used as organic paints are usually based on an epoxy resin and a curing agent. Epoxy cured resins are used as electro-coats or as organic paints for anticorrosion applications [9,10] when deposited on a metal structure. The second material was a three-dimensional acrylic-melamine thermoset, which results from the crosslinking of an acrylic resin with a melamine hardener. Acrylic resins with lateral hydroxyl groups crosslinked with melamine derivatives have many applications [11,12] due to their interesting properties. In particular, they are useful as topcoats in the automotive industry because of their key role in the multi-layer system [13] currently used on many automobiles.

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For both PKHJ® resin and acrylic-melamine thermoset, it has been demonstrated that there is a global oxidation of the material through a chain scission mechanism. Oxidative degradation of phenoxy resins (PR) exposed to UV light mainly involves the aromatic ether functions, and in the case of acrylic-melamine-based clearcoats, several authors [14–17] have noticed a disappearance of the ether linkages, which was described as a loss of crosslinks (chain scissions). In the case of acrylic-melamine thermoset, recent papers devoted to ageing studies by mechanical analysis, such as Dynamic Mechanical Analysis (DMA) [18,19] and micro-hardness measurements [20], have shown that the acrylic-melamine clearcoat hardness significantly increases under UV light irradiation because of an important densification of the network [21].

However, there are still several questions that remain unanswered. The main problem is that IR spectroscopy indicates only that chain scissions occur under photo-oxidation. These chain scissions are not consistent with the global densification of the network observed by mechanical analysis. As a consequence, understanding the competition between chain scissions and crosslinking and the formation of new crosslinks under light exposure needs some more data based on new experimental approaches.

The first part of this paper is dedicated to understanding the ageing phenomena of the PR, considering the changes of the chemical structure and physical properties. The second part attempts to provide a quantitative analysis of the main degradation parameter changes during photo-ageing by using the *Fakirov* law and comparing the degradation rates calculated from a first order kinetic law. The third and fourth parts transpose the methodology developed for the well-defined PR to the study of an acrylic-melamine network.

2. Experimental

2.1. Materials

Phenoxy resin (PR) is produced through the condensation of bisphenol-A [2,2-bis(4’-hydroxyphenyl)propane] and epichlorohydrin (1-chloro-2-3-epoxy propane). In PR, the chain ends are mainly phenolic and the content of epoxy end-groups is fairly low. The studied resin was a phenoxy resin denoted PKHJ® (Fig. 1) and was provided by InChemRez Chemicals Corp. The molecular weights M_w and M_n were, respectively, 57,000 and 16,000. Investigations were conducted on self-standing films (~40 μm) or on deposits on steel panels with a thickness of around 40–50 μm. These substrates were obtained by compression moulding at 200 bars for 10 min at 225 °C.

Acrylic thermoset is a solvent-based acrylic-melamine, which is a mixture of an acrylate-polyol copolymer and butyl-oxylated melamine crosslinker. An acrylic polymer solution which is a solution of acrylic resin in butyl diglycol, with solid content of 68% (w/w) was provide by PSA. The “acrylic” polymer system had a hydroxyl value of 66 and an acid value of 10.1–13.8 mg KOH. The selected melamine system was a non-plasticized, partly butylated, “melamine” resin precursor that was also provided PSA. The melamine resin precursor, with a solids content of 70% in isobutanol, had the acid value of 0.7 mg KOH/g. To prepare the acrylic matrix, the acrylic polymer solution was mixed with a melamine-based derivative crosslinker (provided by PSA) in ratio of 3:1 by weight. Upon heating for 20 min at 140 °C, a trans-etherification occurred, which led to the formation of a three-dimensional polymer network. This approach was used to replicate the procedures recommended by the manufacturer of the components. Bulk analyses were done on the free films. They were obtained by curing the clearcoat on Tedlar® sheets. The cured samples were then removed from the Tedlar® sheets. For surface analyses, the clearcoat was cured on a steel panel with a thickness of around 40–50 μm.

1,4 dioxane, which was used as both the solvent and thermoporosimetry probe, was supplied by Aldrich and was of HPLC grade. This solvent was used without further purification.

2.2. Irradiation

Irradiation was performed under artificial ageing conditions. The ageing device was a SEPAP 12/24 unit [22] from Atlas equipped with four medium pressure mercury lamps (Novalamp RVC 400 W) located in a vertical position at each corner of the chamber. Wavelengths below 295 nm were filtered by the glass envelopes of the sources. Irradiance in the range 300–400 nm is 100 W/m^2. The temperature at the surface of the samples was fixed at 60 °C.

2.3. Analyses

Infrared (IR) spectra were recorded in transmission mode with a Nicolet 760-FTIR spectrophotometer (nominal resolution of 4 cm^{-1}, 32 scan summations) on films with thicknesses of around 30–40 μm.

Vickers micro-hardness (Hv) measurements were performed on a Shimadzu hardness tester. Hv can be expressed by equation (1).

$$\mathrm{Hv} = 1.8544 \times 10^6 \frac{P}{d^2} \qquad (1)$$

where P is the load applied in N and d is the diagonal of the indentation in mm. Hv is expressed in MPa. In the present study, P was fixed at 0.343 N, and the application time was 10 s.

The glass transition temperature of the clearcoat was measured with a Mettler Toledo DSC 822 programmed from 10 to 140 °C at a heating rate of 15 °C/min.

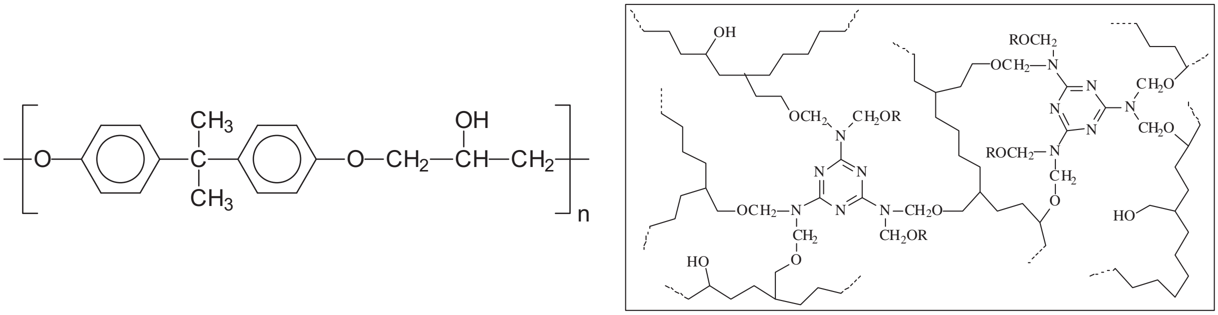

Fig.1. Left: Chemical structure of PKHJ®. Right: Idealised structure of the crosslinked acrylic-melamine network.