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Influence of water on the photooxidation of KHJ® phenoxy resins, 1. Mechanisms

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ABSTRACT

This study is devoted to the influence of water on the mechanisms of photooxidation of anticorrosion coatings based on epoxy resins used in extremely aggressive media like the marine environment. The two principal environmental parameters to be considered are sunlight (UV-light) and water. It is important to understand the role of these two environmental parameters on the ageing of epoxy anticorrosion coatings. On the basis of the effect of photooxidation on the molecular structure under “dry” conditions, water was introduced into the ageing process with either alternating cycles of irradiation/immersion in water or simultaneously by irradiation of the polymer in water. The presence of water had two effects on the photodegradation of PKHJ® phenoxy resin; the first one was on the degradation of the main photoproduct (phenyl formates) formed during irradiation through a hydrolysis reaction leading to the release of formic acid. The second effect consisted of an increase in the photooxidation rate by the formation of photo-initiators.

1. Introduction

The preservation of metal structures against environmental degradation in marine environments has lead to a constant search for new protection methods against corrosion. One of the solutions consists of the use of anticorrosion organic paints [1]. These paints are mainly composed of epoxy resin, polyurethane or polyester; however, new environmentally friendly formulations have been developed [2,3]. During their lifetimes, these coatings are exposed to aggressive environments and must retain their functional properties at an acceptable level to ensure protection against corrosion [4–7]. Therefore, it is of prime importance to characterise their fate and to evaluate their long-term behaviour under these environmental conditions.

Industrial marine paints are complex formulations composed of a mixture that also includes several fillers and pigments in addition to the resin and curing agent. It is necessary to simplify these systems to understand the degradation mechanism of the resin. Polymers with similar units can be chosen as model systems, either a linear resin (a phenoxy one like PKHJ® (Scheme 1)) or a cross-linked system (for example a DGEBA/TETA). Phenoxy resins are usually treated as part of the epoxy polymers family. Because the repeat units are identical, and in spite of its two-dimensional structure, PKHJ® is a good model for simulating the photochemical behaviour of the three-dimensional network of cured epoxy coatings.

The influence of either UV-light or water on the degradation of epoxy or phenoxy resins such as PKHJ® has already been reported. The photooxidation of aromatic amine-cured DGEBA (di-glycidyl ether of bisphenol-A) epoxy systems [8,9] under dry conditions have already been studied and the results showed that the hardener structure had very little or no direct influence on carbonyl product formation. The phenoxy part of the polymer was found to be likely responsible for carbonyl formation, whereas formation of the amide functions depends on the initial amine concentration and electron density on the nitrogen atom.

Previous studies carried out in our research group [10–13] have shown that the photooxidation mechanism of phenoxy resins exposed to UV-light irradiation ($\lambda > 300$ nm) mainly involve the aromatic ether functions. It has been shown that photooxidation results in oxidation of the methylene groups located in the α-position of the ether bond. This leads to the formation of phenyl formate end-groups (band IR at 1739 cm^{-1}), which constitute the main photoproduct obtained by β-scission of the alkoxy radicals. Parallel to this main pathway, the formation of other molecular products in smaller concentrations was also identified, such as various carboxylic acids (formic, acetic, oxalic and benzoic acid).

More recently, a study of the photochemical evolution of a flexible amine-cured epoxy system [14] showed that photooxidation mainly involved the phenoxy part of the resin (DGEBA)

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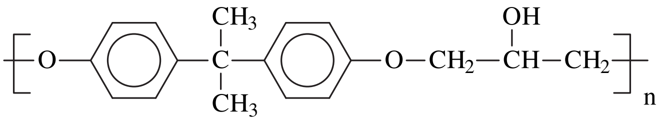


Scheme 1. Chemical structure of PKHJ®.

forming carbonyl functions, whereas the amine crosslinked bonds were oxidised to form amides. The rates of formation of the photoproducts and their spatial distribution in the depth of the sample were also studied [15] by IR microspectrometry and AFM nanoindentation.

Several studies of the photooxidation of anhydride-epoxy systems [16–20] have indicated that the chemical nature of the curing agent (amine or anhydride) has an influence on the photoageing of epoxy-based crosslinked materials [21] and shows a higher stability in the anhydride-cured epoxy. Concerning the effect of water on the ageing of epoxy polymers, it has been shown that water can have a double effect, either a physical effect [22] linked with the hydrophilic character of the polymer that involves the diffusion of water molecules inside the material and leads to plasticisation [23,24] and/or swelling of the material [25] or hydrolysis [26] that can provoke chain scissions. This last reaction leads to a decrease of the molecular weight and a loss of the mechanical properties.

The aim of this work was to study the influence of water on the photodegradation of epoxy anticorrosion coatings that are currently used as marine paints. To evaluate the long-term behaviour of these materials under their use conditions, three kinds of accelerated artificial weathering were carried out to determine the effects of light and water (alternating or simultaneously): UV-light irradiation under dry conditions, alternating irradiation/immersion cycles in water and irradiation in water. This paper focuses on the effect of water on the photodegradation mechanism of the phenoxy resin PKHJ®. The effect of these conditions on the physical properties of the materials will be reported in a forthcoming paper.

2. Materials and methods

2.1. Materials

The phenoxy resin is product of the condensation of bisphenol-A [2,2-bis(4′-hydroxyphenyl)propane] with epichlorohydrin (1-chloro-2-3-epoxy propane) , chain ends are mainly phenolic, the content of epoxy end-groups being fairly low. The phenoxy resin studied was denoted PKHJ® (Scheme 1) and was provided by InChemRez Chemicals Corp.

The investigations on the photodegradation mechanism of PKHJ® were carried out on two different types of samples, either self-standing thin films (35–40 μm) or thicker deposits (200 μm) on metallic substrates (low-carbon steel Q-Panel substrates (SAE1008/1010, R type)). The thin films were made by compression moulding at 200 bar for 3 min at 200 °C, and the thick ones were deposited on metallic substrates by dip-coating from a solution of PKHJ® in THF (0.2 g/mL).

2.2. Irradiation

Three different conditions of ageing were carried out:

- *Irradiation under dry conditions* (without water) was carried out in a Sepap 12-24 unit. This apparatus was designed for the study of polymer photodegradation under artificial ageing conditions [27] and samples were irradiated at $\lambda > 300$ nm in the presence of oxygen at a temperature of 60 °C and relative humidity of less than 2%. The Sepap 12-24 unit was equipped with four medium-pressure mercury lamps (400 W). A borosilicate envelope filtered wavelengths below 300 nm [27].
- *Alternating irradiation/immersion cycles in water* where the samples were submitted to successive cycles of ageing, with each cycle consisting of two successive periods of irradiation and immersion, as shown in Scheme 2.

The first period of a cycle ($h\upsilon$) corresponded to irradiation in the Sepap 12-24 unit (60 °C and $\lambda > 300$ nm), and the second one (H_2O) corresponded to immersion in a water bath. The bath was either deionised water or salted water (NaCl at 3.5 g/L), both at 20 °C and with slight stirring. The effect of various times of immersion was studied. The samples were analysed before and after each period to follow the chemical modifications resulting from the UV-light irradiation and water immersion. After 2 h of immersion, no change was detected and 2 h was chosen as the immersion time.

- *Photodegradation in water* was carried out in a Sepap 14-24H units. This device has been used in previous studies of the photodegradation of water-soluble polymers [28–30]. The chamber was an elliptical reactor equipped with one medium-pressure mercury lamp (400 W) in a vertical position at one focal axis of the chamber [28]. Wavelengths below 300 nm were filtered by a glass envelope. Polymer samples in aqueous solution were irradiated in a Pyrex reactor cooled by water circulation placed at the second focal axis of the chamber. The temperature of the solution was maintained at 27 °C to avoid water evaporation.

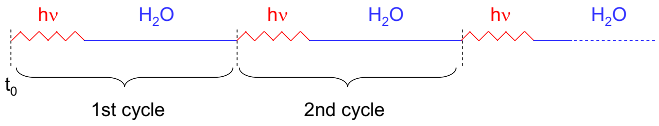
2.3. Characterisation

Infrared spectra in transmission mode were recorded with a NICOLET Magma IR 760 with OMNIC. Spectra were obtained using 32 scan summations at a 4 cm^{-1} resolution. Infrared spectra obtained with ATR were recorded on a NICOLET Magma IR 860 equipped with a diamond crystal and were obtained using 64 scan summations at a 4 cm^{-1} resolution. UV–Visible analysis was performed using a Shimadzu UV 2101 PC spectrometer equipped with an integrating sphere.

3. Results and discussion

3.1. Photodegradation in dry conditions

The IR spectra of PKHJ® irradiated in the form of thin films or thick layers on metallic substrates are shown in Fig. 1. One can observe in this figure that dramatic modifications of the spectra occurred in the carbonyl domain (1900–1500 cm^{-1}) and the hydroxyl domain (3800–3200 cm^{-1}). Previous studies carried out in our laboratory [10,11] showed that the modification in the carbonyl domain could be attributed to the formation of phenyl formate end-groups as the main oxidation product in



Scheme 2. Cycles of ageing with alternating periods of irradiation/immersion in water.