Polymer Degradation and Stability 96 (2011) 144–150

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

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

Yassine Malajati [a,b], Sandrine Therias [a,b,*], Jean-Luc Gardette [a,b]

[a] Clermont Université, Université Blaise Pascal, Laboratoire de Photochimie Moléculaire et Macromoléculaire, BP10448, F-63000 Clermont-Ferrand, France
[b] CNRS, UMR-CNRS 6505, LPMM F-63173, France

ARTICLE INFO

*Article history:*
Received 2 June 2010
Received in revised form
4 October 2010
Accepted 21 October 2010
Available online 3 November 2010

*Keywords:*
Photodegradation
Water
Epoxy coatings
Anticorrosion
Phenoxy resin

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.

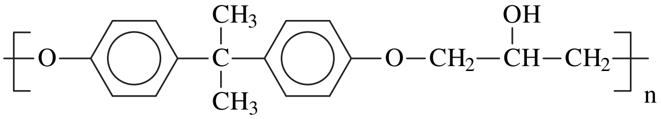
Previous studies carried out in our research group [10–13] have shown that the photooxidation mechanism of phenoxy resins exposed to UV-light irradiation ($\lambda > 300$ nm) mainly involve the aromatic ether functions. It has been shown that photooxidation results in oxidation of the methylene groups located in the $\alpha$-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)

---

* Corresponding author at: Clermont Université, Université Blaise Pascal, Laboratoire de Photochimie Moléculaire et Macromoléculaire, BP10448, F-63000 Clermont-Ferrand, France. Tel.: +33 (4) 73 40 71 43; fax: +33 (4) 73 40 77 00.
*E-mail address:* sandrine.therias@univ-bpclermont.fr (S. Therias).

0141-3910/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2010.10.007



**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 photo-ageing 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 ($h\nu$) 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.

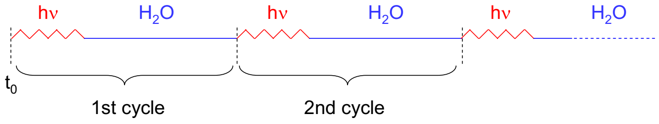
### 2.3. Characterisation

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.

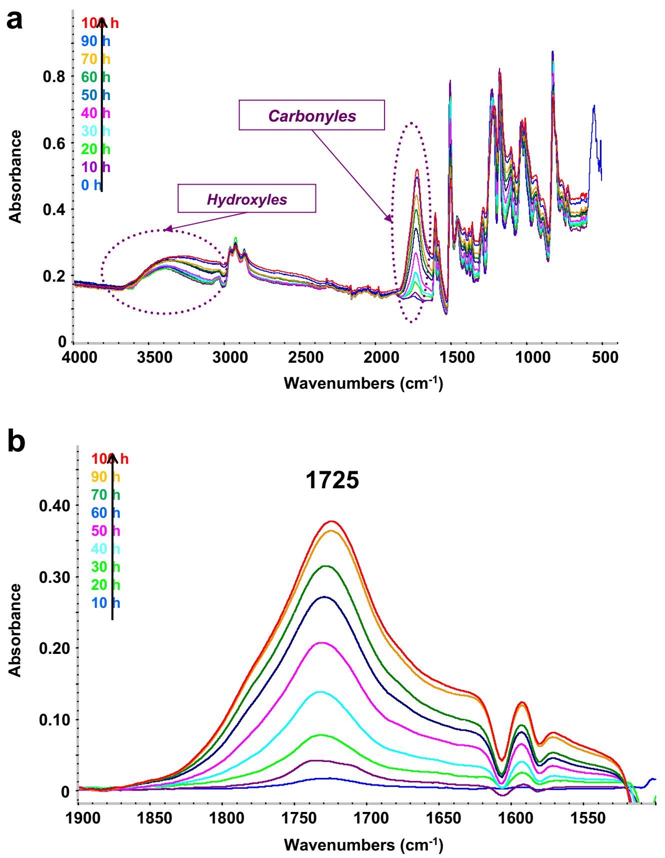


**Fig. 1.** IR spectra of thick PKHJ® layers on metallic substrates during photooxidation under dry conditions ($\lambda > 300$ nm, $T = 60$ °C): (a) direct spectra, (b) difference of spectra, $t - t_0$, in the carbonyl domain.

photooxidised films. These products were characterised by an IR band at 1739 cm$^{-1}$. The various photoproducts accounting for the modifications of the infrared spectra were identified, and a detailed mechanism of the PKHJ® photooxidation was proposed [10–12].

Fig. 1 shows the ATR spectra of PKHJ®. It is recalled that the thickness layer which is analysed by this technique is 2–3 μm from the surface. One can observe that in the early stage of oxidation the maximum of the carbonyl band is 1735 cm$^{-1}$. This maximum shifts to 1725 cm$^{-1}$ for longer irradiation time. In the case of analysis carried out in transmission mode on free films of PKHJ® with thickness around 100 μm, it was shown that the maximum was 1735 cm$^{-1}$. Analysis in transmission mode involves the whole thickness of the sample. The difference between transmission and surface analysis can be attributed to a loss of volatile low molecular weight oxidation photoproducts at 1735 cm$^{-1}$, which leads to a shift of the absorption maximum of 10 cm$^{-1}$. This effect is only observed when the analysis is focused on the surface layer.

### 3.2. *Influence of water on PKHJ® photoageing*

First, we determined that water had no effect on the IR and UV–Visible spectra of PKHJ®. Thin films (~36 μm) were immersed in deionised water at 27 °C in the dark for 27 days. No modification of the spectra was observed.

#### 3.2.1. *Exposure to conditions including alternating cycles of irradiation/immersion in deionised water and/or salted water*

*3.2.1.1. IR analysis.* The IR spectra of PKHJ® (thin film of 36 μm) during ageing, including alternating cycles of irradiation followed by immersion in water only, revealed a weak decrease of intensity in the absorption band at 1735 cm$^{-1}$. This behaviour corresponded to the disappearance of phenyl formate functions. Fig. 2 represents the evolution of the absorbance at 1735 cm$^{-1}$ as a function of time during the cycles of irradiation/immersion in water or salted water compared to the results obtained under dry conditions.

To facilitate interpreting the curves plotted in Fig. 2, we determined the absorbance difference ($\Delta A$) as a function of irradiation time. Thus, for the same $x$-coordinate, two points were plotted. The first one corresponded to the $\Delta A$ after irradiation in Sepap 12-24, and the second corresponded to $\Delta A$ after immersion.

Fig. 2 shows that after 40 h of irradiation, a decrease of absorbance at 1735 cm$^{-1}$ occurred after each immersion of the film in water or salted water. This decrease of absorbance became more and more important as irradiation proceeded. An irradiation carried out after an immersion provoked a new increase in the absorbance. If one compares the curve obtained after immersion in water with that obtained under dry conditions, the amount of phenyl formates formed under dry conditions seemed to be more important than those formed in the case of ageing plus immersion cycles. Diminution of the phenyl formate formed during the step of dry irradiation could result from hydrolysis reactions of this photoproduct and/or from the release of low molecular weight products by extraction from the polymer matrix. Considering the macromolecular nature of the formates, as proposed in the general scheme of the photooxidation of PKHJ®, one has to take into account that the extraction of these photoproducts necessarily implies that a chemical reaction (hydrolysis) occurs. This reaction would provoke end-chain scissions followed by extraction of the low molecular weight products obtained.

Moreover, it is important to note that the rate of formation of formates by irradiation carried out after immersion was always higher than their rate of formation under pure irradiation conditions, with no immersion. This behaviour reflects a photoinductive effect played by phenol which is described later in the discussion. This indicates that, if water leads to a decrease in concentration of the formates, immersion results in a higher rate of photooxidation of the PKHJ® phenoxy resin.

A similar behaviour was observed in the case of metallic substrates coated by thick PKHJ® layers and analysed by ATR-IR spectroscopy (Fig. 3). The influence of water was even more important than in the case of the thin films reported in Fig. 2. Because ATR analysis only comes into contact with the first microns at the surface

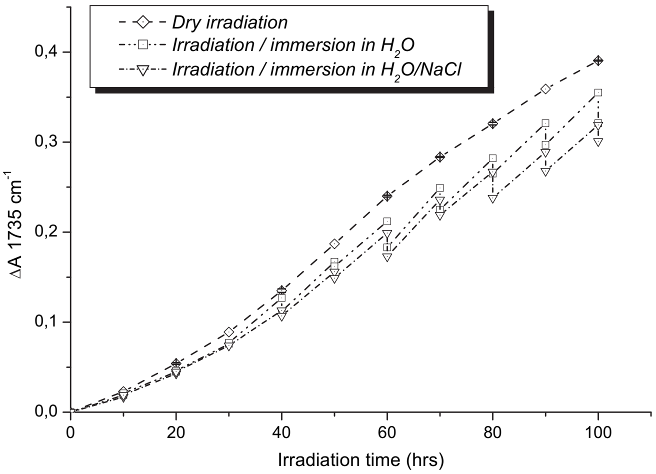


**Fig. 2.** Rates of formation of phenyl formates (at 1735 cm$^{-1}$) for PKHJ® thin films ($e = 36$ μm) as a function of irradiation time during dry irradiation (Sepap 12-24) and during alternating cycles of irradiation/immersion in water or salted water.

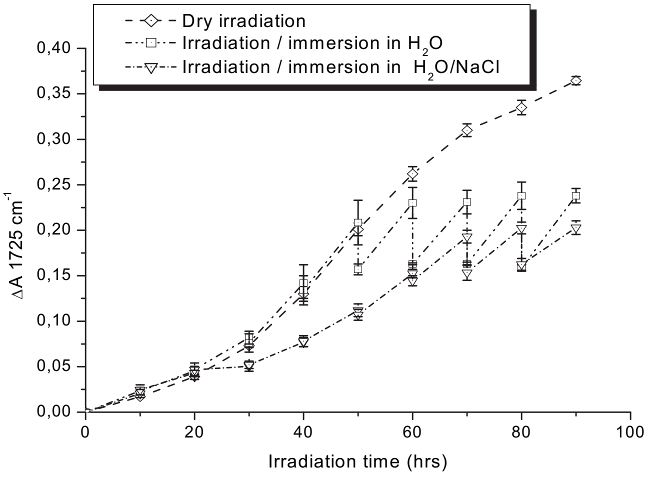


**Fig. 3.** Rates of formation of phenyl formates (at 1725 cm$^{-1}$) for PKHJ® deposits on metallic substrate as a function of irradiation time during dry irradiation (Sepap 12-24) and during alternating cycles of irradiation/immersion in water or salted water.

of the sample, whereas analysis by transmission corresponds to the whole thickness of the film, this result indicates that the effect of water is more important at the surface of the coating.

*3.2.1.2. UV–Visible analysis and correlation with IR.* As shown in Fig. 4, UV-light irradiation of PKHJ® in the presence of air leads to the formation of chromophoric photoproducts absorbing in the UV–Visible range, which provokes a progressive yellowing of the resin. Fig. 4 compares the UV–Visible absorption spectra of a free film (36 μm) before and after 90 h of irradiation under dry conditions and after 90 h of irradiation followed by immersion in water. One observes that immersion in water causes practically no modifications of the spectrum, which means that the photoproducts responsible for yellowing of the resin are not extractible by water and do not react with water (the same effect was observed for immersion in salted water).

The comparison of the effect of water on the correlations between the modifications of the infrared spectra and those of the UV–Visible spectra was very interesting. Fig. 5 shows the variations of absorbance at $\lambda = 335$ nm as a function of IR absorbance at 1735 cm$^{-1}$ either for dry photooxidation in Sepap 12-24 or for ageing including alternating cycles of irradiation/immersion in deionised or salted water.

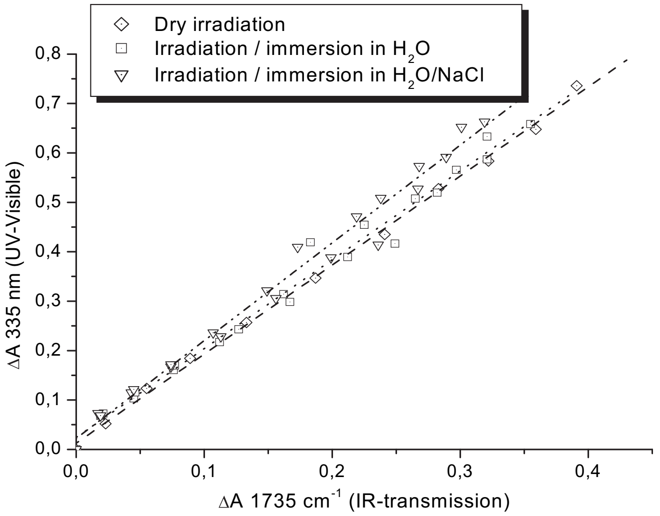


**Fig. 5.** Correlation between kinetics of photoageing determined by IR (transmission) and UV–Visible spectroscopy of PKHJ® thin films (36 μm).

This figure indicates that, despite the kind of ageing, the three curves were similar. The correlation between the variation of the optical density at 335 nm (in the UV–Visible spectra) and that of the IR absorption at 1735 cm$^{-1}$ was almost unchanged by the introduction of the second environmental parameter, i.e., water in the ageing process.

*3.2.1.3. Influence of the chemical nature of the solvent on photooxidised PKHJ®.* As explained above, a decrease in the absorbance at 1735 cm$^{-1}$, provoked by immersion in water, involved the disappearance of macromolecular phenyl formate end-groups. To better understand this phenomenon, PKHJ® films (36 μm) irradiated for 100 h in the SEPAP unit were immersed in four solvents with different polarities: water, salted water, methanol and cyclohexane. The modifications of intensity of the phenyl formate bands at 1735 cm$^{-1}$ are given in Fig. 6.

Fig. 6 shows that largest decrease of absorbance at 1735 cm$^{-1}$ occurred after immersion in methanol. In the case of the non-polar solvent (cyclohexane), no notable modification was observed. The

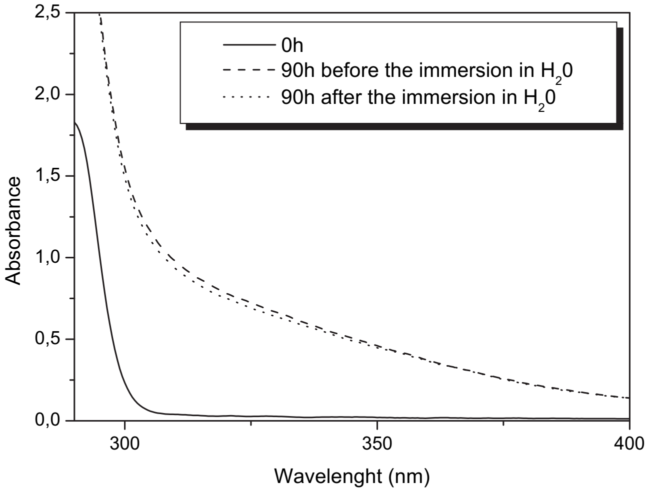


**Fig. 4.** UV–Visible spectra of a PKHJ® film (36 μm) before and after 90 h of ageing, including alternating cycles of immersion in water.

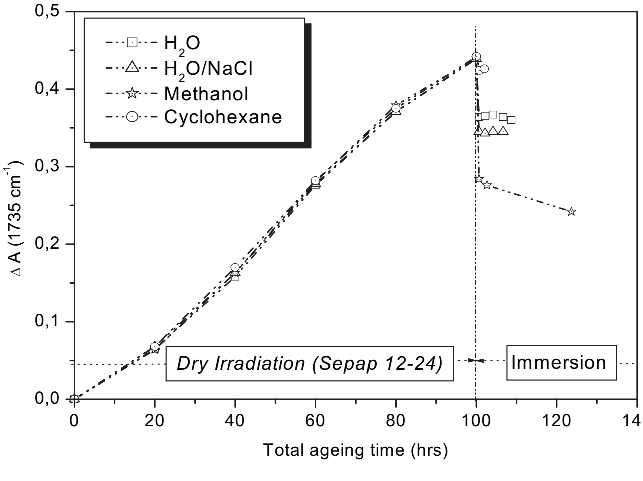


**Fig. 6.** IR absorbance at 1735 cm$^{-1}$ for PKHJ® thin films (36 μm) irradiated for 100 h in Sepap 12-24 and immersed in solvent (deionised water, salted water, methanol or cyclohexane).

effect of water or salted water was intermediate, with a decrease of absorbance twice lower than that observed in the case of methanol.

*3.2.1.4. Analysis of the solution of immersion.* The aqueous solution of immersion of irradiated polymer films was characterised by its pH and ionic chromatography to detect the molecular products that were released. Fig. 7 shows the modifications in the pH of the aqueous solution of immersion. One can observe a decrease in the pH value of the solution, which initially was a neutral medium (deionised water), after the successive immersion of two irradiated PKHJ® films (80 h in Sepap 12-24).

Immersion of the first irradiated film of PKHJ® (253 mg, ~180 µm) provoked a rapid decrease in the pH value of the aqueous solution (initially pH = 6.2), which reflected the release of acid products from the polymer matrix into the solution. After less than 2 h, the pH of the solution stabilised at around 4.8. These results were in good agreement with those obtained by IR spectroscopy, which showed that the absorption band at 1735 $cm^{-1}$ did not decrease any after 2 h of immersion (Fig. 6). This result is in agreement with those reported for other epoxy species [31,32]. Immersion of a second irradiated PKHJ® film 2.5 h after the first one led to another decrease in the pH value of the solution to 4.3, which confirmed the release of acid products into the solution.

To confirm that acidification of the aqueous solution was linked to the hydrolysis and extraction of photoproducts, a virgin PKHJ® film was immersed in water for several hours, which produced no modification in the pH value of the solution. This confirmed that the acidification of the water solution observed in Fig. 7 came from the oxidation photoproducts.

Analysis of the water solution of immersion was also carried out by ionic chromatography, which detects various acid species in the medium. Various carboxylic acids were detected. Formic acid was present at the highest concentration, but oxalic, acetic, succinic and malonic acids were also present (Table 1). This explained the decrease in the pH value of the solution.

The formation of formic, oxalic and acetic acids under photooxidation has been reported in previous works, where these low molecular weight photoproducts were identified by GC/MS and $SF_4$ treatments [10,11]. The formation of formic acid can be attributed to the hydrolysis of formate, which explains the decrease in absorbance at 1735 $cm^{-1}$.

*3.2.1.5. Mechanism of formate hydrolysis in water.* Hydrolysis of the phenyl formate function produces formic acid, which is released into the water bath, and also a phenol function as the end-chain. Scheme 3 summarises the proposed mechanism of formate hydrolysis.

**Table 1**
Concentrations of carboxylic acids obtained by ionic chromatography in the water of immersion of irradiated PKHJ® (473.7 mg irradiated for 80 h in Sepap 12-24).

| Compound | Molecular weight | Range (µg/L) | Limit of detection | *C* (µg/L) | *C* (µM) |
|---|---|---|---|---|---|
| Acetic acid $CH_3$-COOH | 60.05 | 0.5–250 | 0.021 | 33.844 | 0.564 |
| Formic acid H-COOH | 46.03 | 0.5–250 | 0.025 | 57.487 | 1.249 |
| Succinic acid HOOC-$CH_2$ $CH_2CH_2$-COOH | 118.09 | 0.5–250 | 0.003 | 58.609 | 0.496 |
| Malonic acid HOOC-$CH_2$-COOH | 104.06 | 0.5–250 | 0.001 | 32.498 | 0.312 |
| Oxalic acid HOOC-COOH | 90.04 | 0.5–250 | 0.002 | 95.288 | 1.058 |

The phenol functions can have an inductive effect on the photooxidation of PKHJ®, as phenol absorb UV photons and produces radicals that can initiate oxidation of the polymeric matrix. The consequence is an increase in the photooxidation rate, which can be observed on the oxidation kinetic curve of the polymer after immersion (Fig. 3). In the case of immersion in methanol, a similar mechanism can be considered. In presence of methanol, it is a transesterification reaction between methanol and phenyl formates that leads to the formation of phenols and methyl formate (Scheme 4).

The presence of water and NaCl gave similar results to those reported above in the case of deionised water (Figs. 2 and 3). The loss of formate functions was even more pronounced in the presence of salt. This indicated that the release of hydrolysis products is favoured in salted water, which might be explained by ionic interactions acting as a driving force for release.

*3.2.2. Photochemical ageing in water*

To evaluate the effect of UV-light and water simultaneously, a second kind of photochemical ageing was applied to films of PKHJ® phenoxy resin. Irradiation of samples immersed in water in the SEPAP 14-24H unit were carried out ($\lambda > 300$ nm, 27 °C).

*3.2.2.1. IR analysis.* The IR spectra of a PKHJ® film recorded during photooxidation in water in Sepap 14-24H showed the same behaviour as previously observed in the case of ageing, including cycles of irradiation/immersion. The presence of water during irradiation led to the same variations in absorbance at 1735 $cm^{-1}$, which correspond to the formation of phenyl formates. Fig. 8 compares the photooxidation kinetics of PKHJ® thin films (36 µm)

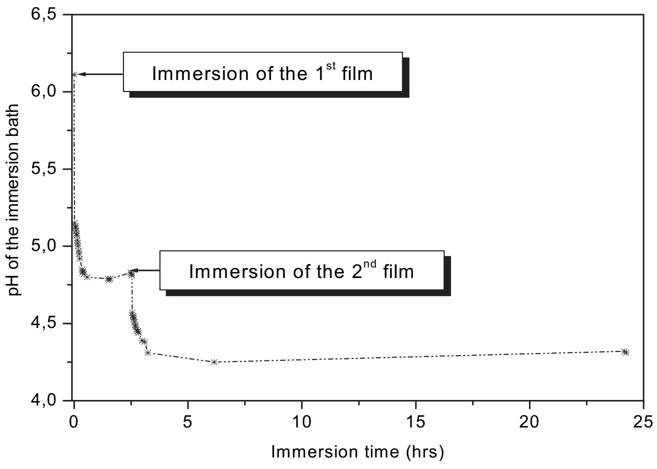
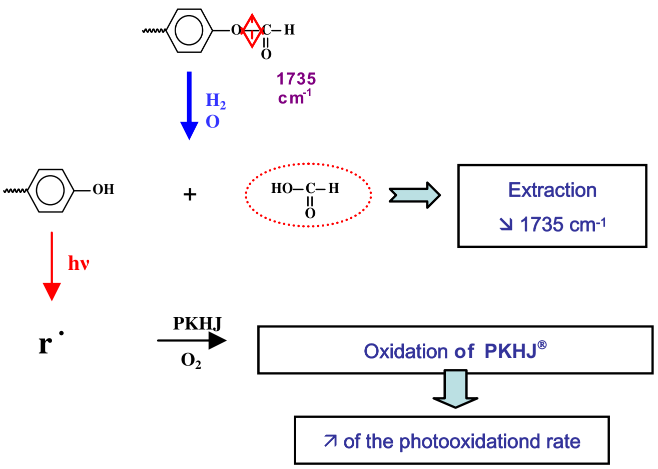
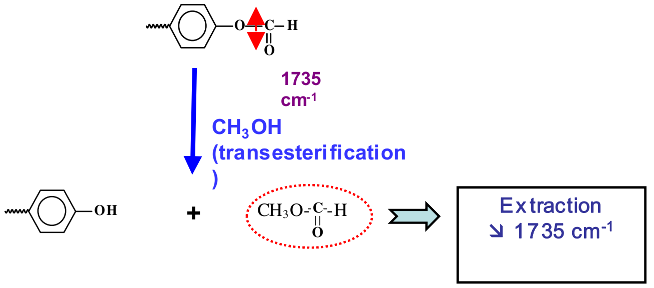


**Fig. 7.** Evolution of the pH of the immersion solution after the successive introduction of two thick PKHJ® films (~180 µm) (irradiated for 80 h in Sepap 12-24).



**Scheme 3.** Mechanism of the effect of water on photooxidised PKHJ® phenoxy resin.



**Scheme 4.** Mechanism of the effect of methanol on photooxidised PKHJ® phenoxy resin.

during photooxidation carried in Sepap 14-24H ($\lambda > 300$ nm, 27 °C) in both dry conditions and water.

Oxidation started after 20 h of irradiation, and the absorbance at 1735 $cm^{-1}$ increased at a much higher rate in the case of irradiation in water (Fig. 8). This effect can be attributed to the photoinductive effect of phenols, which are produced by partial hydrolysis of the formates. It is expected that the simultaneous presence of water during irradiation leads to hydrolysis/extraction reactions that occur continuously. Thus, phenols are produced in larger amounts during irradiation, and their inductive effect due to their absorption of UV-light is more important, which results in a higher oxidation rate of the polymer. Moreover, the release of formic acid and carboxylic acids in the aqueous solution during irradiation was also checked by pH determination, as shown in Fig. 8.

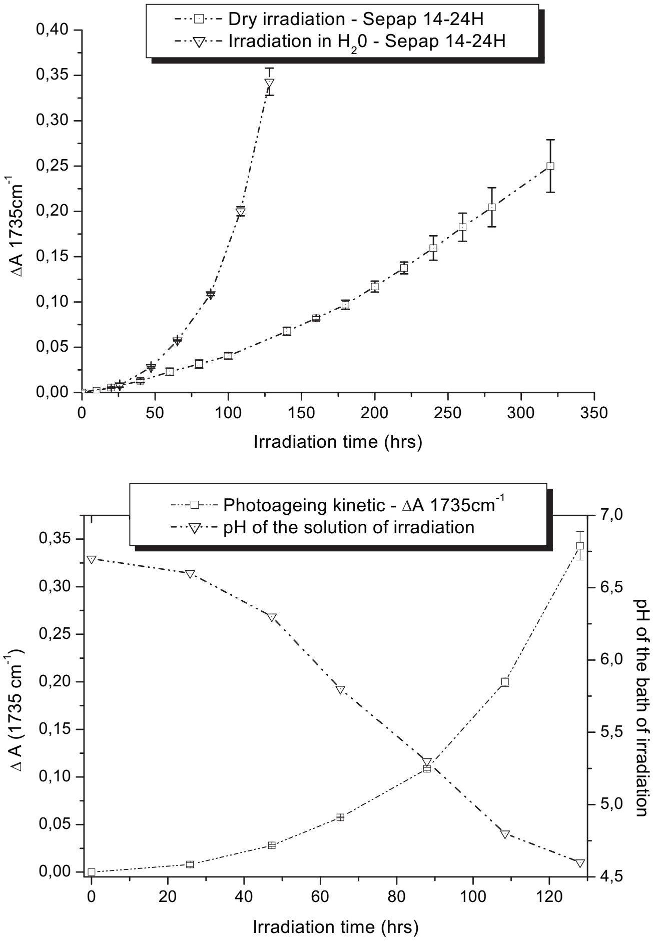


**Fig. 8.** Kinetic curves of PKHJ® thin films (36 μm) during photooxidation in Sepap 14-24H in either dry conditions or in water, and the pH evolution of the aqueous solution.

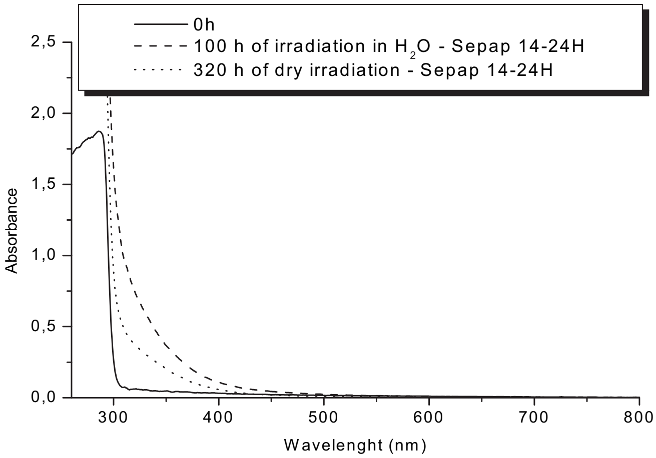


**Fig. 9.** UV–Visible spectra of thin PKHJ® films (36 μm) before irradiation (0 h), after 320 h of dry irradiation in Sepap 14-24H and after 128 h of irradiation in water in Sepap 14-24H.

*3.2.2.2. UV–Visible analysis and correlation with IR analysis.* Fig. 9 shows the UV–Visible absorption spectra of PKHJ® thin films (36 μm) before and after dry irradiation (320 h) or irradiation in water in SEPAP 14-24H (128 h).

After irradiation, UV–Visible spectra presented a shift of absorption towards longer wavelengths in both cases, which revealed a characteristic yellowing phenomenon of the PKHJ® phenoxy resin during ageing. Irradiation in water led to a higher yellowing effect than observed during the dry irradiation, despite the shorter irradiation time (128 h vs. 320 h). This is consistent with an increase in the polymer oxidation rate in water due to the formation of photoinductive phenol groups.

## 4. Conclusions

This study of the influence of water on the chemical modifications of the PKHJ® phenoxy resin during photooxidation confirmed that the main photoproduct was phenyl formate end-groups, which indicates reactivity of the aromatic ether functions by oxidation of the $CH_2$ groups located at the $\alpha$ position of the ether oxygen. The presence of low molecular weight photoproducts in small amounts, such as carboxylic acids (formic, acetic, oxalic) was also detected. Ageing of PKHJ® phenoxy resin under UV-light irradiation and a second environmental parameter, i.e., water through alternating cycles of irradiation/immersion or irradiation in water showed that water provoked two main effects. The first effect was a partial hydrolysis of phenyl formates formed during UV-light irradiation, which lead to macromolecular phenols and formic acid that was easily extracted from the polymer matrix by water. The second effect was an increase in the polymer photooxidation rate as a consequence of the formation of phenols, which act as initiators of polymer photooxidation.

## References

[1] Jackson P. Marine paints, Shreir's corrosion; 2010. p. 2683–2701 [chapter 4.14].
[2] Almeida E, Santos D, Fragata F, De La Fuente D, Morcillo M. Prog Org Coat 2006;57:11–22.
[3] Milne A. Paints and coatings. KGaA, Weinheim: Wiley-VCH Verlag GmbH &Co.; 2005. doi:10.1002/14356007.a18_359.
[4] Miszczyk A, Darowicki K. Corros Sci 2001;43:1337–43.
[5] Yang XF, Li J, Croll SG, Tallman DE, Bierwagen GP. Polym Degrad Stab 2003;80:51–8.

[6] Touzain S, Le Thu Q, Bonnet G. Prog Org Coat 2005;52:311–9.
[7] Fredj N, Cohendoz S, Feaugas X, Touzain S. Prog Org Coat 2008;63:316–22.
[8] Bellenger V, Verdu J. J Appl Polym Sci 1983;28:2599–609.
[9] Bellenger V, Verdu J. J Appl Polym Sci 1983;28:2677–88.
[10] Rivaton A, Moreau L, Gardette JL. Polym Degrad Stab 1997;58:321–32.
[11] Rivaton A, Moreau L, Gardette JL. Polym Degrad Stab 1997;58:333–9.
[12] Rivaton A, Gardette JL. Die Angewandte Makromolekular Chemie 1998;261/262:173–88.
[13] Rivaton A, Gardette JL, Mailhot B. Recent research developments in polymer science, vol. 3; 1999. p. 93–103.
[14] Mailhot B, Morlat-Therias S, Ouahioune M, Gardette JL. Macromol Chem Phys 2005;206:575–84.
[15] Mailhot B, Morlat-Therias S, Bussiere PO, Gardette JL. Macromol Chem Phys 2005;206:585–91.
[16] Ollier-Dureault V, Gosse B. J Appl Polym Sci 1998;70:1221–37.
[17] Monney L, Rouge N, Dubois C, Chambaudet A. Polym Degrad Stab 1998;62:367–71.
[18] Monney L, Belali R, Vebrel J, Dubois C, Chambaudet A. Polym Degrad Stab 1998;62:353–9.
[19] Monney L, Dubois C, Chambaudet A. Die Angewandte Makromolekular Chemie 1999;273:6–11.
[20] Monney L, Bole J, Dubois C, Chambaudet A. Polym Degrad Stab 1999;66:17–22.
[21] Delor-Jestin F, Drouin D, Cheval PY, Lacoste J. Polym Degrad Stab 2006;91:1247–55.
[22] Carfagna C, Apicella A. J Appl Polym Sci 1983;28(9):2881–5.
[23] Carfagna C, Apicella A, Nicolais L. J Appl Polym Sci 1981;27(1):105–12.
[24] Ellis TS, Karasz FE. Polymer 1984;25(5):664–9.
[25] Ngono Y, Marechal Y. J Polym Sci Part B Polym Phys 2000;38:329–40.
[26] Pearce PJ, Davidson RG, Morris CEM. J Appl Polym Sci 1981;26(7):2363–72.
[27] Philippart JL, Sinturel C, Gardette JL. Polym Degrad Stab 1997;58:261–8.
[28] Morlat S, Gardette JL. Polymer 2003;44:7891–7.
[29] Morlat-Thérias S, Hassouna F, Mailhot G, Gardette JL. Polym Degrad Stab 2007;92:2042–50.
[30] Hassouna F, Morlat-Thérias S, Mailhot Gand J-L, Gardette JL. J Photochem Photobiol A Chemistry 2008;195:167–74.
[31] Bonniau P, Bunsell AR. J Compos Mater 1981;15:272.
[32] Ngono Y, Marechal Y, Mermilliod N. J Phys Chem B 1999;103:4979–85.