Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer Degradation and Stability 91 (2006) 1247–1255

Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Thermal and photochemical ageing of epoxy resin – Influence of curing agents

F. Delor-Jestin*, D. Drouin, P.-Y. Cheval, J. Lacoste

Ecole Nationale Supérieure de Chimie de Clermont-Ferrand, Laboratoire de Photochimie Moléculaire et Macromoléculaire – UMR CNRS 6505, Ensemble Universitaire des Cézeaux – 63177 Aubière Cedex, France

Received 4 July 2005; received in revised form 12 September 2005; accepted 13 September 2005
Available online 2 November 2005

Abstract

The thermal and photochemical ageing of epoxy resin was studied using photoacoustic-FTIR spectroscopy. This technique was satisfactory for both unfilled resin and glass fibre filled epoxy composite. The influence of the curing agent (anhydride or amine) was significant for ageing. The durability of anhydride–epoxy system was the best for both thermal and photoageing.

Keywords: Epoxy resin; Curing agents; Ageing; Photoacoustic-FTIR; Thermal analysis

1. Introduction

Epoxy resins are widely used in composite materials and for different activities such as electrical engineering and aeronautics. When considering composites for long-term applications, it is necessary to know how the materials will behave during the intended service life. A lot of recent papers are focussed on the characterization of epoxy resins after ageing. Several techniques have been used to estimate and to explain the changes of these polymers. The main studies are summarized below.

A study of phenoxy resin photoageing (DGEBA – diglycidyl ether of bisphenol A-without curing agent) has been reported by Rivaton et al. [1,2]. They identified the photoproducts by UV and FTIR spectrophotometries, then by chemical derivatization reactions. They also proposed some mechanism of photoproducts formation after long and short wavelength irradiation.

Other papers relate to the case of various cured epoxy materials based on DGEBA. One study proposed by Bellenger and Verdu [3] deals with the influence of curing agents on photo-oxidation of crosslinked epoxy resins. Three systems based on diamines (diaminodiphenyl methane, diaminodiphenyl ether or diaminodiphenyl sulfone) were compared by UV and FTIR analysis. The structure variation with the methylene, ether or sulfone bridges has a noticeable influence on photoageing. The comparison shows that the photoinitiating species essentially derive from the phenoxy part, whereas the propagation essentially depends on amine concentration and electron density on the nitrogen atom. Other studies [4–8] about photo-oxidation give results on anhydride–epoxy systems. An FTIR study has been reported for two epoxy systems (DGEBA–HHPA, hexahydrophthalic anhydride and DGEBA–MTHPA, methyl tetrahydrophthalic anhydride) by Ollier-Dureault and Gosse [4]. This paper reports modifications of the chemical structure and the influence of the addition of a diacid–diester type flexibilizer. Monney et al. [5–7] have published a photochemical study of DGEBA–MTHPA system by using different analytical techniques. ATR–FTIR study [5] gives the molecular changes and confirms mechanisms proposed in other literature. Electron beam X-ray microanalysis [6] allows characterization of the changes of C/O ratio and it shows the relative changes of the different oxidation levels of the organic matrix on the

---

* Corresponding author. Tel.: +33 4 73 40 71 53; fax: +33 4 73 40 70 95.
E-mail address: florence.jestin@univ-bpclermont.fr (F. Delor-Jestin).

0141-3910/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2005.09.009

surface. Another study with DGEBA–MTHPA and DGEBA–IPDA (isophorone diamine) makes a comparison of the matrix durability by ablation measurement [8]. The photochemical removal of products during ageing has been quantified using a two-dimensional profile measurement technique.

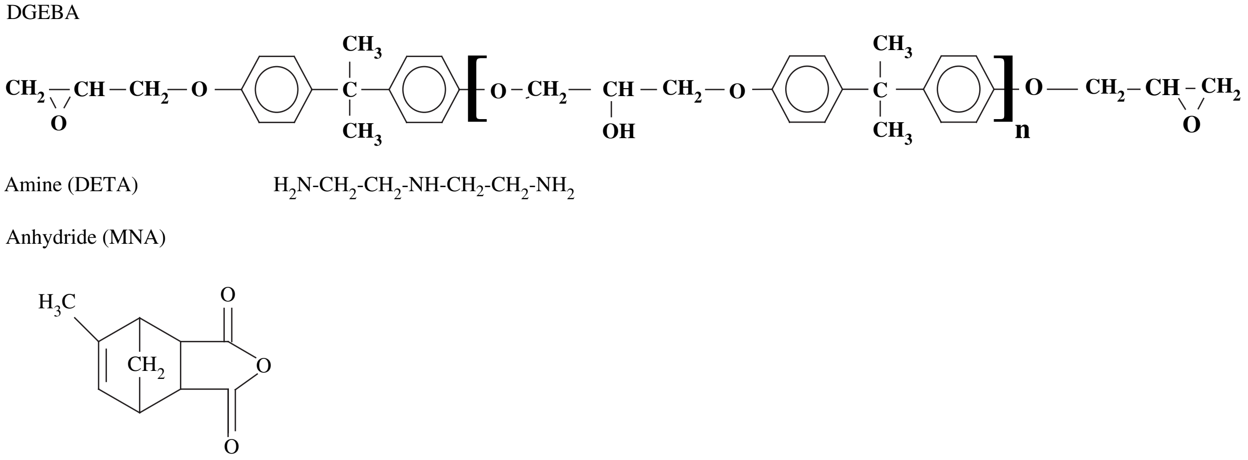
The thermal ageing of epoxy resin has also been investigated. Most of papers relate the case of cured DGEBA polymers [9–17]. A review was published in 1983 on thermo-oxidation of DGEBA–amine systems [9]. Some mechanisms of oxidation are given which depend on the temperature of ageing. The origin of the colouring after thermal degradation is then explained for the DGEBA–TETA (triethyl tetramine) system. A kinetic study on DGEBA–MTHPA system [10] allowed the distribution of oxidation products to be assessed by IR and the rate of oxygen consumption by modelling technique. Another paper [11] presents a thermogravimetric study of DGEBA cured with different amines (aniline, phenylene diamine, etc.) in the absence of oxygen. Some correlation between thermal stability and cure-agent structures are explained. The thermal decomposition under nitrogen of DGEBA/4,4-methylene-dianiline (MDA) with rubber (butadiene–acrylonitrile) modified MDA occurred in one stage. Lee et al. [12] showed that the thermal stability of such a system increased when the content of rubber was higher (because of the four rings with high thermal resistance due to the resonance structure). The thermal stability and the curing behaviour (at 150 and 220 °C) were also investigated for three systems with DGEBA and multifunctional aromatic amine used as flame retardant [13]. These special curing agents contain phosphine oxide. We can also note a kinetic study for DGEBA–DDM (diamine diphenyl methane) [14]. Damian et al. give the order of the reaction as a function of the oxygen pressure and the limiting thickness of homogeneous oxidation. Another approach on epoxy ageing is the use of elevated pressure to accelerate thermo-oxidative degradation in composites (carbon fibre and epoxy resin) [15]. We can finally emphasize a study about a specific epoxy matrix based on tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) with excellent thermal stability [16,17]. This resin cured with diaminodiphenyl sulfone can be mixed with bismaleimide (BMI) to give an interpenetrating polymer network. The TGA and DMA analyses [16] showed an increase in the thermal stability when BMI was added. A two-dimensional FTIR spectroscopy study gave the details about the reaction mechanism of thermal degradation [17]. The method provided information about intra- and intermolecular interactions by selective correlations of peaks.

The studies performed to date indicate the complexity of the possible degradation routes during epoxy resin ageing. The purpose of our study is to analyse structural modifications after ageing on specific crosslinked epoxy system by photoacoustic-FTIR spectroscopy, then to give oxidation kinetics. We compare the thermal and photoageing of two crosslinked DGEBA (first formulation with amine, second one with anhydride). We would also like to analyse the influence of curing agent and the differences observed for both, because there has been no similar previous approach. Thermal analysis in the presence of oxygen with TGA–FTIR was an additional analytical tool which was used to improve the understanding of epoxy degradation.

2. Experimental

2.1. Materials

The prepolymer used in this study was an epoxy system DGEBA (diglycidyl ether of bisphenol A), DER 331, product of Dow Plastics. Typical properties are: epoxide equivalent weight 186 g eq^{-1}, percentage epoxide 23%. Two curing agents were used: diethylene triamine (Ciba) and methyl nadic anhydride (Dow).



The reagents were used as received, without further purification. The crosslinking reaction with anhydride was initiated with an imidazole-type accelerator (1-methyl imidazole supplied by Dow). After DSC (Differential Scanning Calorimetry – Mettler Toledo DSC 30) measurements, we have chosen the curing time and the temperature for each formulation. Optimal curing temperature is obtained when conversion rate is maximum, i.e. we cannot obtain a higher peak height on DSC thermogram. Formulation 1 was done with 40 g of amine for 60 g of epoxy prepolymer. Formulation 2 was done with 90 g of anhydride for 100 g of epoxy. The curing cycle was 60 min at 100 °C then samples were cooled in the open air. Glass fibre filled epoxy–anhydride system prepared by pultrusion technique was also studied.

2.2. Accelerated ageing

Photoageing was carried out in an SEPAP 12-24 device. This irradiation system has been described previously [18]. It is characterized by the source, medium pressure Hg lamps filtered with borosilicate envelope ($\lambda > 300$ nm) and by careful control of the temperature with a thermocouple in close contact with one of the samples. Samples are rotated at a constant distance (20 cm) from the sources. The epoxy samples were irradiated at 60 °C in an SEPAP chamber equipped with four lamps. Epoxy samples were prepared in aluminium photoacoustic crucibles then placed in front of the lamps in the SEPAP device.

For thermo-oxidation, aluminium photoacoustic crucibles with epoxy system were exposed in an aerated oven at 100 °C (Memmert UM100).

2.3. Analytical tools

Photoacoustic-FTIR has been used in particular for the study of cured epoxy resin degradation. Our materials are thermosetting. We also studied glass fibre filled epoxy and we found that this particular accessory for spectroscopy was the best for each kind of samples. Micro-ATR did not give good results. Photoacoustic (PAS) was the only technique which we can use for filled epoxy materials. The PAS accessory from MTEC is coupled with a Nicolet 860 FTIR spectrophotometer. The surface of the sample is lit by an intense IR beam. The rise of temperature at the sample surface provokes an increase of pressure in the PAS cell which is full of helium. The pressure wave spreads inside the cell and reaches the acoustic membrane of the detector which transforms the received signal [19]. The analysed thickness (around 15–20 μm) is function of the frequency of absorbed IR beam and thermal properties of materials. TGA–FTIR used a coupled system Mettler Toledo TGA/SDTA851 – Nicolet Nexus. The gazes coming from the TGA are transferred by a heated tube for analysis in the gas cell of the IR spectrometer. The temperature program in the TGA part was an increase of temperature by 10 °C min^{-1} from 20 to 800 °C, under oxygen (40 ml min^{-1}).

3. Results and discussion

3.1. Analysis of initial materials

Firstly we have identified the initial spectra of the two crosslinked systems obtained by PAS-FTIR spectroscopy. We compared the spectra of the two formulations with one spectrum of phenoxy resin (uncrosslinked DGEBA), as illustrated in Fig. 1. We have given in Table 1 the peak frequencies and tentative assignments after curing protocol on DGEBA. It gives information about the difference between the two crosslinking networks. The presence of curing agent is clearly identified. Amine links are characterized specially at 3320 and 1650 cm^{-1}. The bands at 1860 and 1740 cm^{-1} are attributed to anhydride carbonyl groups.

3.2. Analysis of photo-oxidation

The IR analysis as a function of the irradiation time shows a rapid spectral evolution of the two systems under accelerated UV-ageing. It can be observed from the initial few hours of exposure as illustrated in Figs. 2A, B and 3A, B. The modifications are essentially in the hydroxyl and carbonyl absorption areas.

For the epoxy–amine system, the appearance of several carbonyl groups absorbing in the range of 1670–1800 cm^{-1} is given in Fig. 2A. The maxima are obtained at 1760, 1740

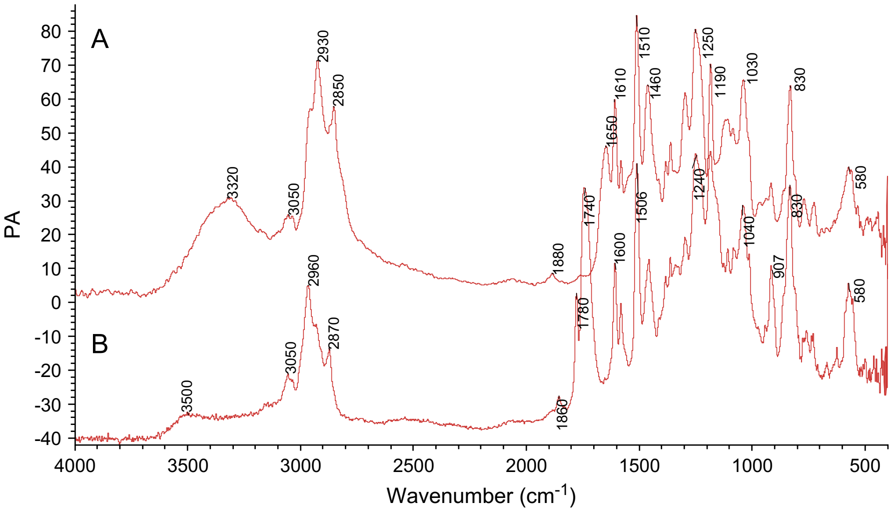


Fig. 1. FTIR spectra of initial materials; A – DGEBA–amine after curing; B – DGEBA–anhydride after curing.

Table 1
Main absorption (wavenumbers, cm^{-1}) observed for raw materials (uncrosslinked DGEBA, amine, anhydride) and the two formulations DGBA–amine and DGEBA–anhydride, then assignments of IR bands

DGEBA	Amine	Anhydride	DGEBA–amide (Fig. 1A)	DGEBA–anhydride (Fig. 1B)	Tentative assignment
3500			3500	3500	ν O–H
	3300		3320		ν N–H
3050			3050	3050	ν phenyl-H
2960–2930–2870	2920		2930–2850	2690–2930–2870	ν C–H and ν CH_2
		1860–1780		1780–1740	ν C=O
	1650		1650		ν N–H
1610–1580–1510			1610–1580–1510	1600–1580–1510	Aromatic ring
1450			1460	1460	δ CH_2
		1230		1230	ν C–O–C
1250–1190				1250–1190	ν phenyl–C–ph, ν C–O–C
		907		907	δ C=C
830			830	830	δ phenyl-H

ν = stretching vibration; δ = in-plane deformation.

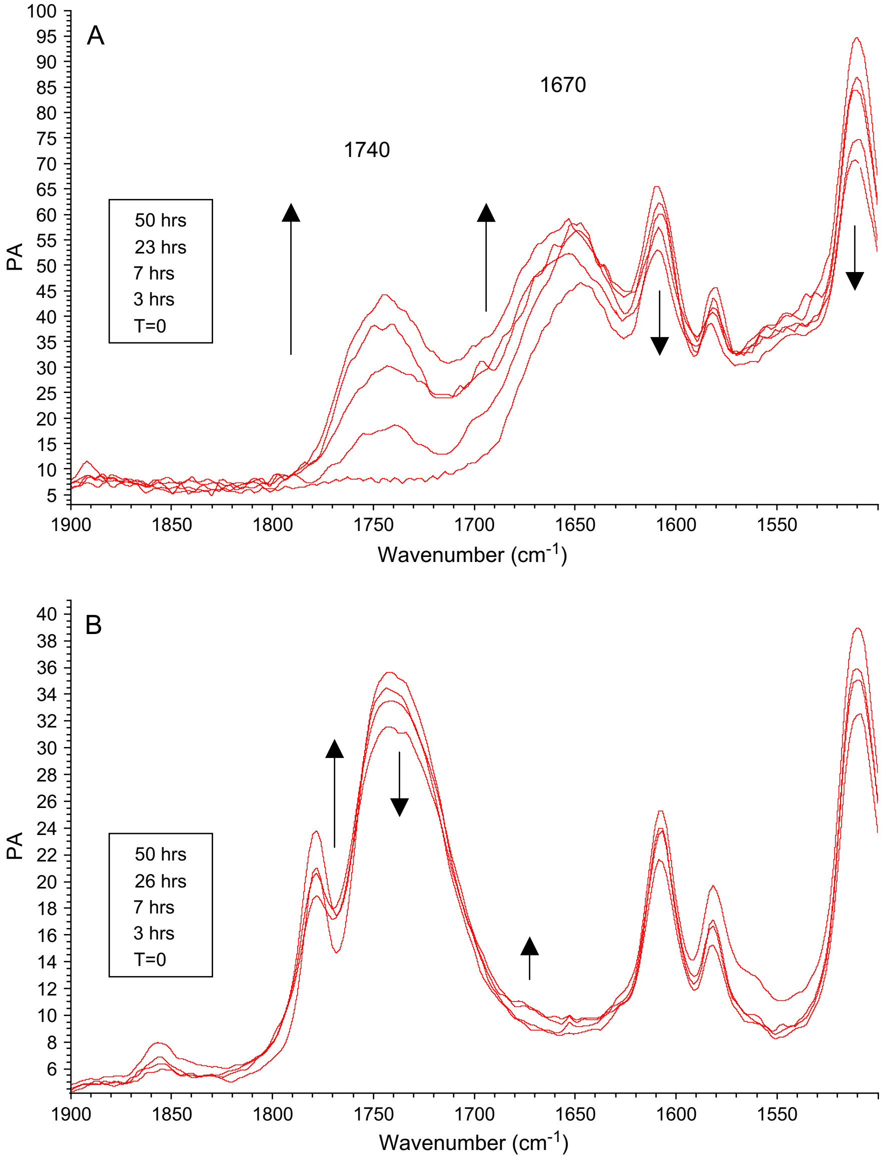


Fig. 2. FTIR-PAS spectra upon photo-oxidation; A – carbonyl absorption area for epoxy–amine. B – carbonyl absorption area for epoxy–anhydride.

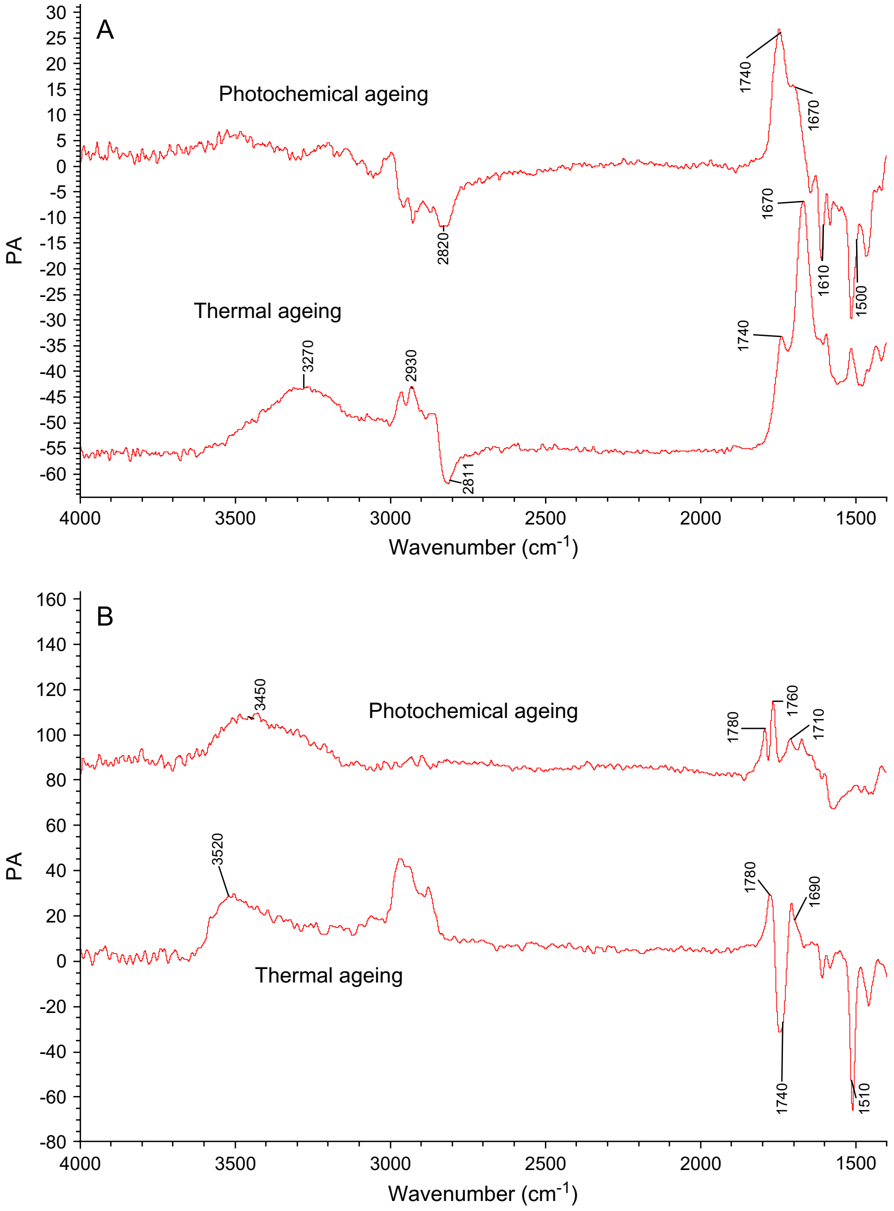


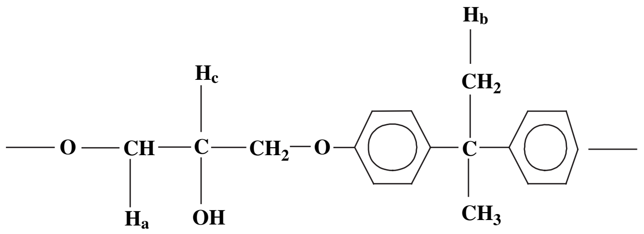
Fig. 3. Subtraction result: aged material − initial material; A − photochemical and thermal ageings for epoxy–amine. B − photochemical and thermal ageings for epoxy–anhydride.

and 1670 cm^{-1}. We can simultaneously observe the decrease of the bands at 1610 and 1510 cm^{-1}, which are characteristic of aromatics. We can notice a small increase at 3250 cm^{-1} on the subtraction result (Fig. 3A − first spectrum).

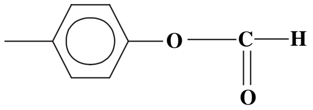
The evolution of the DGEBA–anhydride system is quite different and less developed than on the DGEBA–amine system. We can observe the appearance of new bands such as hydroxyl group absorption at 3450 cm^{-1} (Fig. 3B − first spectrum), carbonyl absorption at 1780, 1760 and 1710 cm^{-1} (Fig. 3A − first spectrum). The main band for anhydride at 1740 cm^{-1} decreased. The main decrease is then noticed at 1570 cm^{-1} (Fig. 3B − first spectrum) due to aromatic C=C bands. The disappearance or modification of numerous absorption bands, associated with the strong increase of the hydroxyl and carbonyl bands or the broadening of the carbonyl band in formulation 2, is evidence of an important phenomenon in both systems. The results show that UV irradiation leads to a specific attack upon the aromatic functions (disappearance of aromatic C=C and C–H bonds).

It is well known that polymer degradation in the presence of oxygen leads to a complex mixture of oxidation products, such as alcohols, hydroperoxides, lactones, esters, carboxylic acids and ketones…. The hydroxyl and carbonyl bands are often very broad and result from the overlapping of bands that are characteristic of numerous oxidation products. The results obtained for two formulations are very different so we try to understand the influence of the curing agent on photo-oxidation.

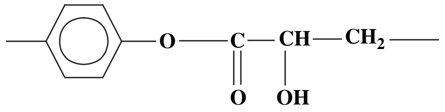
Numerous oxidation sites are possible because of the structure of crosslinked DGEBA systems. We compare our FTIR results on DGEBA–DETA with phenoxy resin study (uncrosslinked epoxy [1,2]) and other works on DGEBA–amine systems [3]. The main evidences are as follows: the general change of DGEBA–amine resembles the ageing of phenoxy resin. The change in the carbonyl region seems the same with main maxima at 1740 and 1760 cm^{-1}. Another maximum (shoulder) at 1670 cm^{-1} is different and is due to amide groups absorption. Hence processes involved in photo-oxidation ($\lambda > 300$ nm) of DGEBA (cured or uncured) have common routes. After phototransformation of chromophoric impurities, the resulting radical species initiate photoageing by abstraction of hydrogen from the polymer backbone. This photoinduced oxidation leads to the formation of macroradicals which can be oxidized to hydroperoxide groups. Due to the chemical structure of DGEBA, three possibilities (H_a, H_b and H_c) are noticed as the origin of oxygen abstraction [2].



The photoreactivity of aliphatic polyethers and bisphenol-A polycarbonate has been previously studied. On the basis of these different works it results that the photo-oxidation proceeds through a primary abstraction of H_a, labile secondary hydrogen. The new radical reacts with oxygen and leads to hydroperoxide. The thermal and photochemical decomposition of hydroperoxides leads to alkoxy radicals. After a β-scission we can have phenyl formate end groups (identified at 1740 cm^{-1}) and another macroradical can also form. Formates are the most important decomposition products of hydroperoxides formed through chain breaking. A cage reaction of alkoxy radical may occur leading to phenyl alkylate (1760 cm^{-1}).



1740 cm^{-1}



1760 cm^{-1}

The main photoproducts for DGEBA–amine are carbonyls and amides. The oxidation of amine links is then investigated. The evolution of DGEBA–amine proceeds as quickly as the evolution of uncrosslinked DGEBA resin. At the same time we get the degradation of DGEBA structure and we can also observe the modifications of amine links, attested by the changes observed on FTIR spectra at 1670 and 1540 cm^{-1}.

From the literature [3] we know that oxidation yields depend on amine concentrations. The comparison of photo-oxidation rates for different curing agents such as aliphatic (DETA), cycloaliphatic (isophorone diamine) or heterocyclic (amino-ethyl piperazine) amines allowed us to find that amide yields are directly related to the initial α-amino methylene concentration. With dianiline-type amines (diaminodiphenyl methane – DDM, ether – DDE or sulfone – DDS), the bridge has a noticeable effect on photoxidation. The stability was found in decreasing order DDS > DDM > DDE. The amide formation depends finally on initial amine concentration and nitrogen atom electron density (which is higher for DGEBA–DDE). The initial rate of amide growth is also higher for DDE system. The photosensitivity of phenyl amine is therefore essentially due to chromophores arising from the phenoxy part, whereas the strongly absorbing chromophores arising from the diamine part are considerably less efficient in photo-initiation. With the new results on DGEBA–DETA we can notice the strong impact on photo-oxidation of the α-amino methylene. The oxidation of the amine bridges is quickly detected.

Next we compare our FTIR results on DGEBA–MNA with the phenoxy resin study [1,2] and work on DGEBA–MTHPA [4–7] or DGEBA–HHPA [4]. The chemical change with the anhydride system is quite different from that of phenoxy resin ageing. The formation of photoproducts is the same for the three phthalic anhydrides, even if the irradiation system is not the same. These results show that the influence of anhydride links is high because the oxidation photoinitiation on phenoxy part with abstraction of H_a is not the main pathway of degradation. The anhydride links brings a slight stabilization of the cured DGEBA system. The mechanism of hydrogen abstraction is probably due to different pathways H_a, H_b, H_c. No main route can be underlined as for DGEBA–amine. The main photoproducts observed can be identified as phenyl alkylate end groups at 1760 cm^{-1} and acids at 1710 cm^{-1}.

3.3. Analysis of thermo-oxidation

The PAS-FTIR analysis as a function of the exposure time in oven shows changes after an induction period. The changes are illustrated in Fig. 3A, B (second spectrum) and Fig. 4A and B. For DGEBA–DETA, the induction period is around 400 h. The main photoproducts are observed in the hydroxyl and carbonyl regions. We can notice the increase of a band centered at 3400 cm^{-1} (hydroxyl groups). The main absorption in the carbonyl area is at 1670 cm^{-1} probably due to amide and ketone end groups. We also observed the 1740 cm^{-1} band. But the ratio ΔDO(1670)/ΔDO(1740) is quite different if we compare photochemical and thermal ageing. The amide formation is favoured with thermal oxidation at 100 °C. Different hypotheses can be proposed; some amides are unstable under UV irradiation or the oxidation pathway to produce amides is preferred under thermal conditions.

The change of DGEBA–MNA is less significant (Fig. 4B) after 1980 h in the oven. The induction period is around 900 h.

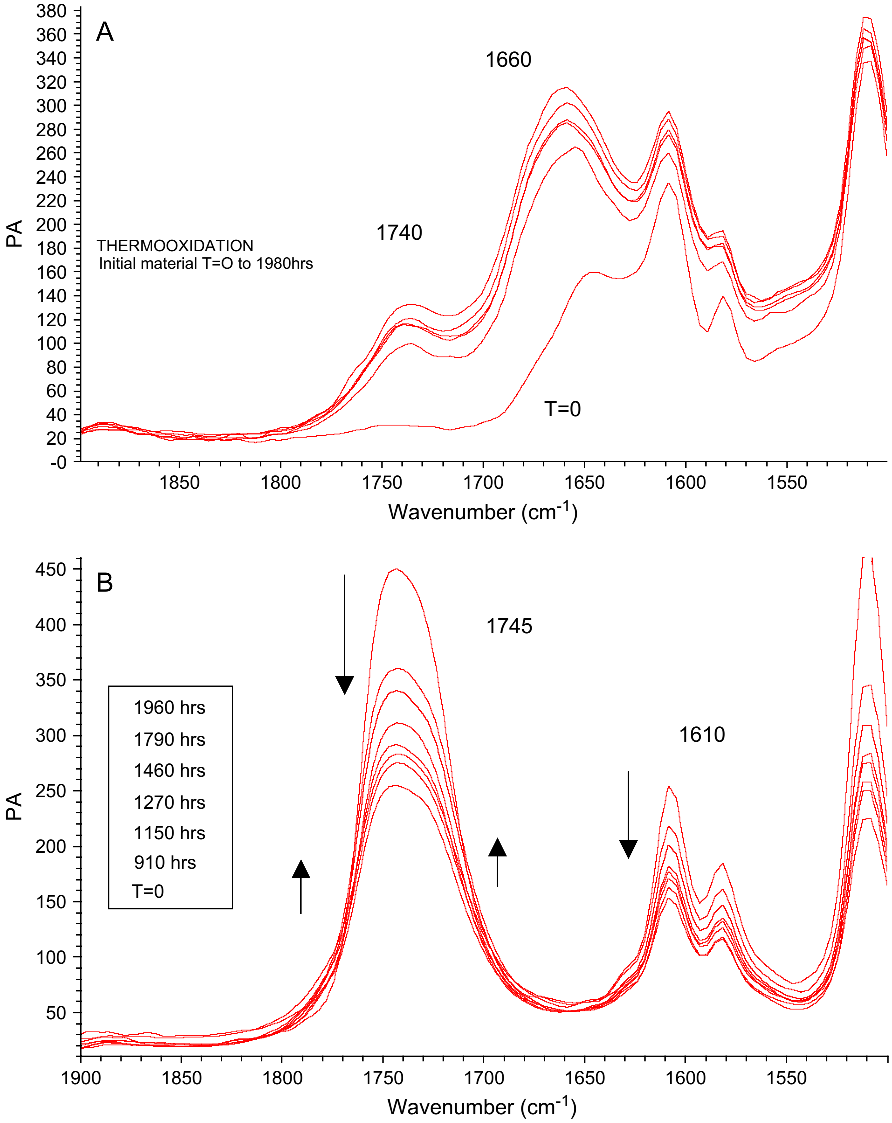


Fig. 4. FTIR-PAS spectra after thermo-oxidation; A – carbonyl absorption area for epoxy–amine. B – carbonyl absorption area for epoxy–anhydride.

New bands with low intensity are detected at 3400, 1780 and 1680 cm^{-1}.

We can compare the results on epoxy–DETA with IR studies on DGEBA–TETA [9]. Visible colour changes can be detected in both cases. The development of colour is due to the formation of polyenyl structures with the possible formation of quinonoid or cyclised conjugated nitrogen compounds. In our case, the colouring is enhanced during thermal ageing. We also estimate that amine cured epoxy resin tend to have excess amine on material surface, and it leads to enhanced degradation by the mechanism proposed by Patterson-Jones (given in the review [9]).

The results obtained with epoxy–MNA were compared with the thermal degradation of DGEBA–MTHPA [10]. Both systems gave some anhydride products identified at 1850 and 1785 cm^{-1}. With MNA the two ageings also give very different results.

With TGA–FTIR (Fig. 5) we can see the difference of thermal stability between uncrosslinked DGEBA and amine

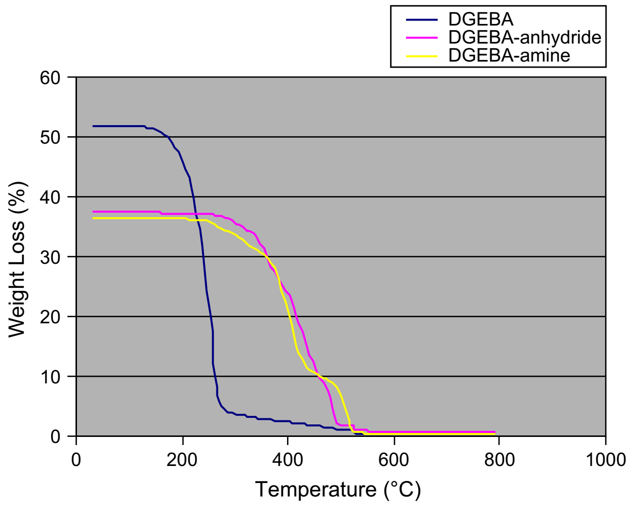


Fig. 5. TGA of three unaged samples.

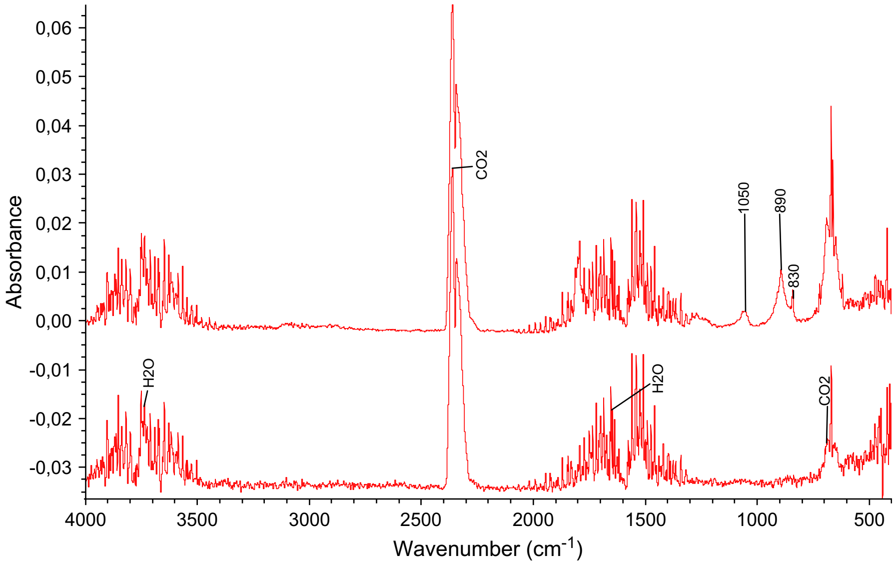


Fig. 6. TGA–FTIR spectra of unaged DGEBA–amine system for two temperatures (300 °C and 500 °C).

or anhydride cured DGEBA. The weight loss starts at 110 °C for DGEBA. For DGEBA–amine the weight loss is significant at 200 °C. For DGEBA–anhydride it is at 240 °C. A small delay is noticeable. The DGEBA–amine is degraded at a lower temperature than DGEBA–anhydride. The analysis by FTIR (Fig. 6) after TGA shows that the thermal decomposition under oxygen of DGEBA (crosslinked or uncrosslinked) gave mainly two products, water and carbon dioxide (at 300 °C). The spectrum obtained at the end of the weight loss at 500 °C shows new bands at 1060 and 890 cm^{-1}. The assignment of these bands was not conclusive.

3.4. Comparison of ageing and determination of curing agent influence

Fig. 7 illustrates the comparison of the two studied epoxy systems during thermal or photoageing. We have calculated the oxidation rate at 1740 or 1780 cm^{-1} for each exposure time and each material. Photo-oxidation is quickly detected. No induction period is noticed. For thermo-oxidation the induction period depends on the curing agent, and is higher for the anhydride–epoxy system (respectively 400 and 900 h). The epoxy resin crosslinked with anhydride is less sensitive to ageing than the epoxy–amine system. The choice of curing agent depends on the required specific properties. The long-term behaviour of crosslinked epoxy system depends on the chosen curing agent. We can conclude that the epoxy–anhydride system was finally more satisfactory towards ageing.

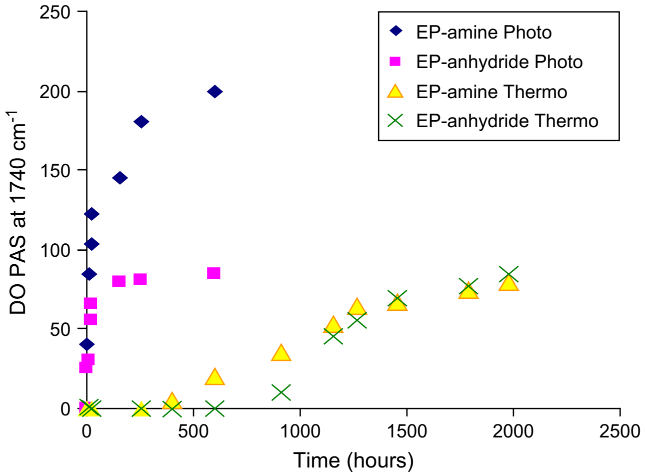


Fig. 7. Kinetics of oxidation after thermal or photochemical ageing for epoxy–amine (1740 cm^{-1}) and epoxy–anhydride systems (1780 cm^{-1}).

3.5. Analysis of glass fibre filled epoxy composite

The filled system was an epoxy–anhydride material. The PAS-FTIR analysis was also satisfactory for glass fibre filled resin. The PAS-FTIR spectrum of initial filled material was similar to the unfilled DGEBA–anhydride. The photochemical and thermal ageing of the final formulation gave the same analytical results. We obtained low oxidation and the induction periods were almost the same. Under UV irradiation the induction period was 350 h. It was 900 h during thermal ageing. The addition of glass fibre did not affect the materials' behaviour towards oxidative degradation.

4. Conclusion

The need for a better understanding of basic relationships between resin structure and performance is classical in ageing studies. The analysis of two crosslinked DGEBA systems (DETA and MNA) after thermal and photochemical ageing allows us to propose a complementary approach in terms of oxidation reactions, curing agent influence and comparison of ageing. We can notice the simultaneous chemical changes of the DGEBA structure and of the bonds due to crosslinker. The behaviour of curing agents such as anhydride appears to be much better both upon thermal and photoageing. It follows that curing agents play an important role in epoxy resin degradation and stability.

References

[1] Rivaton A, Moreau L, Gardette J-L. Polym Degrad Stab 1997;58: 321–32.
[2] Rivaton A, Moreau L, Gardette J-L. Polym Degrad Stab 1997;58:333–9.
[3] Bellenger V, Verdu J. J Appl Polym Sci 1983;28:2677–88.
[4] Ollier-Dureault V, Gosse B. J Appl Polym Sci 1998;70:1221–37.
[5] Monney L, Belali R, Vebrel J, Dubois C, Chambaudet A. Polym Degrad Stab 1998;62:353–9.
[6] Monney L, Rouge N, Dubois C, Chambaudet A. Polym Degrad Stab 1998;62:367–71.
[7] Monney L, Bole J, Dubois C, Chambaudet A. Polym Degrad Stab 1999;66:17–22.
[8] Guillot L, Monney L, Dubois C, Chambaudet A. Polym Degrad Stab 2001;72:209–15.
[9] Maxwell ID, Pethrick RA. Polym Degrad Stab 1983;5:275–301.
[10] Le Huy HM, Bellenger V, Paris M, Verdu J. Polym Degrad Stab 1992;35:171–9.
[11] Dyakonov T, Mann PJ, Chen Y, Stevenson TK. Polym Degrad Stab 1996;54:67–83.
[12] Lee JY, Shim J, Kim SW. J Appl Polym Sci 2001;81:479–85.
[13] Jain P, Choudhary V, Varma IK. Eur Polym J 2003;39:181–7.
[14] Damian C, Espuche E, Escoubes M. Polym Degrad Stab 2001;72: 447–58.
[15] Tsotsis TK, Keller S, Bardis J, Bish J. Polym Degrad Stab 1999;64: 207–12.
[16] Musto P, Ragosta G, Russo P, Mascia L. Macromol Chem Phys 2001;202:3445–58.
[17] Musto P. Macromolecules 2003;36:3210–21.
[18] Penot G, Arnaud R, Lemaire J. Die Angew Makromol Chem 1992;30:493–9.
[19] Delprat P, Gardette JL. Polymer 1993;34(5):933–7.