ELSEVIER

Polymer 41 (2000) 4077–4087

polymer

Thermal ageing of a supported epoxy-imide adhesive

N. Piccirelli[1], M.E.R. Shanahan*

Centre National de la Recherche Scientifique, Université d'Evry Val d'Essonne, Ecole Nationale Supérieure des Mines de Paris,
Centre des Matériaux P.M. Fourt, B.P. 87 91003 Evry Cedex, France

Received 23 March 1999; received in revised form 6 August 1999; accepted 19 August 1999

Abstract

A supported epoxy-imide adhesive has been aged in air at elevated temperatures (180–250°C). Evolution of the material has been studied using gravimetry, optical microscopy, X-ray microanalysis, and viscoelasticimetry. Mass loss was manifest and has been shown to be more significant from adhesive surfaces exposing fibres (the support) than from those presenting only polymer. Microscopic examination and X-ray microanalysis indicated the formation of oxidised regions near the exposed surfaces of the polymer. Regions with exposed fibres degraded more rapidly due to facilitated oxygen ingress. This surface governed form of degradation seems to be accompanied by bulk thermolytic ageing, not requiring oxygen, as shown by viscoelasticimetry, indicating a drop in the glass transition temperature, T_g, after ageing. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ageing; Epoxy-imide; Thermo-oxidation

1. Introduction

The use of structural adhesives for the assembly of systems required to withstand elevated temperatures is becoming more widespread. This indicates the use of polymeric adhesives presenting good thermal and chemical resistance. The combined effects of oxygen in the air and heat can lead to thermo-oxidative degradation and subsequent loss in mechanical properties. Various factors, such as the chemical nature of the crosslinking agent in a thermoset polymer [1], or the presence of glass or carbon fibre reinforcement [2–6], can influence long-term ageing behaviour. It is thus essential to identify factors limiting durability during extended exposure to air at elevated temperatures with an aim to understand the ageing process(es) and related kinetics.

In this context, we have studied the behaviour of a structural epoxy-imide adhesive under thermo-oxidative conditions (exposure to air at temperatures in the range 180–250°C) for extended periods. The present study complements work presented earlier on the creep behaviour of the same material [7]. Here, the objective is a macroscopic analysis of the effects of thermal ageing on the adhesive considered. From a practical standpoint, correlation of such ageing effects as observed with the bulk adhesive and the behaviour of structural adhesive joints, constructed with the same polymeric material, is sought. The techniques employed in this study do not unfortunately allow us to furnish explanations about the macromolecular mechanisms occurring during degradation of the epoxy-imide adhesive under consideration. The influence of the presence of a fibre support within the adhesive on the kinetics of mass loss during ageing has been considered. Effects of ageing on the glass transition, T_g, of the polymer have been exploited in an attempt to understand better the role played by thermal degradation on the polymeric structure. X-ray analysis on aged polymer samples has allowed us to correlate the kinetics of advancing degradation and gravimetric evolution with exposure time.

2. Experimental

2.1. Material

The material studied is an epoxy-imide adhesive distributed by CYTEC and known commercially by the reference FM32. As studied previously [7], the film was supplied as a film of ca. 0.4 mm thickness supported on a glass fibre mat intended to facilitate handling of the adhesive during application. The volume fraction of glass fibres in FM32 is ca. 10% and it contains ca. 0.15% of volatile substances. Analyses effected on the adhesive by FTIR and by

---

* Corresponding author. Tel.: +33-1-6076-3022; fax: +33-1-6076-3150.
E-mail address: shanahan@mat.ensmp.fr (M.E.R. Shanahan).

[1] Present address: Renault, Direction de la Recherche, Guyancourt, France.

PII: S0032-3861(99)00644-8

Table 1
Dimensions of ageing samples

	Nature of sample	Width (mm)	Length (mm)	Thickness (mm)	S_1 (mm^2)	S_2 (mm^2)	$\frac{S_2}{S_1+S_2}$
Gravimetry	Small	7.5	14.5	3	218	132	0.38
	Square	14.5	14.5	3	421	174	0.29
	Large	22.5	26.5	3	1193	294	0.20
X-ray microanalysis	Observation	14	15	3	420	174	0.29
Viscoelasticimetry	DMTA	5	28	3	280	198	0.41

chromatography have revealed the presence of the prepolymer diglycidyl ether of bisphenol A (DGEBA) and of two amine-based crosslinking agents: dicyandiamide (DDA) and 4,4′-diamino-diphenylsulphone (4,4′-DDS). However, no imide compounds or groups were detected with these techniques. Notwithstanding, the high thermal resistance of the adhesive suggests the presence of imide containing constituents. According to the manufacturers, FM32 presents good mechanical properties at temperatures up to 180°C and can withstand short periods at up to 250°C.

Sheets of cured adhesive were obtained for cutting into samples by superimposing eight layers of the polymer film, leading to a final thickness of the “composite” material (polymer and fibrous support) of ca. 3 mm. The eight layers were placed between two films of poly(tetrafluorethylene) (PTFE), used as non-stick agents, the assembly placed in a steel support, and covered by a 2 mm thick sheet of silicone elastomer fixed by means of a steel frame (80×80 mm^2). The silicone sheet effectively prevented any leaking of the adhesive, whilst in a liquid state, during crosslinking. Crosslinking was effected under a pressure of 3 bars maintained by the application of a compressed, calibrated spring. Heating from ambient temperature (and subsequent cooling) was affected at 3°C/min. Curing corresponded to 4 h at 180°C followed by a post-cure, also of 4 h, but at 205°C (cure cycle recommended by the manufacturer).

After crosslinking and post-cure, samples were cut from the sheets of adhesive using a diamond mill, the areas exposed after milling being subsequently polished with glass paper of grade 1200. Prepared samples were dried in an oven for 10 days at 70°C followed by 10 days at 90°C before use. Table 1 gathers together the dimensions of the various sample geometries used in this study.

Thermal ageing of the samples was effected at five temperatures, viz. 180, 200, 215, 230 and 250°C, in natural convection ovens (MEMMERT and PROLABO) capable of maintaining a constant temperature with a precision of ±2°C during the entire ageing periods.

Evolution of the FM32 adhesive during ageing was followed mainly using gravimetry, X-ray microanalysis and viscoelasticimetry. Optical microscopy was also employed.

2.2. Gravimetric analysis

Three different geometries were employed for the samples studied by gravimetry. Weighings were effected periodically on a MEMMERT AT 250 balance. Before each weighing, the sample in question was cooled from the test temperature to ambient for 30 min in a desiccator. Percentage relative mass loss, $L(t)$, during ageing for time, t, is given simply by

$$L(t) = \frac{\Delta m}{m_0} \times 100 = \frac{m_0 - m(t)}{m_0} \times 100 \qquad (1)$$

where m_0 and $m(t)$ are, respectively, initial sample weight and weight after ageing for time t.

2.3. X-ray microanalysis

Samples of adhesive aged at 180, 200 and 250°C were analysed using X-ray microanalysis in order to study the evolution of the degraded zone of the adhesive as a function of ageing time and temperature.

After various exposure periods, observation samples (see Table 1) were cut open, encapsulated in epoxy resin and polished to a surface finish of 1 μm (the method of surface analysis being sensitive to surface defects). Samples were subsequently metallised to obtain an aluminium deposit of thickness 300 Å (30 nm).

X-ray analysis was effected on a wavelength dispersion spectrometer, CAMECA SX 50, using an acceleration voltage of 15 kV and an electron beam intensity of 30 nA. Electron penetration depth within the adhesive is of the order of 1.5 μm. Mappings of relative distribution of oxygen, carbon, nitrogen and sulphur were thus obtained for the adhesive after various ageing periods.

2.4. Thermomechanical analysis of aged samples

We measured the glass transition temperature of the adhesive FM 32 as a function of ageing period by using viscoelasticimetric data. Rectangular samples (dimensions $28 \times 5 \times 3$ mm^3) aged at 180, 200 and 250°C were tested in compression on a METRAVIB Viscoanalysell at a frequency of 5 Hz and scanning a temperature range of 20–300°C at a heating rate of 2°C/min. The glass transition temperature, T_g, of the polymer was determined from the maximal value of the loss tangent, tan δ.

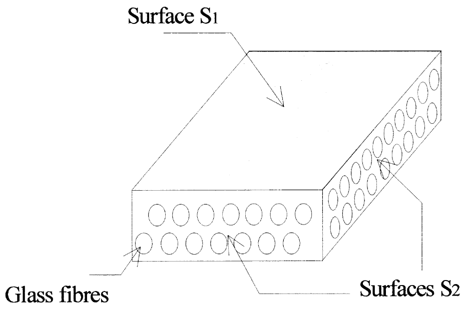

Fig. 1. Schematic representation of adhesive sample.

3. Results and discussion

3.1. Gravimetric study of thermal ageing of adhesive

Relative mass loss (see Eq. (1)) of the adhesive in air in three different geometries (see Table 1) was followed with time at various temperatures. Each sample geometry presents two distinct types of surface. The first, referred to with index 1, corresponds to the polymeric adhesive alone: the part normally intended to be put into contact with the substrate to be bonded and, under normal conditions, representing by far the largest proportion of the adhesive film surface. The second type corresponds to that exposed after a cut perpendicular to surface 1. This surface, noted 2, exposes sections (severed) of the supporting glass fibres. In principle, various sub-types of surface 2 exist since a perpendicular cut, with respect to surface 1, may adopt various angles compared to the fibre axes. However, the fibre support is (orthogonally) reticulate with apparent symmetry for the two sets of fibre axes. Surface 2 corresponds to cuts made perpendicular to either set of fibre axes, it being assumed that the two directions are identical (see Fig. 1).

Defining S_1, S_2 and $S_T = S_1 + S_2$ as surfaces exposed to air during ageing, respectively, of types surface 1, surface 2 and total surface, we considered behaviour for various relative surface ratios. The smallest samples corresponded to the largest ratio S_2/S_T (see Table 1).

Fig. 2 shows gravimetric curves obtained for the three geometries with an ageing temperature of 200°C. It is clear that the relative mass loss is a function of sample size, smaller samples suffering (relatively) greater mass reduction for a given ageing time. This tendency has been observed previously [2,3,5], but mainly for polyimide (PMR 15) matrices reinforced with carbon fibres and at considerably higher temperatures, in the range of 350–400°C.

The influence of geometry on the rate of mass loss is, however, not always evident, as found by Bowles [8], when working with non-reinforced PMR 15 resins. Similarly, in the case of stable fibre/matrix interfaces, it has been found that no geometric effect was detectable [8,9].

Notwithstanding, we have attributed the observed variation in gravimetric behaviour to the presence of two types of surface: with and without exposed fibres, the relative fractions of each, and the integrity of the fibre/matrix interface during ageing. (The fibres themselves are sufficiently stable chemically at the temperatures studied.) Degradation of the fibre/matrix interface may well favour the creation of easier diffusion routes for environmental oxygen to penetrate into the bulk material, thus accelerating decomposition and, as a result, mass loss.

If we consider that during the early stages of ageing, degradation is limited to a thin superficial layer of material, we may hypothesise that the rate of mass loss depends essentially on the local composition and the characteristic mass loss rates of the surfaces exposed [3].

Thus we may model the first part of the gravimetric

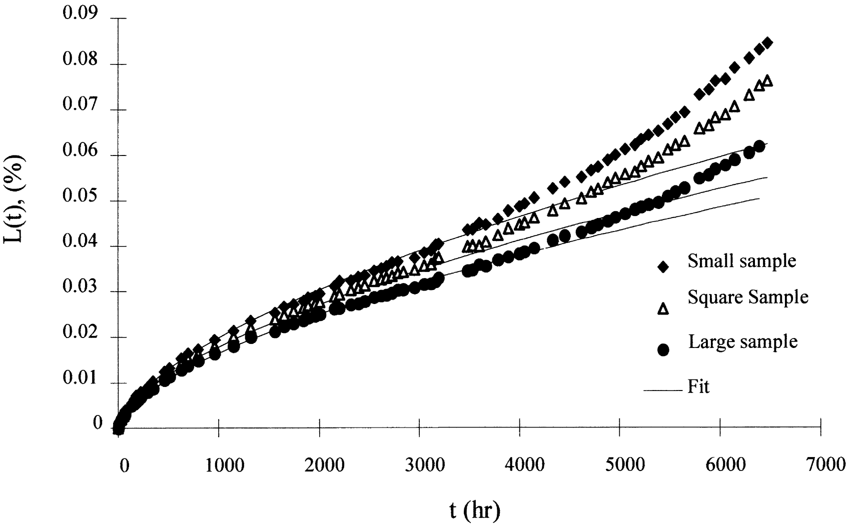

Fig. 2. Gravimetric curves for adhesive samples aged at 200°C—effect of geometry.

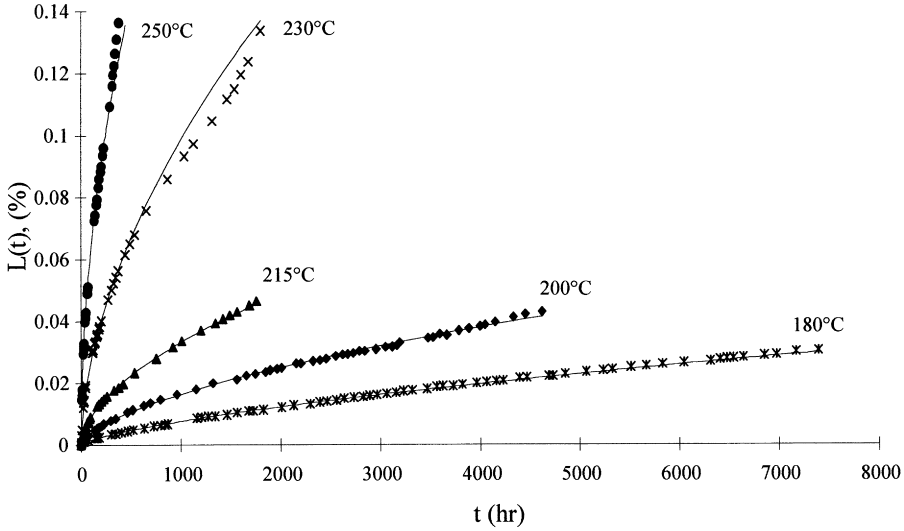

Fig. 3. Gravimetric curves for large samples aged in air: $S_2/S_T \approx 0.2$. Lines correspond to Eq. (2).

curves (Fig. 2) by an empirical relation of the type:

$$\frac{\Delta m}{m_0} = At^n \tag{2}$$

where t is ageing time, n is a constant and A is a parameter depending on sample geometry.

With the above hypothesis, we may relate the fractional mass loss to the various surfaces exposed and to the corresponding rates of weight loss for a given temperature:

$$A = \frac{S_1}{S_T} v_{\mathrm{pl}} + \frac{S_2}{S_T} v_{\mathrm{p2}} \tag{3}$$

with

$$v_{\mathrm{pl}} = \frac{V_{\mathrm{pl}}}{m_s}, \qquad v_{\mathrm{p2}} = \frac{V_{\mathrm{p2}}}{m_s} \tag{4}$$

where V_{p1} and V_{p2} correspond to the rates of mass loss associated to surfaces S_1 and S_2 (see Table 1), units being g mm^{-2} h^{-n}, and m_s represents the mass of adhesive per unit exposed area, in g mm^{-2}.

The values of v_{p1}, v_{p2} and n associated with each of the three geometries tested have been calculated for the five temperatures studied. Figs. 3–5 show the gravimetric curves obtained for the various cases over the time ranges for which we observe a satisfactory agreement between the experimental results and the empirical power law relationship summarised by Eqs. (2)–(4). In Table 2 we present values of v_{p1}, v_{p2} and n as evaluated from the experimental data, using regression analysis.

Whatever temperature is considered in the range covered, we note that $v_{\mathrm{p2}} > v_{\mathrm{p1}}$ and thus the surfaces S_2 with exposed fibres lead to more rapid mass loss than do surfaces S_1, with

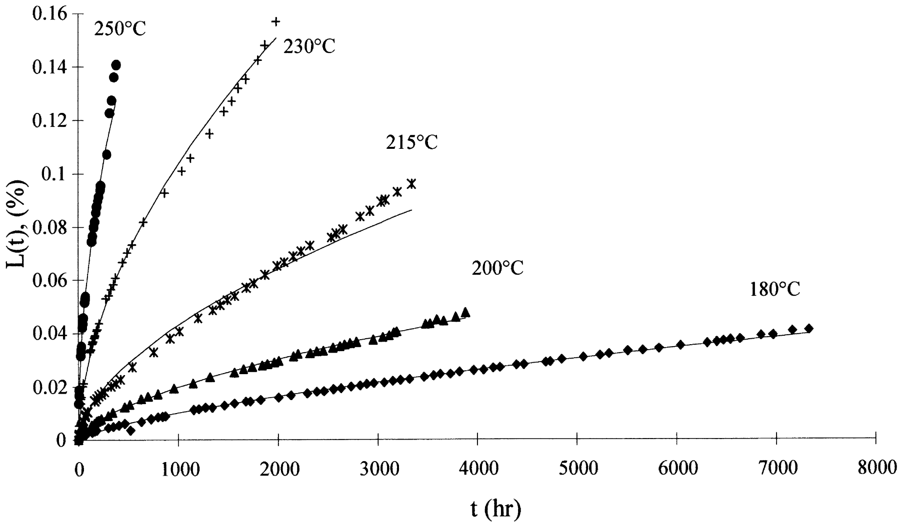

Fig. 4. As for Fig. 3 except square samples with $S_2/S_T \approx 0.29$.

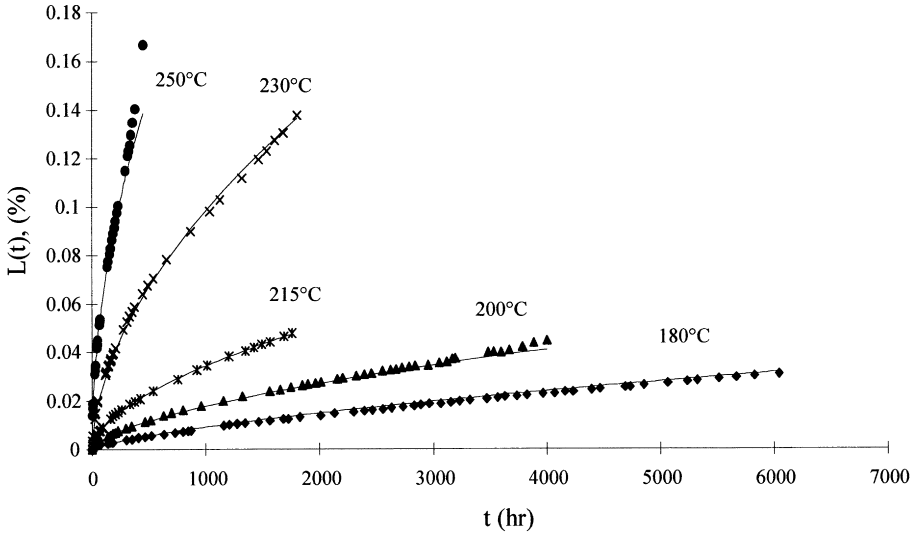

Fig. 5. As for Fig. 3 except small samples with $S_2/S_T \approx 0.38$.

no exposed fibres. We suggest that the more rapid degradation associated with surfaces S_2 is related to local failure of adhesion between fibre and matrix occurring early during the ageing process. This separation may be due to the generation of thermal, differential stresses (linear coefficient of expansion for the polymer is ca. $5 \times 10^{-4}\ °C^{-1}$; that of the glass fibres is ca. $5 \times 10^{-6}\ °C^{-1}$) in the vicinity of the interface. Once fibre/matrix separation has occurred, (presumably) diffusion of oxygen towards the centre of the sample will be facilitated, effectively increasing the surface of the polymer exposed to the deleterious environment and consequently accelerating the overall ageing process.

Consideration of Table 2 shows that the power n of Eq. (2) decreases with increasing temperature. This cannot be presently explained but it may be noted that values are in the range of 0.5–0.7. Dependence on t^n in Eq. (2) with n in this range suggests that mass loss may be some sort of diffusion process not too far removed from Fickian behaviour.

Observations by optical microscope and using X-ray microanalysis have enabled us to add supplementary evidence supporting the above findings and reasoning concerning the influence of the glass fibre support during ageing.

Table 2
Mass loss rate data associated with different surfaces of adhesive exposed to thermal ageing (values calculated from Eqs. (2) and (3))

Temperature (°C)	$v_{p1} \times 10^4 (h^{-n})$	$v_{p2} \times 10^4 (h^{-n})$	n
180	0.50	1.58	0.69
200	2.44	3.40	0.61
215	5.33	17.2	0.57
230	13.5	17.0	0.56
250	55.3	82.9	0.50

3.2. Microscopic characterisation of thermal ageing

In Fig. 6, we present examples of photomicrographs of sections of FM 32 unaged, and after ageing for 500, 1000 and 2000 h at 215°C. The formation of a blackish layer of an apparently porous nature near the edge of the samples can be seen. With ageing time, this layer becomes thicker and this process is favoured by the proximity of micro-cracks (Fig. 6c). In the vicinity of glass fibres, this black degradation layer is able to extend further into the bulk of the sample. Thus, we may suppose that preferential degradation occurs near the fibre/matrix interface, permitting the development of privileged paths for the further diffusion of oxygen.

The composition of this degraded layer has been ascertained using X-ray microanalysis, on samples aged from 500 to 2000 h at 180, 200 and 250°C. Various elemental mappings are presented in Figs. 7–9. The distributions of oxygen, carbon, sulphur and nitrogen have been considered. Both sulphur and nitrogen are (presumably) present in the crosslinking agents in the adhesive. Neither of these elements would seem to evolve significantly in concentration during ageing. In contrast, we observe that a layer rich in oxygen, yet poor in carbon, develops. This may attain a thickness of ca. 75 μm after 2000 h at 180°C or ca. 85 μm at 200°C after the same time.

Analyses effected on samples aged at 250°C showed the formation of a similar layer, yet thinner (ca. 35 μm). Nevertheless, samples aged at this temperature became extremely brittle, due to rapid degradation. It is therefore probable that the true thickness should be somewhat greater but partial disintegration of samples occurred during handling.

We attribute the increase in oxygen in the degraded zones to the chemical fixing of this element to the macromolecular network. Indeed, the thermo-oxidation of thermoset resin based composite materials is often accompanied by the

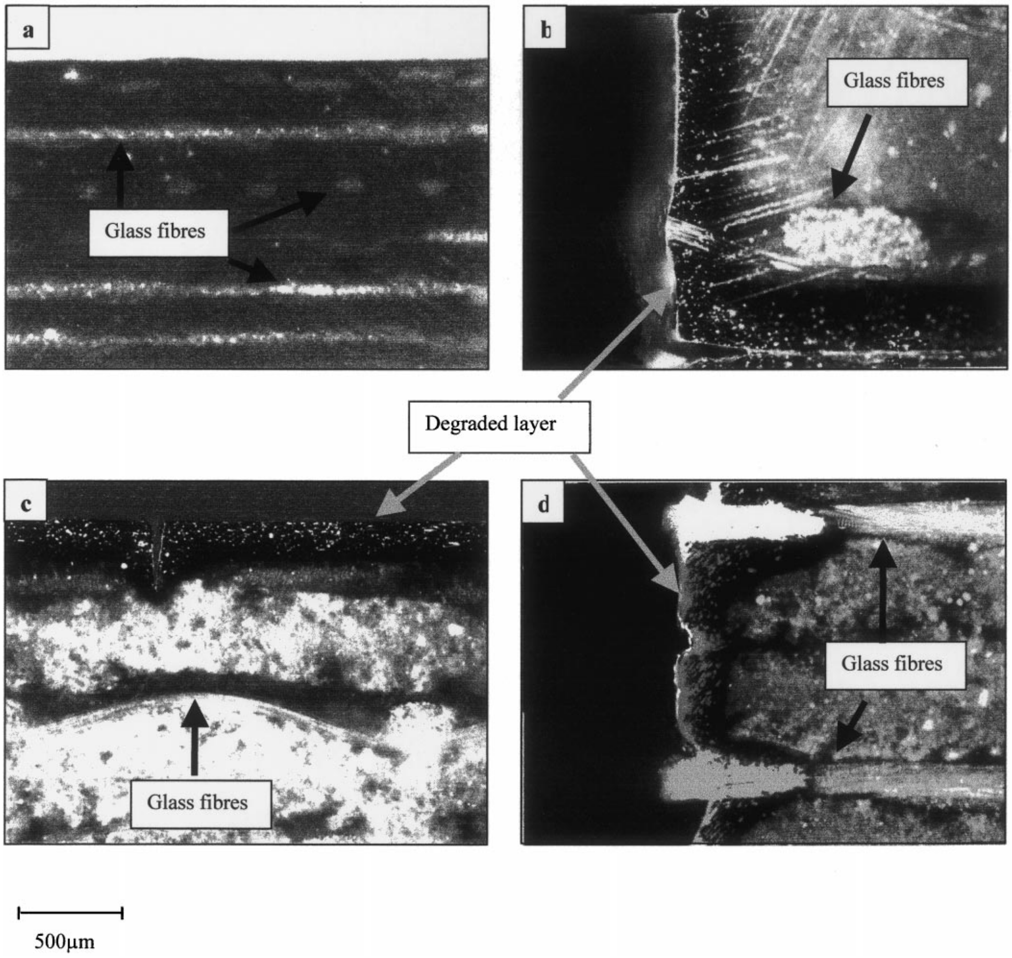

Fig. 6. Optical micrographs of sections of adhesive aged at 215°C: (a) unaged; b) 500 h ageing; (c) 1000 h ageing; (d) 2000 h ageing.

formation of peroxide groups [10]. Following the classical scheme for thermo-oxidation [10], the oxidative reaction leads to the formation of organic compounds obtained from radical induced degradation of the polymeric network initiated by heat and the degradation of the peroxide groups formed. When these carbon containing groups are of sufficiently low molecular weight, they may be eliminated from the network during ageing (leaching). This may explain the reduction in carbon content in the degraded layer and the mass loss of the material. (The implication is that the mass of oxygen attached to the network is less than the total mass of the groups eliminated—an analogous process can occur with degradation of polymers in a water environment at lower temperature [11].)

In Fig. 10, we present the evolution of the thickness of the degraded zone during ageing time perpendicular to the fibres axes, i.e. diffusion into S_1. This thickness increases quite rapidly in the early stages and then attains a plateau. The value of the plateau thickness is an increasing function of temperature and, as may be expected, the rate of increase of thickness also increases with temperature. These results suggest that two processes participate in the oxidation kinetics.

- In the early stages, excess oxygen is available and degradation rate is chiefly governed by the kinetics of oxidation of the polymer. The degraded layer thickens rapidly.
- At later times, the oxidised layer becomes relatively thick and constitutes a barrier to further diffusion. Degradation rate is then largely controlled by the speed of diffusion of oxygen into the, as yet, unaffected polymer.

The degradation kinetics of the adhesive would become, according to this scheme, rapidly dictated by the rate of diffusion of oxygen into the bulk polymer and not by the subsequent chemical reaction—particularly at higher temperatures. In the absence of cracks, ageing rate would be somewhat slowed by the passivating effect of the surface oxidised layer.

Fig. 11 represents the evolution of the oxidised degraded layer thickness with ageing time, both for environmental ingress principally from surface S_1 (direction D_1) and from surface S_2 (direction D_2). Initially, ageing is virtually independent of the type of surface. However after (say), 1000 h, the oxidised layer grows more rapidly in direction D_2 than in direction D_1. This result confirms the hypothesis of an undesirable effect in ageing related to the presence of a

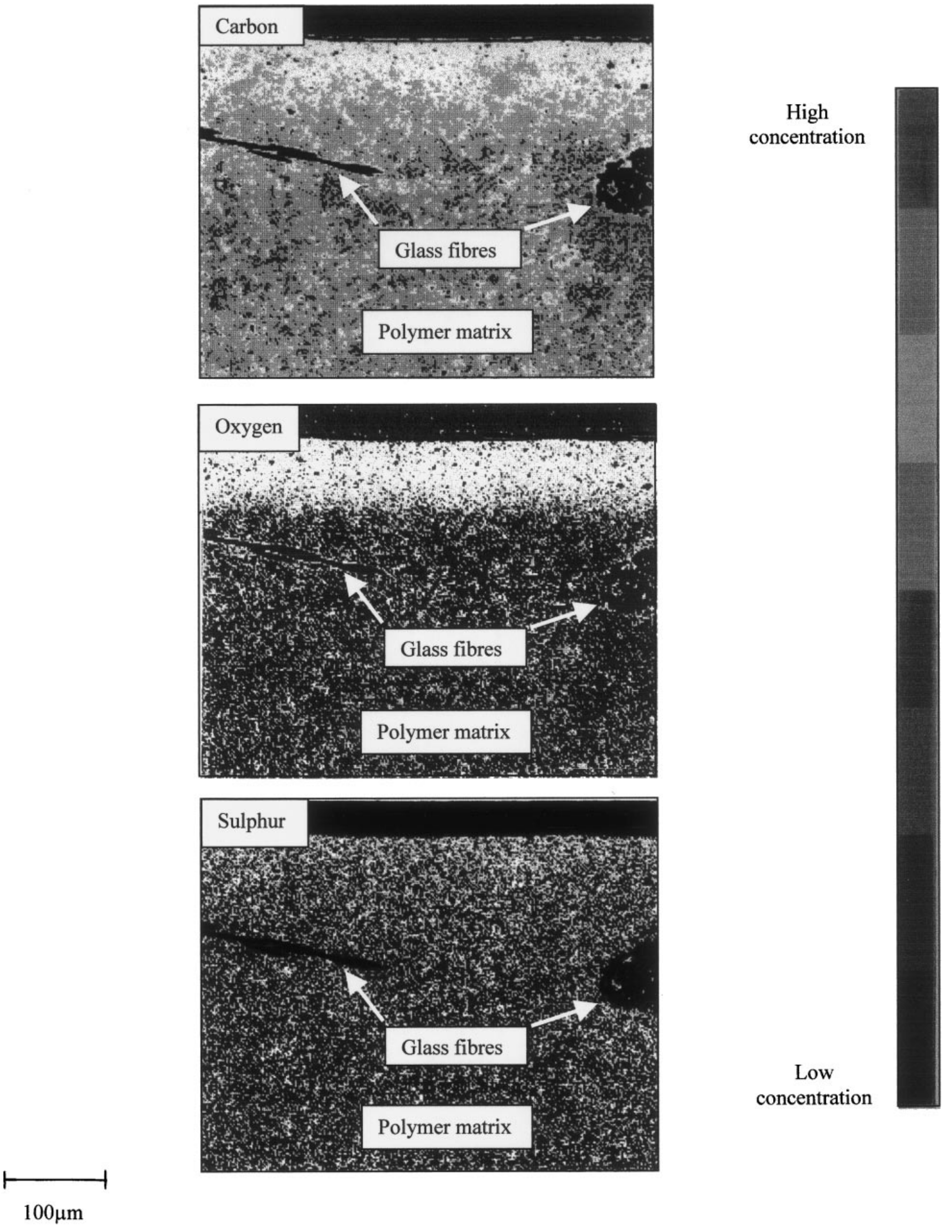

Fig. 7. Elemental mappings for sections of adhesive aged at 180°C for 2000 h (surface analysed: 0.24 mm^2).

fibrous support. At the outset, interfacial cracks and separation should be (relatively) insignificant and thus the two surfaces should present similar overall behaviour. As interfacial damage occurs, oxygen ingress becomes facilitated and ageing rate increases for surface S_2 when compared with surface S_1.

3.3. Evolution of T_g during thermal ageing

For different ageing times at temperatures of 180, 200 and 250°C, we have considered the evolution of the glass transition temperature, T_g, of the adhesive. Results are presented in Figs. 12–14. We observe a drop in T_g with ageing time at all three temperatures, yet both rate of decrease and absolute decrease become more notable with increasing temperature. In particular, the marked drops of T_g at both 200 and 250°C strongly suggest that microstructural modification is occurring to the polymer during ageing. T_g is a function of degree of crosslinking [12] and thus we propose that the modifications involved are principally due to macromolecular chain scission (e.g. [11]). Degradation does not “undo” crosslinks (or, at least presumably does not), yet chain scission will have the same global effect by reducing network density.

At long ageing times, cracks, or microcracks, will allow oxygen to diffuse into the bulk material to oxidise the macromolecular structure. Chain scission and a drop in T_g will therefore presumably be related to thermo-oxidation. Neverthess, results at 180 and 200°C suggest a second

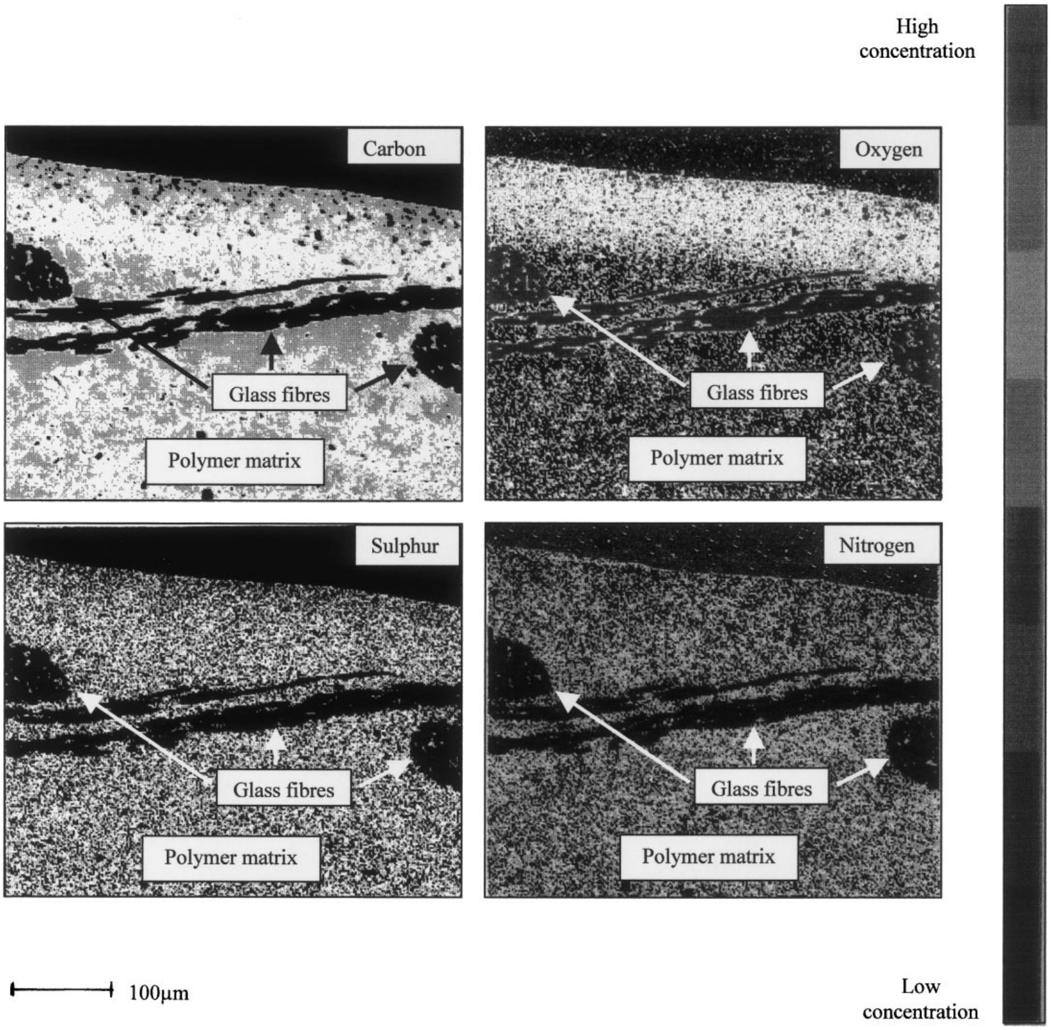

Fig. 8. As for Fig. 7 except ageing at 200°C.

mechanism occurring concomitantly. A process of thermolysis would affect the *entire* sample simultaneously (ignoring any slight time lags in attaining the ageing temperature). Such a degradation mechanism would increase in rapidity with temperature but would not be limited by diffusion processes. Evidence for this comes from the fact that, at lower temperatures, the material would seem to suffer from a relatively homogeneous degradation (drop in T_g) combined with the surface effects and diffusion constituting the main part of this article.

4. Conclusion

The presence of a fibrous support procures many mechanical advantages for composite materials, yet in the case of structural adhesives, the main role is to facilitate handling. In this study, we have shown that the fibres can have undesirable effects when the cured adhesive is submitted to elevated temperatures in the presence of air. Surfaces of the adhesive containing exposed fibres may be more susceptible to oxidation than surfaces consisting uniquely of the polymer. Increased rate of degradation has been shown to be related to interfacial separation between fibres and polymeric matrix. This separation leads to a privileged path for the diffusion of oxygen within the bulk material. Interfacial cracks may be related to thermal stresses due, in their turn, to different coefficients of expansion of the fibres and the matrix.

In the case of the epoxy-imide material studied, we have shown that thermo-oxidation leads to the formation of an oxygen-enriched surface layer, suggesting the fixing of oxygen to the macromolecular network. Degradation is accompanied by the loss of organic matter, leading to reduced local carbon content. At (relatively) low temperature, degradation occurs in a fairly thin surface layer (of the order of 100 μm) and it would seem that the oxidised layer slows further ageing, probably by acting as a passivating barrier. Finally, it would seem that an overall (bulk) process of thermolysis is coupled with the essentially surface predominant oxidative phenomenon.

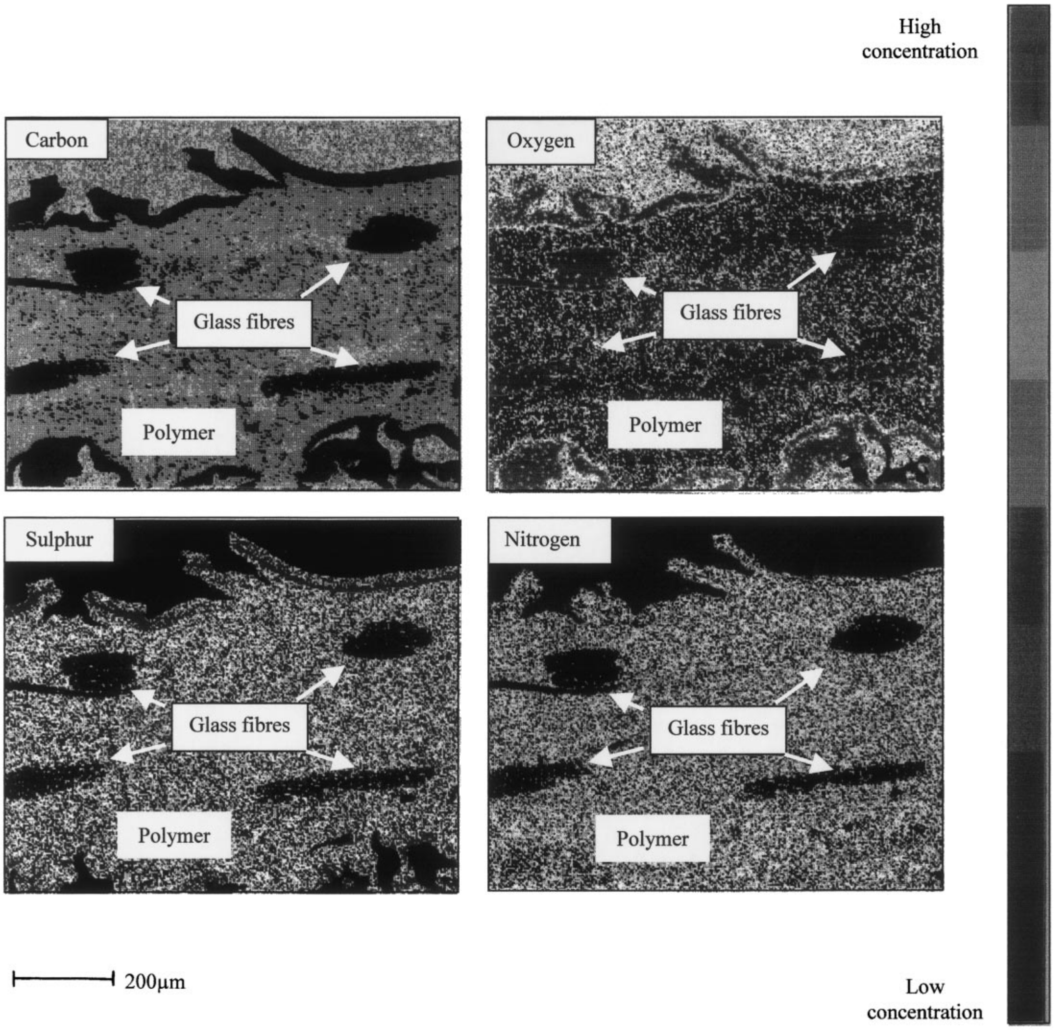

Fig. 9. As for Fig. 7 except ageing at 250°C for 500 h (surface analysed: 0.94 mm^2).

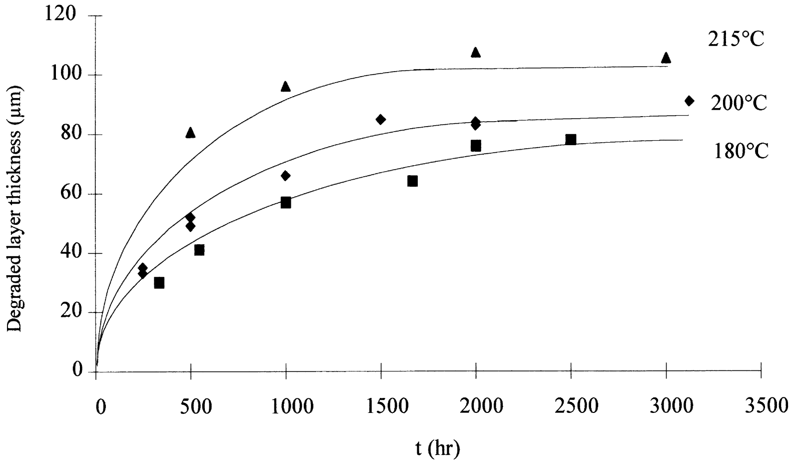

Fig. 10. Thickness of degraded layer (surface S_1) vs. ageing time.

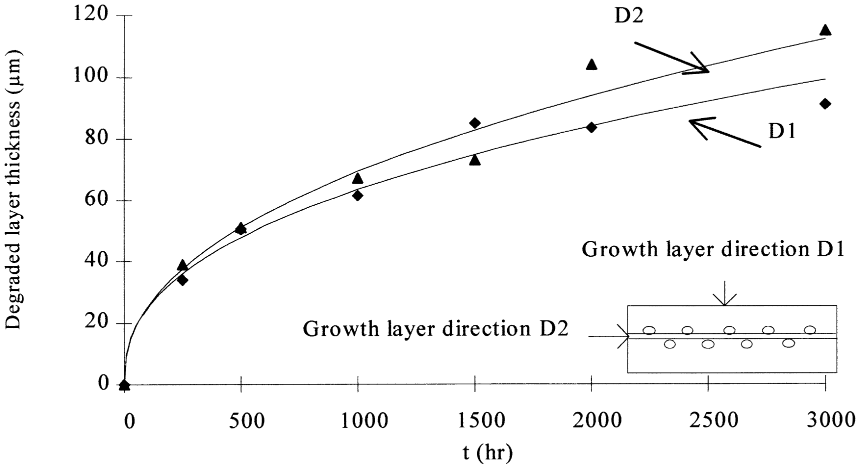

Fig. 11. Thickness of degraded layer vs. ageing time at 200°C following two directions.

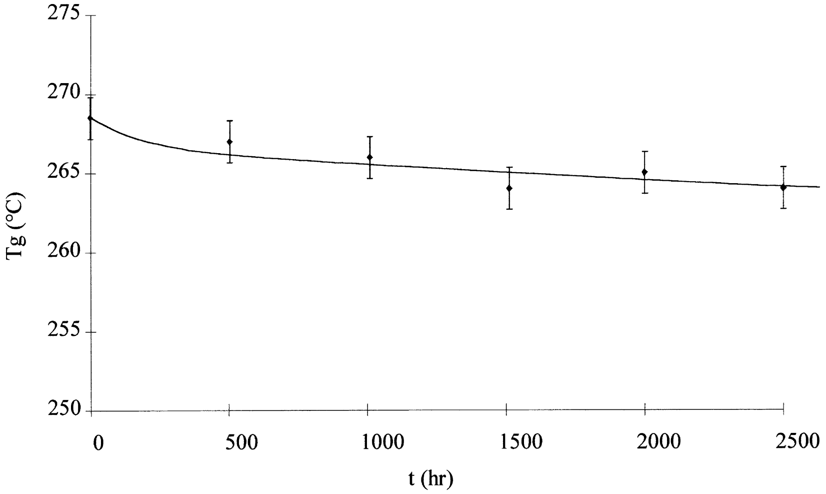

Fig. 12. T_g vs. ageing time at 180°C.

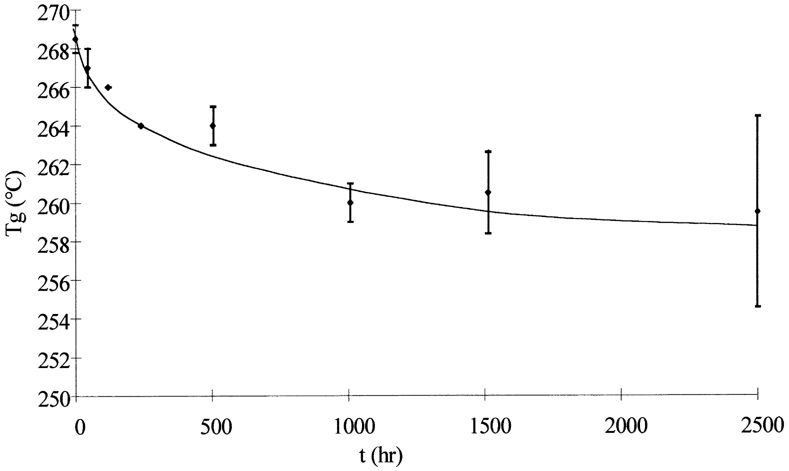

Fig. 13. As for Fig. 12 but at 200°C.

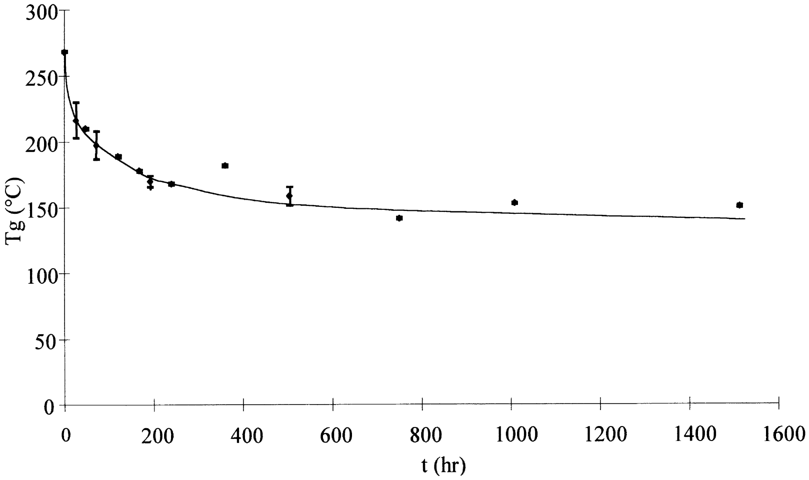

Fig. 14. As for Fig. 12 but at 250°C.

Acknowledgements

The authors thank the Société Nationale d'Etudes et de Constructions des Moteurs d'Aviation (SNECMA) for their financial and material aid and G. Frot for his aid with the X-ray analysis.

References

[1] Bellenger V, Verdu J. J Appl Polym Sci 1985;30:363.
[2] Nelson JB. In: O'Brien TK, editor. Thermal aging of graphite/polyimide composites in long term behavior of composites, ASTM, 1983. p. 206.
[3] Bowles KJ, Meyer A. Specimen geometry effect on graphite/PMR15 composite during thermo-oxidative ageing. 31st International SAMPE Symposium, 1986. p. 1285.
[4] Bowles KJ, Nowak G. J Comput Mater 1988;22:966.
[5] Bowles KJ. Thermo-oxidative stability studies of PMR15 polymer matrix composites reinforced with various continuous fibers. SAMPE Quarterly 1990;21(11):6.
[6] Bowles KJ, Jayne D, Leonhardt TA. Isothermal ageing effects on PMR15 resin. SAMPE Quarterly 1993;18(2):2.
[7] Piccirelli N, Shanahan MER. Polymer 1999;40:1333.
[8] Bowles KJ. Effect of fiber reinforcements on thermo-oxidative stability and mechanical properties of polymer matrix composites. SAMPE Quarterly 1992;23(2):2.
[9] Marceau C, Hilaire B. Polymer 1993;34:2458.
[10] Gillen KT, Wise J, Clough RL. Polym Degrad Stab 1995;47:149.
[11] Xiao GZ, Shanahan MER. J Polym Sci, Part B 1997;35:2659.
[12] Van Krevelen DW. Properties of polymers: their correlation with chemical structure, their numerical estimation and prediction from additive group contributions, Amsterdam: Elsevier, 1991.