ELSEVIER

Ageing of a carbon epoxy composite for aeronautic applications

V. Bellenger*, J. Decelle, N. Huet

Ecole National Suerieure des Arts et Metiers LTVP, 151 boulevard de l'hôpital 75013 Paris, France

Abstract

It is possible to simulate the weight loss and the density increase of an epoxy matrix induced by oxidation with a kinetic model of radical chain oxidation coupled with the equation of oxygen diffusion. In this paper, we checked this kinetic model for UD composite samples and showed that it allows the calculation of the weight loss taking into account two diffusion coefficients of oxygen, the first in the parallel direction to fibres and the second in the transverse direction. Our simulation tool is valid in the validity domain of Arrhenius law and if the crack density remains under a critical value. The carbon fibres do not show a specific effect on the weight loss induced by oxidation at the ageing temperature under consideration.
© 2004 Elsevier Ltd. All rights reserved.

1. Introduction

This work deals with the durability of a structural part for the future European supersonic aircraft ESCT. It is made of a composite material, an epoxy matrix reinforced by carbon fibres. The supposed lifetime corresponds to about 20,000 thermal cycles between −55 and 120 °C with a total length of the plateau at 120 °C of 80,000 h (10 years). Thermal ageing of composite materials shows a weight loss, changes in the glass transition temperature, significant loss of mechanical strength and ultimate strain [1–3]. The chemical degradation strongly depends on the environmental oxygen concentration and on the specimen geometry. The degradation is faster in the 'through-the-thickness fibre end surface' than in the compressed surface and much faster than in the surface cut parallel to the fibres. The oxidation mechanism is limited to superficial layers and from a kinetic point of view, it is diffusion controlled in the parallel direction to fibers whereas it is controlled by the chemical reaction kinetics in the transverse direction [4,5]. There are two ways to accelerate thermo-oxidative ageing [6], an increasing temperature and an increasing pressure of

oxygen. The last one seems better because a test temperature higher or close to the glass transition temperature of the matrix possibly involves other chemical reactions than those observed at moderate temperature [7]. For several years, ENSAM has developed for polymers kinetic models of oxidation coupled with the equation of oxygen diffusion in order to determine the concentration profile of oxidation products in the sample thickness and the weight loss induced by chain breaking reactions [8–10]. In the case of the neat matrix [11], we have shown that it is possible to simulate the behaviour with a kinetic model of radical chain oxidation coupled with the equation of oxygen diffusion. Just now, our aim is to simulate the behaviour of the matrix in a composite part and to check our kinetic model is by studying the weight loss of composite samples induced by oxidation.

2. Experimental

2.1. Material

The composite is a unidirectional carbon/epoxy laminate. The density of carbon fibres is 1780 kg/m^3 and the volume fraction is 64.8±0.6%. The matrix is made of a mixture of aromatic epoxy (triglycidyl amino

---

* Corresponding author. Tel.: +33-1-4424-6308; fax: +33-1-4424-6382.

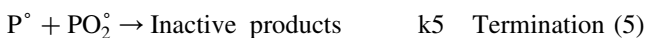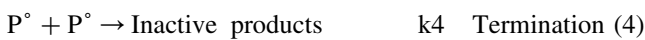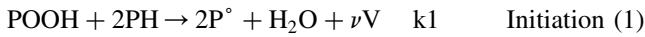*E-mail address:* veronique.bellenger@paris.ensam.fr (V. Bellenger).

phenol-diglycidyl ether of bisphenol F) crosslinked by an aromatic diamine, the diamino diphenylsulphone. There is 30% by weight of a thermoplastic polyether sulphone for increasing impact strength. The initial density of the UD laminate is 1560 ± 10 kg/m^3 and the micro voids fraction is equal to 4.1%. Samples are cured 3 h at $150\,°C + 2$ h at $180\,°C$, then post-cured under vacuum during 1.5 h at $210\,°C$ to achieve a complete cross linking reaction. The initial glass transition temperature is $195 \pm 3\,°C$.

2.2. Ageing

Before ageing, samples were dried under vacuum at $70\,°C$ until they reach a constant weight. It is an important preliminary condition because this matrix is hydrophilic. Samples are exposed in isothermal conditions at 150 and $180\,°C$, with a partial pressure of oxygen included between 2×10^4 and 6×10^4 Pa. The weight variation is measured with an analytical balance of which relative accuracy is 10^{-4}.

2.3. Modelling

For the theoretical calculation of the weight loss, we started from a closed loop oxidation mechanistic scheme [12]. The main difference with the standard mechanistic scheme of oxidation is the initiation step: the main source of alkyl radicals is the hydroperoxide decomposition

POOH + 2PH → 2P° + H$_2$O + νV   k1   Initiation (1)

P° + O$_2$ → PO$_2^°$ k2   Propagation (2)

PO$_2^°$ + PH → POOH + P°   k3   Propagation (3)

P° + P° → Inactive products   k4   Termination (4)

P° + PO$_2^°$ → Inactive products   k5   Termination (5)

PO$_2^°$ + PO$_2^°$ →

   Inactive products + O2   k6   Termination (6)

The reason of this choice is that the matrix is a thermostable polymer and that the thermolysis is quite low at the ageing temperatures under consideration.

From this mechanistic scheme, we can derive a set of differential equations, which describe the concentration evolution of reactive species including the concentration of reactive hydrogen atoms [PH]. [PH] represents the secondary C–H groups or C–H groups, which are located in α position of a heteroatom.

$$\frac{d[P^°]}{dt} = 2k_1[POOH] - k_2 C[P^°] + k_3[PH][PO_2^°]$$
$$- 2k_4[P^°]^2 - k_5[P^°][PO_2^°] \tag{1}$$

$$\frac{d[PO_2^°]}{dt} = k_2 C[P^°] - k_3[PH][PO_2^°] - k_5[P^°][PO_2^°]$$
$$- 2k_6[PO_2^°]^2 \tag{2}$$

$$\frac{d[POOH]}{dt} = -k_1[POOH] + k_3[PH][PO_2^°] \tag{3}$$

$$\frac{d[PH]}{dt} = -k_3[PH][PO_2^°] - 2k_1[POOH] \tag{4}$$

$$\frac{d[O_2]}{dt} = -k_2 C[P^°] + k_6[PO_2^°]^2 + D\frac{\partial^2 C}{\partial x^2} \tag{5}$$

where C is the oxygen concentration and D the oxygen diffusion coefficient. This last Eq. (5) is a balance equation between oxygen which is consumed in chemical reaction (2) or regenerated in reaction (6) and oxygen, which is brought by diffusion according to the second Fick's law.

It is impossible to solve this system analytically, but it can be solved numerically with the Matlab software by the finite difference method of Runge–Kutta (Ode23tb of Matlab) [11]. The sample is discretized into N knots equally spaced with a distance Δx. The lines $i = 1$ and $i = N$ correspond to both surfaces of the sample. At the beginning of ageing, the concentration of alkyl and alkoxy radicals is null. The concentration of hydrogen atoms and hydroperoxide is the same in all the sample thickness (17×10^{-3} and 10^{-7} mol/m^3 for the neat matrix). The surface concentration of oxygen is 3.3×10^{-3} mol/m^3 for experiments carried out at atmospheric pressure.

Then for each direction ($x = 1$, 2 or 3; Fig. 1), each time $t > 0$ and each point $i = 1,…,N$, the system of differential equations can be rewritten for as follows

$$\frac{d[P^°]_i}{dt} = 2k_1[POOH]_i - k_2 C_i[P^°]_i + k_3[PH]_i[PO_2^°]_i$$
$$- 2k_4[P^°]_i^2 - k_5[P^°]_i[PO_2^°]_i \tag{6}$$

$$\frac{d[PO_2^°]_i}{dt} = k_2 C_i[P^°]_i - k_3[PH]_i[PO_2^°]_i - k_5[P^°]_i$$
$$\times [PO_2^°]_i - 2k_6[PO_2^°]_i^2 \tag{7}$$

$$\frac{d[POOH]_i}{dt} = -k_1[POOH]_i + k_3[PH]_i[PO_2^°]_i \tag{8}$$

$$\frac{d[PH]_i}{dt} = -k_3[PH]_i[PO_2^°]_i - 2k_1[POOH]_i \tag{9}$$

For $i = 1, N$ $C_1 = C_N = C_S$ where C is the oxygen concentration and C_S the concentration at the sample surface.
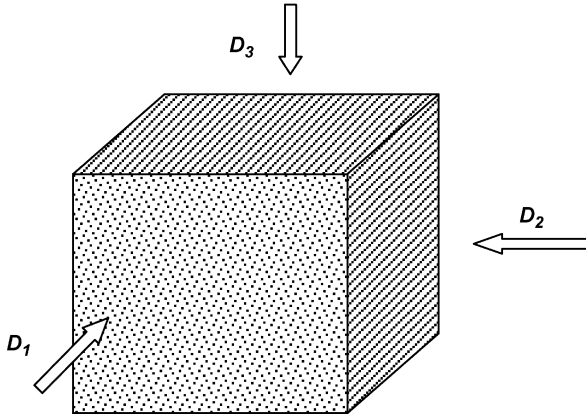
Fig. 1. Scheme of the UD composite sample with the three directions of oxygen diffusion.

For $i = 2,...,N-1$, the variation of oxygen concentration is described by the following equation

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = -k_2 C_i[P^\circ]_i + k_6[PO_2^\circ]_i^2$$
$$+ D_x \frac{C_{i+1} - 2C_i + C_{i-1}}{\Delta x^2} \qquad (10)$$

where D_x is the diffusion coefficient of oxygen in the direction x and Δx the distance between two consecutive knots. The Matlab parameters are reported in Table 1. PH_0 stands for the initial concentration of hydrogen atoms, which can be abstracted by hydroxyl, alkoxy or peroxy radicals in reactions (1) and (3). This concentration is determined from the chemical composition of the matrix, and its calculation is detailed in Table 2. Volat is determined from isothermal experiments of the neat matrix at 150 and 180 °C and atmospheric pressure [11]. The rate constants of the oxidation mechanistic scheme are reported values in literature for rubber [13], polyolefines [14], polar and low molecular weight compounds [15] except for the constant k_3, which is smaller in our case. Concerning the oxygen diffusion in the composite, the diffusion coefficient D_2 in the transverse direction to fibres is slightly lower than the diffusion coefficient measured experimentally for the neat matrix. The diffusion coefficient D_1 in the parallel direction to fibres is calculated from the diffusion coefficient D_2 by the relationship, which Kondo established for the diffusion of water [16]

$$D_1 = \frac{1 - V_f}{1 - 2\sqrt{V_f/\pi}} D_2 \qquad (11)$$

where V_f is the volume fraction of fibres. To calculate the total weight loss of the composite, we add up the weight variations calculated in each direction x and equal to the algebraic sum of O_2 grafted on polymer chains, water and volatile compounds eliminated from the material

$$\frac{1}{m_0}\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{32}{\rho_0}R(C) - \frac{18}{\rho_0}\frac{\mathrm{d}[H_2O]}{\mathrm{d}t} - \frac{M_V}{\rho_0}\frac{\mathrm{d}[V]}{\mathrm{d}t} \qquad (12)$$

Table 1
Matlab parameters used for the modelling

	ΔE (kJ/mol)	Pre-exponential factor
PH_0 (mol/l)	17	–	–
$POOH_0$ (mol/l)	10^{-4}	–	–
$Dens_0$	1.56×10^3	–	–
Volat		14	3.5×10^3
Cs (mol/l)	3.3×10^{-3}	–	–
D_2 (m²/s)		15	4.6×10^{-11}
Cte_1 (l mol^{-1} s^{-1})[a]		130	3.5×10^{11}
Cte_2 (l mol^{-1} s^{-1})[b]	10^8	–	–
2β (l mol^{-1})[c]		45	1.1×10^8
Cte_3 (s^{-1})[d]		65	3.2×10^8
ψ[e]	0.1	–	–
R_0 (mol l^{-1} s^{-1})[f]		73	5.2×10^3

[a] $Cte_1 = k_1$.
[b] $Cte_2 = k_2$.
[c] $2\beta = (k_2 k_6)/(k_5 k_3 PH_0)$.
[d] $Cte_3 = k_3 PH_0$.
[e] $\psi = (k_4 k_6)/(k_5)^2$.
[f] $R_0 = (k_3)^2 (PH_0)^2/k_6$.

where ρ_0 is the initial density,

$$R(C) = k_2 C[P^\circ] - k_6[PO_2^\circ]^2 \qquad (13)$$

$$\frac{\mathrm{d}[H_2O]}{\mathrm{d}t} = k_1[POOH] \qquad (14)$$

and

$$\frac{\mathrm{d}[V]}{\mathrm{d}t} = \nu k[POOH] \qquad (15)$$

3. Results and discussion

The theoretical and experimental curves of weight loss of the composite aged at 150 and 180 °C are shown in Figs. 2–4. The modelling tool gives satisfactory results. To ensure the necessity to use two different values of oxygen

Table 2
Calculation of the concentration of reactive C–H groups towards alkoy, peroxy and hydroxyl radicals

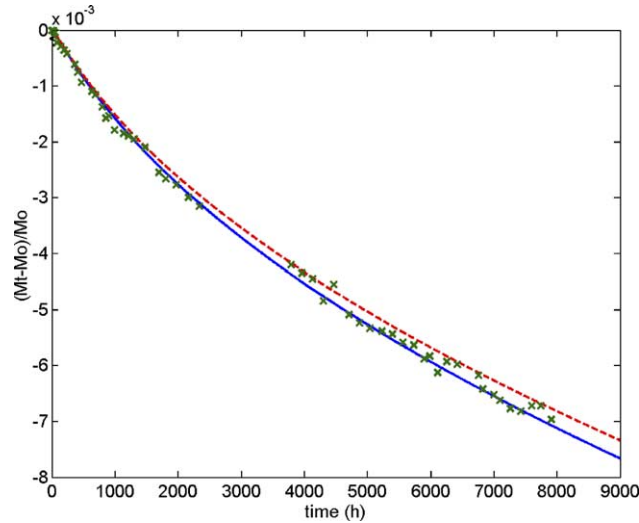| Matrix	DGEBF	TGAP	DDS	PES	Total
Weight (%)	33	22	11	33	99
Reactive C–H groups	12	15	–	–	27
H (mol/kg matrix)	18.5	11.8			30.3

Fig. 2. Experimental (x) and theoretical weight loss (——) of a composite sample $20 \times 20 \times 1$ mm exposed at 150 °C, 2×10^4 Pa, (— — —) theoretical weight loss with a single diffusion coefficient equal to D_2.

diffusion coefficient, the theoretical curve of weight loss calculated with a single diffusion coefficient equal to D_2 has been reported on Fig. 2. Obviously a single diffusion coefficient equal to D_2 gives slightly worse results. However, the fit is not very much sensitive to the value of D if we use a single diffusion coefficient equal to the diffusion coefficient of oxygen in the transverse direction to fibers, due to the low thickness of our samples. Now, the question is: can we extrapolate this behaviour at lower temperature? We checked it with the theoretical and experimental gravimetric curves (Fig. 5) for the neat matrix exposed at 120 and 2×10^4 Pa. Our simulation tool is valid at moderate temperature, in the validity domain of Arrhenius law.

Laminate samples were first exposed to 500 cycles of 2 h between -55 and 150 °C in three various atmospheres, nitrogen, dry air and oxygen. The result of these first experiments was the build-up of microcracks. The crack density was measured by X radiography [17] and is equal to 2.2, 7.2 and 7.9 cracks/cm. The microcracking of samples exposed to nitrogen is simply due to thermal fatigue. For samples exposed to dry air and oxygen, the microcracking is due to the coupling effect of oxidation and thermal fatigue. Then, these pre-cracked samples were aged in isothermal conditions at 150 °C and 6 10^4 Pa of oxygen. The weight loss is shown on Fig. 6. The higher was the initial crack density, the earlier is the discrepancy with the theoretical curve and the more accelerated is the weight loss. When the crack density becomes higher than a critical value, the surface exchange of the sample with atmospheric oxygen is significantly modified and our simulation tool does not work any more. The effect of graphite fibre on the thermo-oxidative stability of PMR polyimide composite is much debated in the literature [18,19], but the ageing tests were carried out at much higher temperatures (600 °F). According to Bowles [20], the behaviour strongly depends on
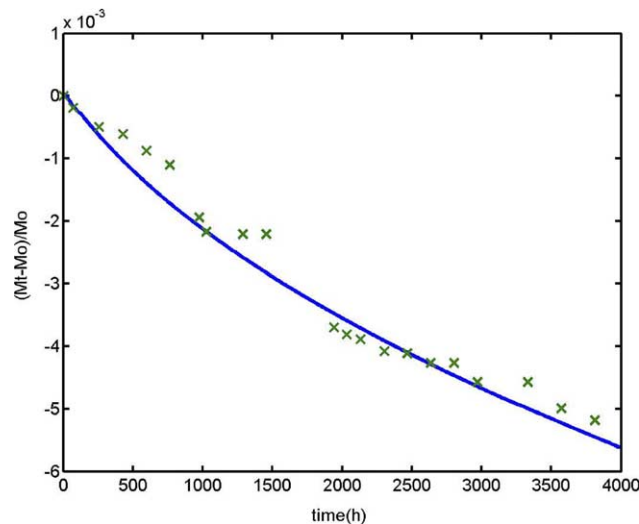

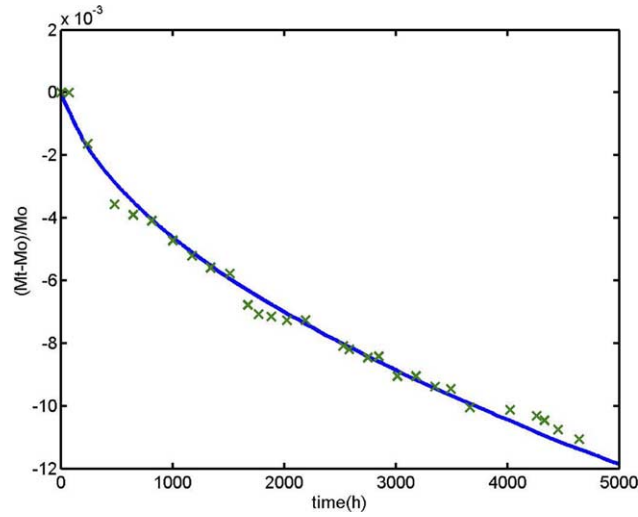Fig. 3. Experimental (x) and theoretical weight loss (——) of a composite sample $20 \times 20 \times 1$ mm exposed at 150 °C, 6×10^4 Pa.

Fig. 4. Experimental (x) and theoretical weight loss(—) of a composite sample $20\times20\times1$ mm exposed at 180 °C, 2×10^4 Pa.
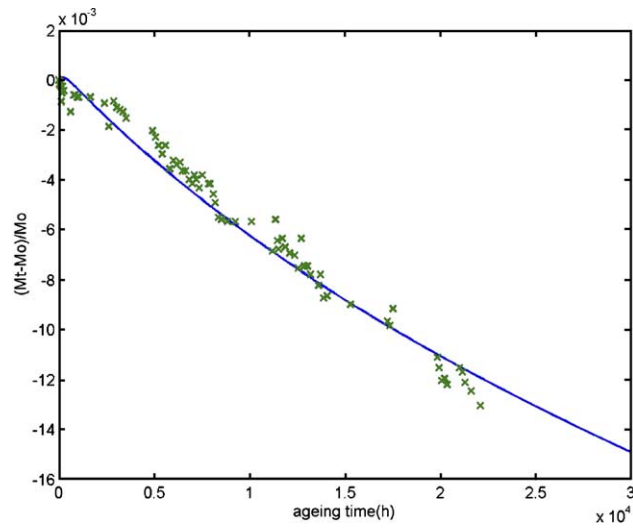

Fig. 5. Experimental (x) and theoretical weight loss(—) of a matrix sample $20\times20\times1.5$ mm exposed at 120 °C, 2×10^4 Pa.
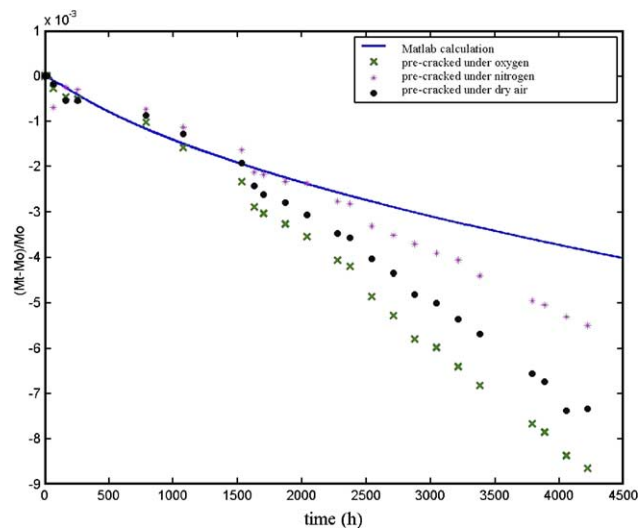

Fig. 6. Theoretical weight loss(—) and experimental weight loss (x) of laminate samples ($1.5\times35\times25$ mm) aged 4500 h at 150 °C, 6×10^4 Pa. These samples were first exposed to 500 cycles of 2 h between -55 and $+180$ °C under nitrogen, or dry air or oxygen.

the fibre-matrix bonding. In our case, we did not observe a specific role of carbon fibres towards the matrix oxidation.

4. Conclusions

We used the kinetic model coupled with the equation of oxygen diffusion established for the neat matrix to simulate the oxidative behaviour of a UD composite sample. The weight loss of the composite sample was calculated taking into account two diffusion coefficients of oxygen, the first (D_1) in the parallel direction to fibres and the second ($D_2 = D_3$) in the transverse direction. D_1 was calculated from D_2 value by the relationship used by KONDO for water diffusion in the same kind of composite materials. Our simulation tool is valid below the glass transition temperature, $T_g = 195$ °C, and we determined the activation energy for all the parameters which obey Arrhenius law. The higher is the temperature; the easier is the diffusion of low molecular weight compounds outside of the sample. When the temperature is higher than T_g, Volat parameter becomes nearly independent of the temperature because the diffusion of volatile compounds in the rubbery matrix is sufficiently fast for an efficient elimination. It was possible to simulate the weight loss of pre-cracked samples when the crack density remains under a critical value. When the exchange surface between the composite material and oxygen is modified, our simulation tool is no more valid. It should be noticed that in the temperature range, which was studied, our modelling does not require a specific role of carbon fibres.

Acknowledgements

References

[1] Bowles KJ, Meyers A. Specimen geometry effects on graphite/PMR 15 composites during thermo-oxidative ageing. 31st Int SAMPE Symp 1986;1285–99.

[2] Parvatareddy H, Wang JZ, Dillard DA, Ward TC, Rogalski ME. Environmental aging of high performance polymeric composites. Effect on durability. Compos Sci Technol 1995;53:399–409.

[3] Madhukar MS, Bowles KJ, Papadopoulos DS. Thermo-oxidative stability and fiber surface modification effects on the inplane shear properties of graphite/PMR-15 composites. J Compos Mater 1997; 31(6):596–618.

[4] Nam JD, Seferis JC. Anisotropic thermo-oxidative stability of carbon fiber reinforced polymeric composites. SAMPE Q 1992;24(1):10–18.

[5] Salin IM, Seferis JC. Anisotropic effects in thermogravimetry of polymeric composites. J Polym Sci B Polym Phys 1993;31:1019–27.

[6] Tsotis TK, Keller K, Lee K, Bardis J, Bish J. Aging of polymeric composite specimens for 5000 h at elevated pressure and temperature. Compos Sci Technol 2001;61(1):75–86.

[7] Tsotis TK, Lee SM. Long term thermo-oxidative aging in composite material. Failure mechanisms. Compos Sci Technol 1998;58(3/4): 355–68.

[8] Audouin L, Langlois V, Verdu J, De Bruijn JCM. Role of oxygen diffusion in polymer ageing: kinetic and mechanical aspects. J Mater Sci 1994;29:569–83.

[9] Abdeljaoued K, Bellenger V, Desarmot G, Verdu J. Thermal oxidation of PMR 15 polyimide matrix. Proceedings of ICCE/7, Denver; 2000. p 75.

[10] Colin X, Marais C, Verdu J. Methodology for lifetime prediction in oxidative ageing application to the study of poly(bismaleimide) thermal ageing. Proceedings of MoDeSt 2000, Palerme, Symp 8; 2000.

[11] Decelle J, Huet N, Bellenger V. Oxidation induced shrinkage for thermally aged epoxy networks. Polym Degrad Stab 2003;81:239–48.

[12] Audouin L, Gueguen V, Tcharkhtchi A, Verdu J. Close loop mechanistic schemes for hydrocarbon polymer oxidation. J Polym Sci A Polym Chem 1995;33:921–7.

[13] Bolland JL, Gee G. Kinetic studies in the chemistry of rubber and related materials. Trans Faraday Soc 1946;42:236–43.

[14] Howard JA, Ingold KU. Absolute rate constants for hydrocarbon autoxidation. Can J Chem 1967;45:793–802.

[15] Korcek S, Chenier JHB, Howard JA, Ingold KU. Can J Chem 1972; 50:2285–97.

[16] Kondo K, Taki T. Moisture diffusivity of unidirectional composites. J Compos Mater 1982;16:82–93.

[17] Rouquie S, Ho NQ, Lafarie-Frenot MC, Bellenger V. Comparison of damage development in C/epoxy laminates during isothermal ageing or thermal cycling. Proceedings of Euromech 453; 2003. p 133.

[18] Vannucci RD. Properties of PMR polyimide composites made with improved high strength graphite fibers. 12th SAMPE Tech Conf 1980;11–30.

[19] Bowles KJ. Thermo-oxidative stability studies of PMR 15 polymer matrix composites reinforced with various continuous fibers. SAMPE Q 1990;6–13.

[20] Bowles KJ, Madhukar MS, Papadopoulos DS, Inghram L, Mc Corkle L. The effects of fiber surface modification and thermal aging on composite toughness and its measurement. J Compos Mater 1997; 31(6):552–79.