Thermal ageing of PMR15 polyimide matrix

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(Received 31 July 1992; revised 21 December 1992)

This study deals with the determination of the role of carbon fibre in the thermal ageing of PMR 15 polyimide matrix composite. The gravimetric behaviour of a neat resin is compared with that of a composite based on the same resin, both polymerized with a very similar cure schedule. Rates of degradation in the stationary stage of gravimetric curves are analysed with an Arrhenius model.

(Keywords: composite; polyimide; PMR 15; neat resin; thermal ageing)

INTRODUCTION

Polynadimide polymers have been widely studied due to their remarkable properties as high temperature matrices for composite materials. Some authors[1-3] have quantified this thermal stability by measuring mechanical properties such as flexural strength or interlaminar shear strength for several composites fabricated with different fibres. Here we present a new approach involving the study of degradation kinetics of the neat resin and the composite.

EXPERIMENTAL

Materials

The neat resin, called hot melt, was formed from three basic monomers: monomethyl ester of 5-norbornene-2,3-carboxylic acid (NE), 4,4'-methylene dianiline (MDA) and dimethyl ester of 4,4'-benzophenonetetracarboxylic acid (BTDE).

The prepreg was manufactured from an alcohol solution of these monomers and HTA7 carbon fibres. This prepreg, an 8 satin weave fabric, was purchased from GEC-Alsthom-IVA (commercial reference CPI 2237).

Composite fabrication and characterization

Panels (300 mm × 300 mm) were autoclave moulded with the following cure cycle: 3 h at 220°C under vacuum (heating rate 1°C min^{-1}) — the pressure (10 MPa) was applied at the end of this stage; 30 min at 250°C (heating rate 1°C min^{-1}); 2 h at 315°C (heating rate 3°C min^{-1}); the composite was cooled to 100°C at 2°C min^{-1} and the pressure was removed. Panels were not post-cured.

The laminates were about 2.3 mm thick with a symmetric form, $(AB/BA)_3$; A and B are two surfaces of the same ply. Composite specimens (20 mm × 10 mm × 2.3 mm) were cut with a diamond saw.

The fibre content was determined to be 66.5 mass% by H_2SO_4/H_2O_2 digestion.

The glass transition temperature, T_g, was determined to be 343°C by thermal mechanical measurements at the highest value of tan δ.

Interlaminar shear strength performed at 20°C before ageing gave a value of 60 ± 1.5 MPa.

Neat resin fabrication

The neat resin plates were manufactured using a two-stage cure process. First, the hot melt was raised to 220°C, held for 3 h and cooled to room temperature under vacuum. This second stage resin was reduced to the smallest powder possible by cryopounding. In the second stage the powder was inserted into a hermetic mould under a hydraulic press. The temperature was raised to 320°C under high pressure (7 MPa), held for 2 h and cooled to room temperature.

The T_g was measured thermomechanically as 393°C.

Isothermal ageing

In previous work[4] we have shown the very important role of moisture absorption on degradation mechanisms. (Water sorption characteristics of some polynadimides will be reported elsewhere[5].) Therefore before the thermal ageing tests, each sample was dried at 90°C until constant weight. After this conditioning thermal treatment, all specimens were weighed at zero time (M_0) and were placed in air at 340, 360 and 380°C for the composite and at 320 and 340°C for the neat resin.

The gravimetric study was carried out by weighing the specimens at various times up to 600 h with an analytical microbalance of relative precision 10^{-4}.

RESULTS AND DISCUSSION

The weight losses at 340°C as a function of exposure time for the neat resin are shown in *Figure 1*. Whatever the

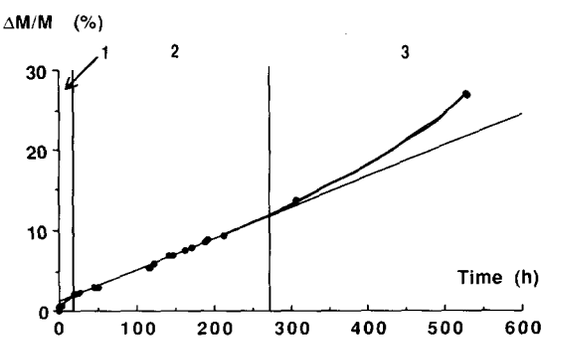

Figure 1 Gravimetric curve of neat resin at 340°C

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0032-3861/93/112458-02

Table 1 Rate of degradation, V_p, for composite and neat resin

Temperature (°C)	V_p, composite ($\% h^{-1} \times 10^{-3}$)	V_p, neat resin ($\% h^{-1} \times 10^{-3}$)
320	–	1.34
340	1.29	3.76
360	3.70	
380	10.00	

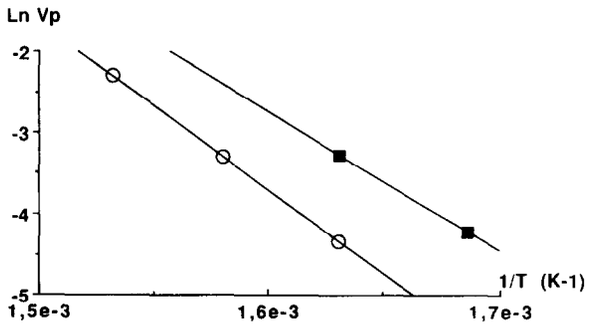

Figure 2 Arrhenius plot of neat resin (■) and composite (○)

temperature or type of sample, the gravimetric curves are of the same form with three areas:

1. a quick transitory state;
2. a stationary state in which the curve could be assimilated to a straight line. This means that the rate of degradation, V_p, can be graphically calculated;
3. the last part corresponding to accelerated degradation.

For each testing condition, V_p could be determined by linear regression. The results are presented in *Table 1*. We note that V_p is an increasing function of temperature. An Arrhenius plot of V_p, reported in *Figure 2*, gives the following apparent activation energies: composite, $\Delta H = 176\ kJ\ mol^{-1}$; neat resin, $\Delta H = 156\ kJ\ mol^{-1}$. It is clear that the two straight lines are not superimposed. So at this stage of the discussion, the following hypothesis could be made. The composite weight loss comes only from the matrix degradation. In other words we suppose that degradation of carbon fibres is negligible (if it takes place) because of the very good thermal oxidation resistance of HTA7 fibres.

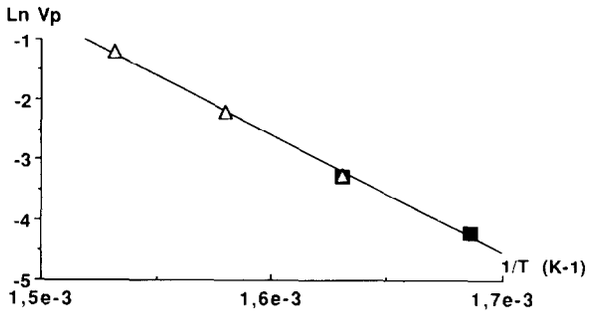

Figure 3 Arrhenius plot of neat resin (■) and resin in composite (△)

With the fibre content, we could calculate the rate of weight loss of the resin in the composite:

$$V_{p,\text{resin in composite}} = V_{p,\text{composite}}(100/T_r)$$

where T_r is resin content $= 100 - T_f$, T_f is fibre content.

Figure 3 shows the Arrhenius plot of the neat resin and the resin in the composite and it is clear that all points fall on one line. The experimental value of the correlation coefficient is $r^2 = 0.999$ and the global apparent activation energy is $156\ kJ\ mol^{-1}$.

This result suggests that fibres have no effect on matrix degradation kinetics. In view of the literature, this is a surprising result. However, to our knowledge, this is the first time that composite and neat resin manufactured by the same company have been compared. In the future, mechanical characterization of thermal ageing and matrix degradation reactions will be determined.

ACKNOWLEDGEMENTS

The authors thank Pr J. Verdu from ENSAM for helpful discussions, Mr G. Dallemagne from Aerospatiale for the thermomechanical test on neat resin, Miss S. Dugue and Mr F. Rossi from ETCA whose consistent efforts have significantly contributed to the success of this study.

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