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Effect of water on the properties of a glass-polyimide laminate

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Effects of accelerated moisture aging on glass–polyimide laminates were investigated using flexural strength measurements and scanning electron microscopy. The degradation rate at 60, 80 and 100° C in water and steam followed first order kinetics. The calculated value of the activation energy for aqueous degradation (E_a = 16.4 kcal mol^{-1}) indicates that the probable mechanism of attack in water and flowing steam is selective hydrolysis of uncycled "amic acid" groups. This causes a decrease in average molecular weight of the matrix with subsequent breakdown of the polymer–fibre interface. The computed value of the activation energy for a single laminate is used to illustrate the calculation of degradation rates and service lifetime of the same or other laminates under various conditions of temperature and water vapour pressure.

1. Introduction

Glass-reinforced composites possessing high mechanical properties and high temperature service capability have achieved increased importance for aerospace applications. Because of their high power transmission, low electric loss, and resistance to thermal oxidative degradation at 175 to 300° C, polyimide resin-based composites are among the most promising of the available systems for meeting the requirements for advanced radomes. However, a major drawback has been difficulty in processing and high porosity that permits extensive moisture absorption and property degradation. Several investigators have studied ways of optimizing the cure and post-cure conditions for glass- and quartz-reinforced polyimides [1, 2] while others [3–5] have studied the effect of water on the properties of polyimide composites under limited test conditions. This investigation was undertaken to examine, in some detail, the effect of water at several temperatures in the liquid state and in flowing steam at 100° C on the flexural properties of glass–PI laminates. Particular emphasis is placed on the role of water on the property degradation and an attempt is made to determine the probable mechanism of attack. The results of a kinetic analysis are used to predict the service lifetime of the laminate.

2. Experimental investigation

A Hexcel Corporation condensation-type F-174-5/7781 prepreg was selected. The F-174 prepreg is composed of style 7781 glass fabric with a 1100S finish impregnated with Monsanto's Skybond 709 polyimide resin. The resin is derived from the reaction of a diacidester mixture of benzophenonetetracarboxylic acid and an aromatic diamine, such as 4,4′-diaminodiphenylmethane. The polymerization occurs in a solution of ethanol, xylene, *n*-methyl-2 pyrrolidone and water by way of a two-step condensation process with a polyamic acid intermediate. The optimum cure cycle for the laminate used in this investigation has been discussed in detail [1]. Essentially, the cure cycle schedule which was carried out at 27 in. Hg (5.1×10^7 dyn cm^{-2}) consisted of a 4.5 h, stepwise heat-up from room temperature to 350° F (177° C). This was followed by cooling to 150° F (66° C) and an eight-step, 7.5 h oven post-cure cycle to 600° F (315° C).

Specimens cut from 2-ply laminates, each of which had been previously weighed, were immersed in water in a reaction vessel at 60, 80 and 100° C for at least 24 h. Other specimens were treated in a specially constructed environmental chamber through which steam at 100° C was passed at a constant flow rate (1.7 litre sec^{-1}). The chamber

TABLE I Effect of vacuum drying on the flexural strength of a glass–polyimide laminate

Temperature (°C)	Treatment time in water (h)	% MOR retained (wet)	% MOR retained (dry)
60	24	75	98
	192	65	85
80	24	67	97
	192	59	83
100	24	61	84
	192	49	57

was vented to the atmosphere such that the pressure of steam was approximately 1 atm. All specimens were brought to constant weight in a vacuum desiccator before properties were measured.

The flexural tests on dried laminates conformed essentially to Federal Test Method Std. No. 406. Tests were made on a three-point loading fixture with a fixed span of 1.588 cm (0.625 in.) (to determine the flexural strength). The specimens were 2.54 cm (1 in.) wide by 6.35 cm (2.5 in.) long and had a nominal thickness of 0.05 cm (0.02 in.). The rate of centre loading was 0.05 cm min^{-1} (0.02 in. min^{-1}).

Infra-red spectral analysis was performed using a Perkin–Elmer 521 spectrophotometer. The spectrum of the water insoluble extract was run in a KBr disc. Scanning electron microscopy was performed on the AMR Model 1000 SEM.

3. Results

Results of flexural tests performed on 2-ply laminates that were treated in water are illustrated in Figs. 1–3. These specimens were cut from three 0.5 m x 0.5 m panels that had been processed according to the same cure and post-cure cycle. Points on the curves represent an average of four tests and the error bars represent the spread in the data. A group of specimens that were treated for 24 and 192 h in water at 60, 80, and 100° C, were tested in the water absorbed condition, i.e. after 10 min of air drying, and in the fully dried condition after being brought to constant weight in a vacuum desiccator. These preliminary results, listed in Table I, indicate a reversible MOR decrease of 20 to 25% for specimens treated for short times and/or lower temperatures, and tested in the water absorbed condition. Although this effect is eliminated by specimen drying, there remains a time and temperature-dependent irreversible effect. Thus the data reported throughout this paper represent tests on specimens which were removed from the boiling water environment, and dried to constant weight in order to separate the reversible effect due to plasticization by the absorbed water from any irreversible chemical effects. The results shown in Fig. 1 clearly indicate the time dependence of the irreversible degradation process. Although the three test panels were given an identical treatment, the degradation rate clearly differs for each panel. The observed decrease in modulus of rupture (MOR) for panel 2 approaches an asymptote after 1200 h of approximately 8 to 10% of the

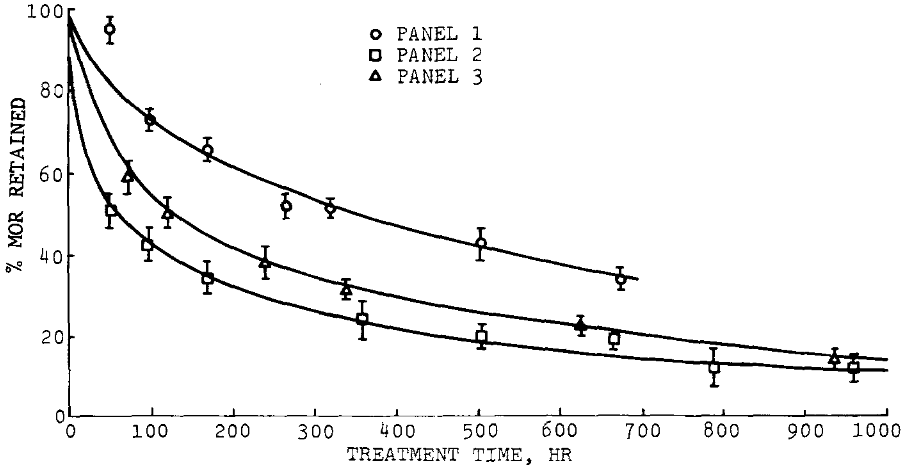


Figure 1 Effect of boiling water on the MOR of glass–PI laminates.

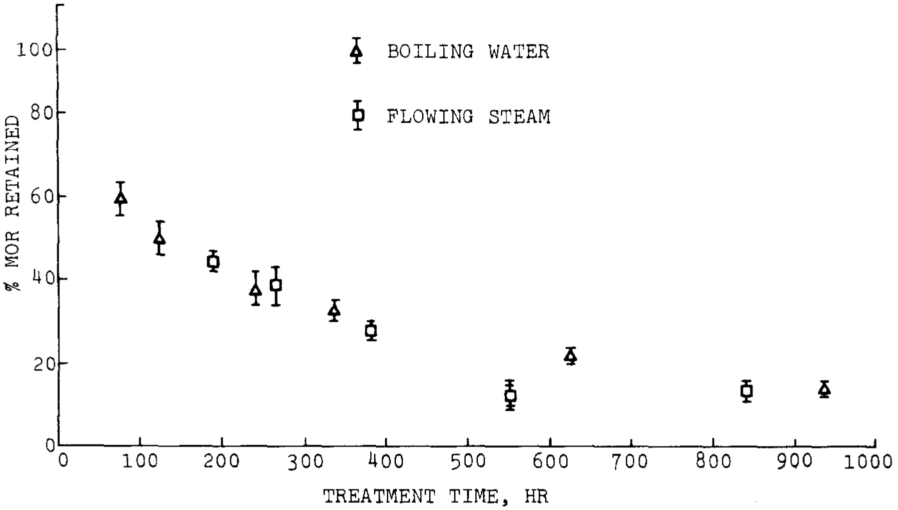


Figure 2 Comparison of boiling water and steam on the MOR of a glass–PI laminate

original MOR $5.55 \times 10^8\ \mathrm{N\,m^{-2}}$ (80.4×10^3 psi) for the untreated material. The time required to approach a similar reduction in MOR for panels 1 and 3 was calculated to be 2100 and 1500 h, respectively. The observed difference in the rate and extent of degradation among the three panels is probably due to small differences in the chemistry and properties of the prepreg. The factors causing these differences would include the volatile content (13.0 ± 2.0%), the dry resin content (34.0 ± 2.0%), the resin flow and the gel time. To a lesser extent, slight differences in the cure and post cure cycles would also affect the retained solvent content as well as the degree of cycling of the amic acid intermediate.

To determine the effect of a lower concentration of water on the decrease in flexural strength of the composite, specimens from panel 3 were treated in flowing steam (1.7 litre $\mathrm{sec^{-1}}$, 100° C). The effect of this treatment on the MOR and a comparison with specimens immersed in boiling water is illustrated in Fig. 2. The overlap of the two sets of data indicates that the rate of degradation is similar for specimens treated in the two media. This suggests that a threshold exists above which the degradation rate is unaffected by the water concentration and that the appreciable degradation of the laminates in boiling water is not in part due to the specimen agitation caused by boiling.

To gain a more complete understanding of the nature of the degradation reaction, the effect of

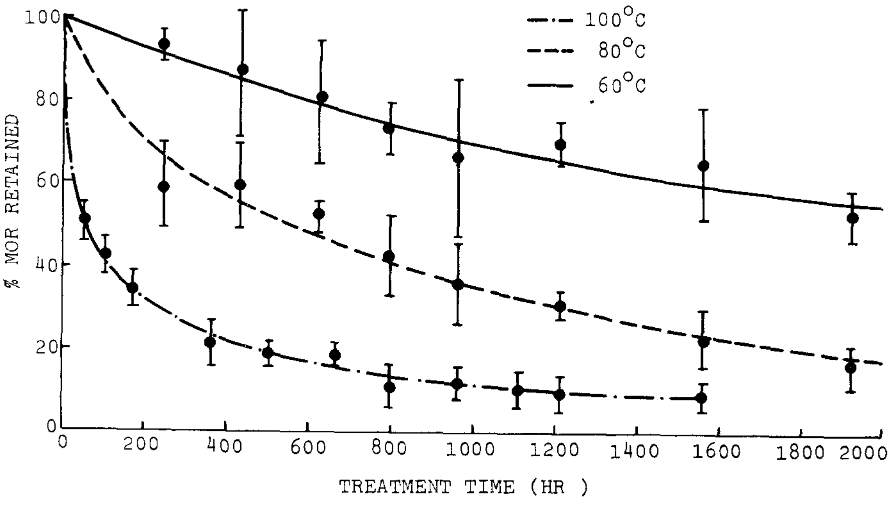


Figure 3 Effect of immersion temperature on decrease in MOR of glass–PI laminate.

water at 60 and 80° C on panel 2 was also studied. This panel was selected because total degradation at 100° C was completed in the shortest time and assuming that the degradation process is thermally activated, following the reaction at lower temperatures would require the shortest time. The results of flexural tests for specimens treated at 60, 80 and 100° C are illustrated in Fig. 3. Although the reaction did not go to completion at the lower temperatures, substantial degradation did occur. After 1920 h, at 80° C, the MOR was reduced to 16.4% of that for the untreated laminate whereas the MOR of specimens treated for the same time at 60° C was reduced to 52.9% of that of the untreated laminate.

Computer-assisted least squares curve fitting of the data illustrated in Figs. 1 to 3 indicates that the decrease in MOR follows first order kinetics. The first order rate constants derived from the best fit of each data set are listed in Table II. The temperature dependence of the reaction rate constants can be obtained from the Arrhenius equation. The first order rate constants for panel 2 at 60, 80 and 100° C were used in a computer-assisted least squares program to calculate the activation energy, E_a, and the pre-exponential frequency factor, A. These values are 16.4 kcal mol^{-1} and 1.73 x 10^7 h^{-1}. If one assumes that the same degradation reaction is occuring for the three panels and that this reaction would occur at room temperature as well as 100° C, the activation energy and empirical rate constants obtained from the decrease in MOR at 100° C for a specific panel can be used to calculate rate constants at lower temperatures utilizing the integrated form of the Arrhenius equation. These results are also listed in Table II.

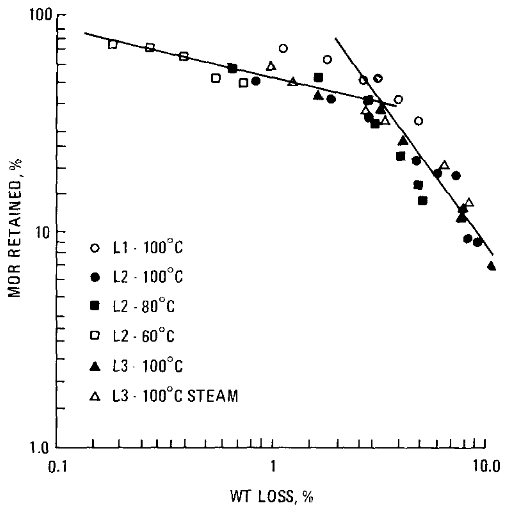


Figure 4 Correlation between MOR decrease and specimen weight loss for glass–PI laminate treated in water.

As indicated previously, the specimens were dried to constant weight after aqueous treatment to separate the reversible plasticization phenomenon from any irreversible chemical reaction. A temperature and time dependent decrease in specimen weight accompanied the decrease in MOR. The possibility of a correlation between MOR and weight loss, independent of treatment time and temperature was indicated. This relationship is shown in Fig. 4 for the three laminates investigated. Each datum point represents an average weight loss and average MOR. Specimen treatment includes 60, 80 and 100° C in water as well as 100° C in steam. Least squares fit of the data indicates the best fit corresponds to two straight lines. The equations for these lines are:

line 1 log (% MOR retained) = 1.72 − 0.22 log (% wt loss);

ling 2 log (% MOR retained) = 2.27 − 1.33 log (% wt loss).

The intersection of these lines corresponds to 40% MOR retained and 3.1% weight loss. These data suggest two distinct mechanisms account for the decrease in MOR and weight loss.

The maximum weight loss (11%) as shown in Fig. 4 represents a percentage of the total composite weight that consists of 22 to 26% polyimide

TABLE II Rate constants for aqueous degradation of glass–PI laminates

Panel	Medium	k (h^{-1})				
		25° C	45° C	60° C	80° C	100° C
1	water	7.5 x 10^{-6}*	4.6 x 10^{-5}*	1.5 x 10^{-4}*	6.0 x 10^{-4}*	2.1 x 10^{-3}
2	water	1.5 x 10^{-5}*	8.9 x 10^{-5}*	2.8 x 10^{-4}	1.3 x 10^{-3}	4.0 x 10^{-3}
3	water	1.0 x 10^{-5}*	6.4 x 10^{-5}*	2.0 x 10^{-4}*	8.3 x 10^{-3}*	2.9 x 10^{-3}
3	steam					2.0 x 10^{-3}

* Calculated from Arrhenius equation.

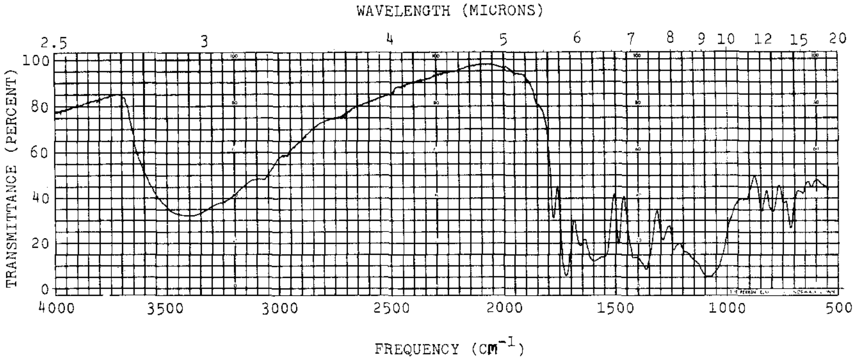
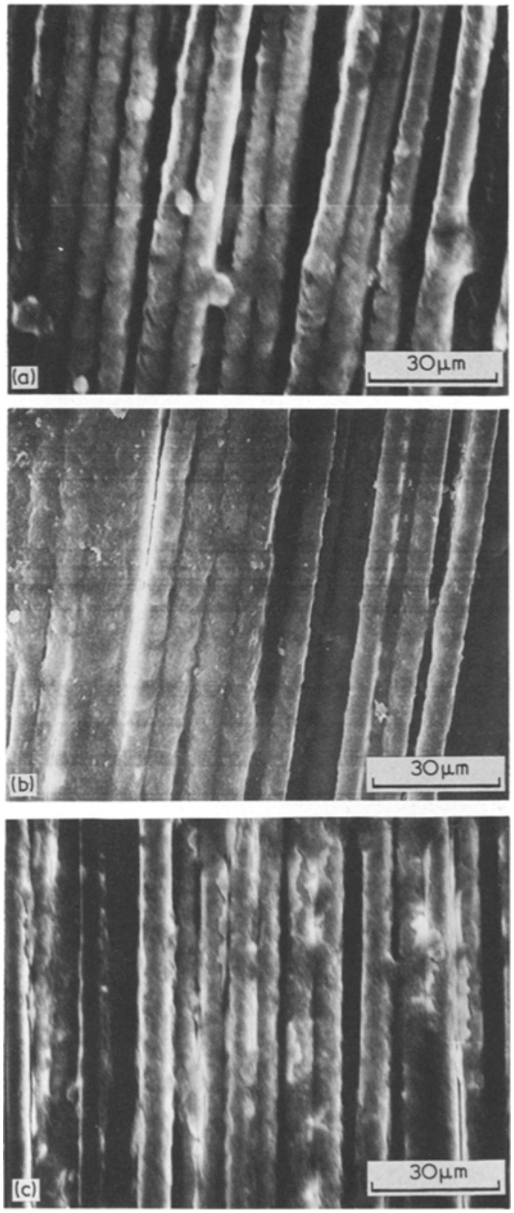


Figure 5 Infra-red spectrum of aqueous extract from glass–PI laminate treated in boiling water.

[4]. If this observed weight loss is due primarily to the loss of polymer, the maximum polymer weight loss would be 42 to 50% of the total polyimide content. This, however, would be unlikely since little polymer would remain to bind the glass fibres. Thus, it was assumed that the weight loss was partially due to loss of fibres. To confirm this assumption the brown solid residue which remained in the reaction vessel after treatment of the speci-



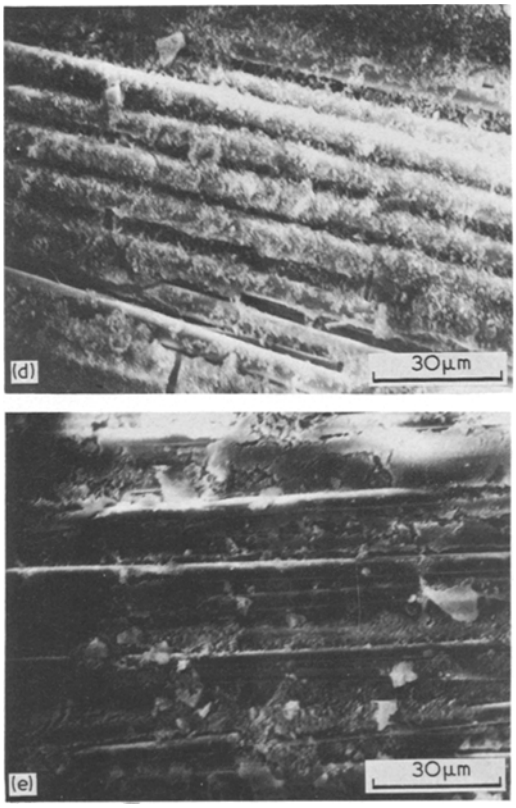


Figure 6 Scanning electron micrographs of glass–PI laminate. (a) Untreated, (b) treated 99 days in water at 60° C, (c) treated 40 days in water at 80° C, (d) treated 65 days in water at 80° C, (e) treated 33 days in water at 100° C.

mens was collected, dried for 60h at 95° C over SiO_2, and an infrared spectrum was run (Fig. 5). The major absorption peaks at 1780, 1724, 1664, 1490, 1424, 1365, 1290 and 1242 cm^{-1} are consistent with those expected for the Skybond series resins [6], indicating that a major product is low molecular weight polyimide. The broad peak at 1080 cm^{-1} is due to the Si–O–Si vibration of the glass fibres that are removed from the surface of the laminate either following or accompanying the loss of the polymer matrix. The broad absorption band at 3400 cm^{-1} is due to water absorbed in the KBr disc or to water of hydration at the surface of the glass fibres.These results confirm that the weight loss is due to the loss of both polymer and fibres.

In order to determine whether the glass fibres are removed continuously during the solution treatment of the laminate or only after prolonged treatment, scanning electron microscopy was carried out on specimens treated at 60, 80 and 100° C. Representative micrographs are shown in Fig. 6. The untreated laminate (Fig. 6a) contains a uniform coating of polyimide over the glass fibres, permitting the transfer of load from fibre to fibre. Specimens treated at 60° C for 99 days in water (Fig. 6b) contain a uniform coating of polymer similar to that of the untreated specimens. However, some evidence of polymer flaking and embrittlement does exist. The MOR of these specimens is only 50% of that of the untreated specimens. The very small weight loss (0.7%) of these specimens on drying under vacuum before mechanical testing as well as the surface appearance suggest that the degradation of strength is due to selective hydrolysis. Specimens from the same laminate which where treated for 40 days at 80° C in water retained only 36% of the original MOR and at the same time lost 2.8 wt%. A typical specimen is shown in Fig. 6c. The coating in part resembles that of the untreated laminate in that it still appears to be distributed over the fibres. However, there is indication of polymer breakdown as evidenced by the extensive surface flaking and coating separation from the fibres, which would account for the rather substantial weight loss. Additional exposure to water at 80° C (65 days) results in a complete breakdown of the polymer coating (Fig. 6d). The MOR of these specimens is only 23% of that of the untreated laminate. The weight loss of 3.9% is due primarily to polymer loss since the fibres still appear to be held in place. Fig. 6e shows the effect of the most severe attack, i.e. 33 days in boiling water. Many of the outer fibres have been leached from the specimen and the lower layer of polymer is brittle and discontinuous. The weight loss of 7.9% is due to both polymer and fibres. These specimens retain only 11% of their original strength which was the lower limit for this investigation.

4. Discussion

Agreement among the activation energies for the aqueous degradation of 2-ply glass-polyimide laminate reported in this work ($E_a = 16.4\,\mathrm{kcal\,mol^{-1}}$) and that for the hydrolytic degradation of "Kapton" ($E_a = 16.2\,\mathrm{kcal\,mol^{-1}}$) and "Poly-X" ($E_a = 16.8\,\mathrm{kcal\,mol^{-1}}$) suggests a similar mode of attack [7, 8].* The proposed mechanism for the degradation of the polyimide films involves selective hydrolysis of uncycled "amic" acid linkage involving a cooperative mechanism with the ortho-substituted carboxyl group. Selective hydrolysis of the Skybond matrix is not unexpected since the resin is polymerized by way of a two-step condensation process with a "polyamic" acid intermediate similar to that formed in the two polyimide films previously investigated. The scanning electron microscopy results show that the breakdown of the structural integrity of the resin is a gradual process rather than a catastrophic one which would be expected if the breakdown occurred at the fibre–matrix interface. In a rigid system, such as a polyimide matrix composite, exposure to boiling water will not break sufficient bonds between the coupling agent and the fibre as long as the resin retains its integrity [9]. Furthermore, our tests were performed on specimens that were dried to constant weight. This drying would eliminate water that competes with the silane coupling agent for the formation of hydrogen bonds at the glass fibre surface. Therefore, it is suggested that the probable mechanism of hydrolytic degradation of the flexural properties of glass-PI is selective hydrolysis of uncycled amic acid linkages causing loss of matrix integrity with subsequent breakdown of the matrix–glass adhesion.

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* "Kapton" and "Poly-X" are trade names for condensation type polyimide films based upon pyromellitic dianhydride, and either 4,4′ diaminodiphenylether or a long chain aliphatic diamine, respectively.

Generation of kinetic data under specific conditions can be very useful in predicting an upper limit service lifetime of a part which experiences a continuous exposure to water. For example, if a glass–PI laminate is designed to be used at loads of approximately 3.86×10^8 N m^{-2} (56×10^3 psi), it is possible to calculate the time required for the properties to decrease to that value from the generated rate constants utilizing the integrated form of the first order rate equation, that is,

$$t = \frac{1}{k} \ln \frac{(\mathrm{MOR})_0}{(\mathrm{MOR})_{\mathrm{DL}}}$$

where k = first order rate constant, $(\mathrm{MOR})_0$ = modulus of rupture of the untreated laminate, 5.55×10^8 N m^{-2} (80.4×10^3 psi), $(\mathrm{MOR})_{\mathrm{DL}}$ = modulus of rupture at design limit, 3.86×10^8 N m^{-2} (56×10^3 psi). Calculations of this type predict a lifetime of 181 h for laminates exposed to flowing steam. Specimens that were not dried before testing or which were tested at elevated temperatures would be expected to fail after a shorter exposure time because of the additional contribution due to the plasticization by the absorbed water as well as the effect of elevated temperature on the mechanical properties of glass-reinforced composites. Cyclic or discontinuous exposure similar to aircraft use conditions would not be expected to appreciably affect the matrix degradation rate since irreversible hydrolysis would be expected to be cumulative, dependent upon temperature and concentration of water vapour, and number of hydrolyzable linkages present. However, in the case of both the statically and cyclically loaded specimens one would expect an additional loading effect on the rate of degradation of the specimen or part. Therefore, service lifetime calculations based upon matrix degradation would serve, at best, as an upper lifetime limit.

An analysis of this type can be extended to include relative humidity profiles. It is unnecessary to perform hydrolytic stability tests for polyimide resins at any temperature other than 100° C because the activation energy has been determined over the temperature range of 60 to 100° C for the glass–PI composite and over the 25 to 100° C range for Kapton. Since the agreement is good, these results can be used to calculate the degradation rate at reduced pressures at any temperature below 100° C after rate constants are calculated at 100° C at the same water vapour pressure. It is probable that the Arrhenius plot still holds at temperatures greater than 100° C, thus enabling the calculation of the rate constants for low water vapour pressure at temperatures of approximately 150 to 200° C and extending this to a calculation of k at lower temperatures. The upper temperature limit would, of course, be specified by the thermal stability of the matrix and coupling agent.

5. Conclusions

Moisture attack of a 2-ply glass–PI laminate occurs within the polyimide matrix, rather than at the fibre–matrix interface. The probable mechanism of attack is selective hydrolysis of the uncycled amic acid linkages which causes a decrease in average molecular weight and embrittlement of the matrix resulting in the inability of the matrix to transfer load. Prolonged immersion in water results in a complete breakdown of the structural integrity of the composite with a loss of the outermost fibres.

The three laminates investigated were all subjected to the same cure and post-cure treatment. However, differences in the rate of attack were apparent and these appear to be due to the small variation in chemistry among the panels. In spite of these differences the modulus of rupture for the three panels subjected to varying water treatment times the temperatures has been related to the specimen weight loss. In fact, it appears that specimen weight loss can be employed to predict the modulus of rupture of these laminates without prior aqueous treatment history.

The use of reaction rate constants generated at one temperature coupled with the activation energy for the degradation process has been demonstrated as a suitable technique for determination of laminate failure time under specific conditions of environment temperature and water vapour concentration. These techniques can be expanded to include more typical environmental conditions, which would be useful in the prediction of the service lifetime of a product.

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