

ISOTHERMAL AGING OF AN ADVANCED HIGH TEMPERATURE CARBON FIBRE COMPOSITE

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SUMMARY: Preliminary results from isothermal aging at 250°C of high temperature carbon fibre reinforced composites are presented. Composites made from two different thermosetting polyimide resin systems have been compared: one the novel CBR 320/328 resin developed by CSIRO and the other the commercial Matrimid 5292 A/B system. The two materials were found to behave quite differently after being aged at this temperature for periods of up to six weeks. The mode I interlaminar fracture toughness of the commercial system decreased substantially after four weeks of aging due to matrix embrittlement. This coincided with significant chemical changes (as detected by Raman and Fourier Transform Infrared Spectroscopy) and the loss of a measurable glass transition temperature. None of these observations were noted in the CSIRO composites which showed only surface degradation after four weeks at 250°C. Contrary to this, the thermal stability evaluated on the basis of weight loss data over the same period of time, indicated that the commercial composite (12% weight loss) was more stable than the CSIRO composite (16%).

KEYWORDS: thermosetting polyimide, aging, interlaminar fracture toughness, FTIR, Raman, DMTA.

INTRODUCTION

In the years since the Concorde first led the race for supersonic passenger aircraft, significant advances in technology have taken place. These have facilitated research and development in introducing a new breed of high speed civil transport (HSCT) to be launched early in the next century. The demands placed on materials for these aircraft are intense; not only must they have outstanding mechanical properties and yet still remain lightweight, but they must also be able to withstand the extremely high (177°C) surface temperatures of an aircraft cruising at mach 2.5. Components are expected to maintain their performance for up to 20,000 flights, thus long term thermal stability is a major driving force in the selection of these materials.

The current study involves aging of carbon fibre reinforced composites of CBR320/328. CBR 320/328 is a resin system invented by CSIRO for high temperature applications[1] and this is one of many resin systems developed to satisfy the above requirements. The resin is based on bismaleimides which have superior processability to conventional polyimides in terms of composite fabrication. [2]. These composites have a high T_g (of approximately 300°C) and good thermal stability. A commercial high temperature resin system has also

been investigated for the purpose of comparison, the CIBA GEIGY Matrimid 5292 A/B system.

The chemical structures of the resin components are given in Figure 1 along with the proposed cure mechanism. All compounds are highly aromatic structures which result in a matrix with high thermal stability. It is generally accepted that these systems are cured via an ene reaction followed by Diels Alder addition as depicted, although there are also many other side reactions which take place. Thus, the final structure of the cured matrix is extremely complicated and has not been completely determined.

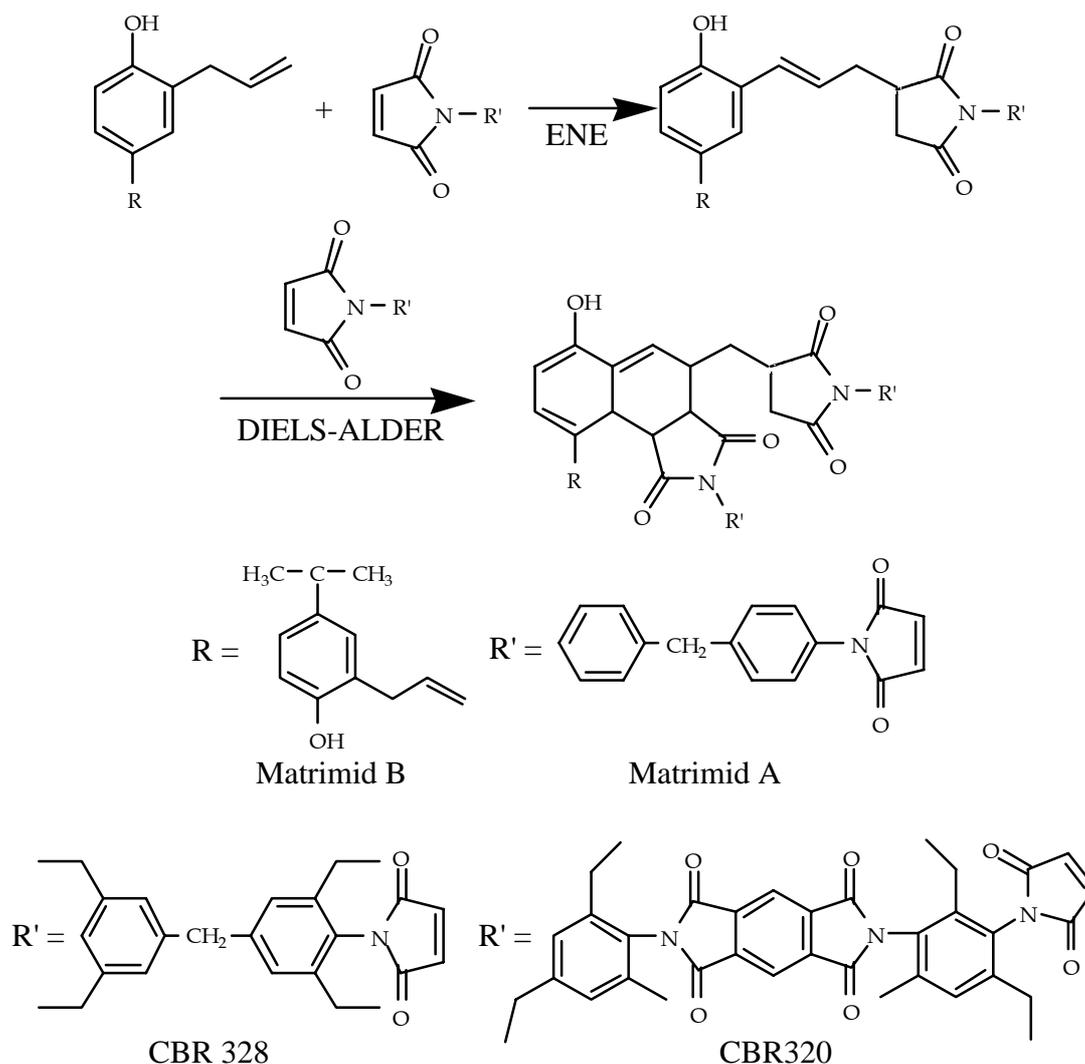


Fig. 1: Proposed scheme for cure chemistry, indicating the chemical structures of the resin components.

EXPERIMENTAL DETAILS

Materials

Matrimid 5292 A and B (4,4'-bismaleimidophenylmethane and 3,3'-diallylbisphenol A respectively) were obtained from CIBA GEIGY. CBR 320 and 328 were prepared in large scale batches via previously reported synthetic routes from the respective diamines. [1], [3] Unidirectional carbon fibre cloth with E glass weft (FC150U100) was obtained from Advanced Composites and had a density of 150 gm/m².

Specimen manufacture

The components of each resin system were combined and heated to 200°C under vacuum to remove any residual solvents from their synthesis. Failure to do this adequately can lead to voids in the cured laminate. The ratio of the components used to formulate the commercial resin system were specified in the material data sheet to be Matrimid A: Matrimid B, 1.3 : 1 (w/w). The formulation of the CSIRO resin was CBR 320 : CBR 328 : Matrimid B, 1 : 1.5 : 1.2 (w/w).

Prepregging was performed by solution casting. A mould was built for this purpose from a plate of aluminium with four strips of glass affixed to each edge to create a well approximately 6 mm deep. Teflon coated glass was used to line the base of the mould as a release film. The cloth was placed in the mould and most of the glass fibre tows were carefully removed from the cloth to create unidirectional carbon fibres in the region of crack propagation in the mode I tests. A few of the glass fibre tows were retained to prevent the carbon fibre tows from warping during prepregging. These remaining tows were found to exhibit no effect on the properties of the composite. The resin loading was 1.09g/g cloth and the appropriate quantity of resin was dissolved in dichloromethane (10% w/w) and the solution was carefully poured over the unidirectional cloth in the mould which was placed on a level surface in a fume cupboard. The solvent was allowed to evaporate for 1-2 hours before the prepreg was removed and B-staged in an oven preheated to 100°C for 1 minute.

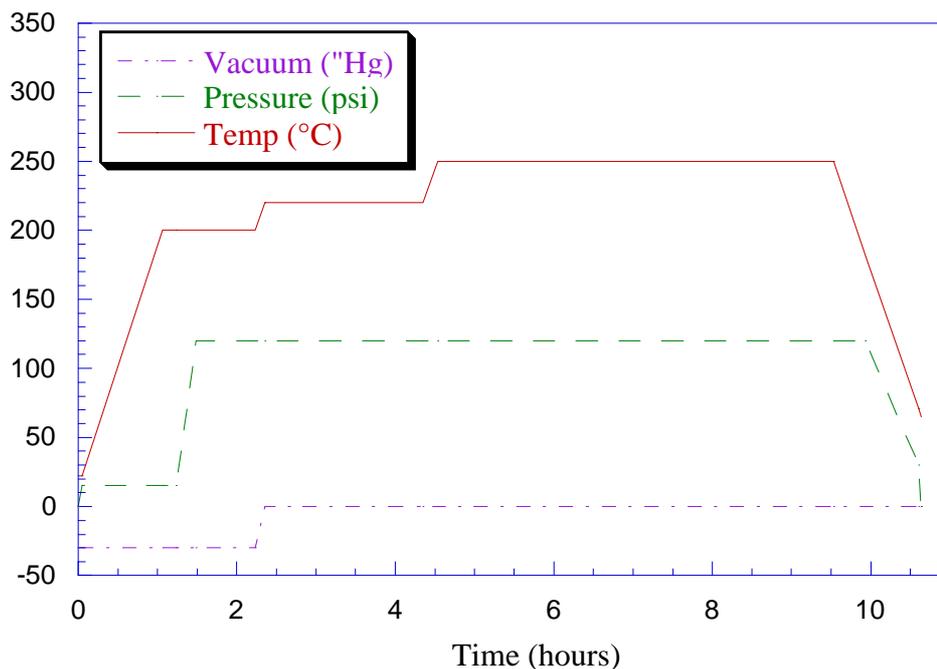


Fig. 2: Optimal autoclave cure cycle for CBR320/328

Prepregs were then aligned and stacked to create a 28 ply laminate. A piece of aluminium foil 15 μ thick and 70 mm long was treated with a release agent and carefully placed in the mid-thickness of the specimen to act as the crack starter in the mode I DCB tests. An aluminium frame, just slightly larger than the dimensions of the prepregs and 4 mm thick was used to prevent the unidirectional carbon tows moving or warping during the cure. If this was not done then mixed mode behaviour was observed during testing rather than pure mode I behaviour. The prepregs and frame were vacuum bagged and cured in an autoclave using the cure cycle shown in Figure 2.

Prior to aging in air in a furnace preheated to 250°C, the specimens were preconditioned at 120°C for 24 hours to drive out any moisture the samples might have absorbed. Samples were also wrapped in glass fibre cloth before aging to protect them from contamination.

Characterisation

The percent fibre volume of each laminate was determined by image analysis of at least 5 representative SEM photographs of a cross section of the sample. The percent fibre volume calculated was approximately 45-48%. Mode I fracture toughness tests were in accordance with the protocol of the European Structural Integrity Society [4]. Specimens were cut to size using a diamond saw and were 20 mm in width, 4 mm in thickness and 160 mm in length with a 70 mm long crack starter film. To load the specimen, aluminium tabs were adhered to the end which contained the precrack film and one side of the specimen was coated with white correction fluid to assist in monitoring the crack length. An Instron 4505 Universal Testing Machine was used to perform the tests with a crosshead speed of 1 mm/min and a load/displacement curve produced for each test. From this data, the mode I critical strain energy release rate was calculated using corrected beam theory according to Eqn 1.

$$G_{IC} = 3P\delta/2B(a+|\Delta|) \quad (1)$$

where P = load, δ = displacement, B = specimen width, a = crack length and $|\Delta|$ = the crack length correction factor which is determined to be the x-axis intercept of the plot of the cube root of the compliance ($C = \delta/P$) vs the crack length (a). Values of G_{IC} were plotted as a function of crack length (a) to produce a resistance (R) curve. $G_{IC-init}$ is defined as the first deviation from linearity on the load/displacement curve. $G_{IC-prop}$ is defined as the value of G_{IC} during steady state crack propagation, which corresponds to a plateau in the resistance curve. The fracture surface of the specimens were examined using a Cambridge S360 Scanning Electron Microscope.

Fourier Transform Infrared Spectroscopy (FTIR) was performed using KBr discs of the samples on a Perkin Elmer 1800 double beam Fourier Transform Infrared Spectrometer. Raman spectra were obtained using a Renishaw Raman Imaging Microscope, model 2000 with a 718 nm NIR laser source. Dynamic Mechanical Thermal Analysis (DMTA) was run on a Polymer laboratories Mk2 instrument using 2 mm thick composite specimens in single cantilever mode.

RESULTS AND DISCUSSION

Mode I Interlaminar Fracture Toughness

Mode I delamination tests were completed after one, two, four and six weeks of aging at 250°C in the case of composites made from the Matrimid A/B resin system. This temperature was selected to investigate the effect of aging at a temperature just below the glass transition temperature of the material. Figure 3 shows the change in interlaminar fracture toughness over this period of time. The value of $G_{IC-init}$ can be seen to decrease steadily as the material is aged due to embrittlement. Prior to thermal treatment $G_{IC-init}$ was measured to be 150 J/m² which is consistent with other published values for high temperature composites [5]. This value was observed to decrease steadily over the six weeks of aging, eventually reaching 16 J/m². The value of G_{IC} during steady crack propagation however, initially increases due to the resin continuing to crosslink even after cure, evidence of this is discussed later. After the first two weeks, $G_{IC-prop}$ decreases dramatically from 400 J/m² to 100 J/m².

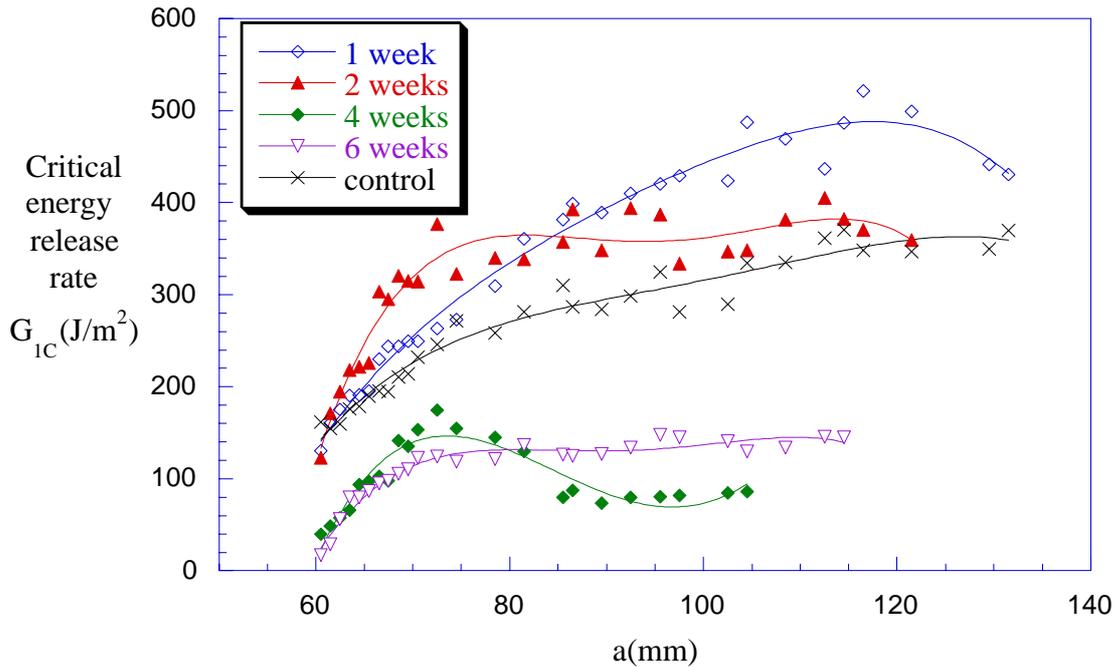


Fig. 3: The effect of isothermal aging at 250°C on the interlaminar fracture toughness of a composite of Matrimid A/B.

The corresponding study of the CSIRO resin system showed that no change in either $G_{IC-init}$ or $G_{IC-prop}$ occurs during the first two weeks of aging. Samples tested after four and six weeks of aging at 250°C also did not show any significant changes in either value, however upon close examination of the fracture surfaces, the distinctive hackle mark deformation indicative of mode II type fracture was observed. This was a result of preparing samples without use of the aluminium frame mentioned previously. At this stage the results are inconclusive and further study is required.

Fourier Transform Infrared Spectroscopy

Changes in the infrared spectra of the composites aged at 250°C were monitored over a period of four weeks. KBr discs were made from small amounts of composite which were both scraped from the surface of the specimen or scraped from the centre of the specimen after it had been split open. Although small amounts of carbon fibre fragments were also present after the KBr disc had been pressed, these only had the effect of broadening the baseline and did not greatly affect the quality of the spectra recorded.

In both composites made with the CSIRO resin and the commercial resin, oxidation of the surface of the panels was observed during the first four days of aging. After this, no further changes were observed at the surface. The FTIR spectra showing these initial changes are shown in Figure 4. The most noticeable change as aging progresses is the broadening of the spectra and the loss of the detail which can be seen in the control spectrum. Sharp, distinctive peaks at 2969, 2935, 2875 cm^{-1} which have previously [6] been assigned to asymmetric stretches of CH_3 and CH_2 groups and the symmetric stretch of a CH_3 group respectively disappear. The imide carbonyl group at 1779 cm^{-1} also disappears and the ingrowth of a broad peak at 1615 cm^{-1} is seen. This is consistent with oxidation of the matrix in this surface layer, although it is difficult to say more precisely what is occurring at this stage due to the inherent broadness of the spectra.

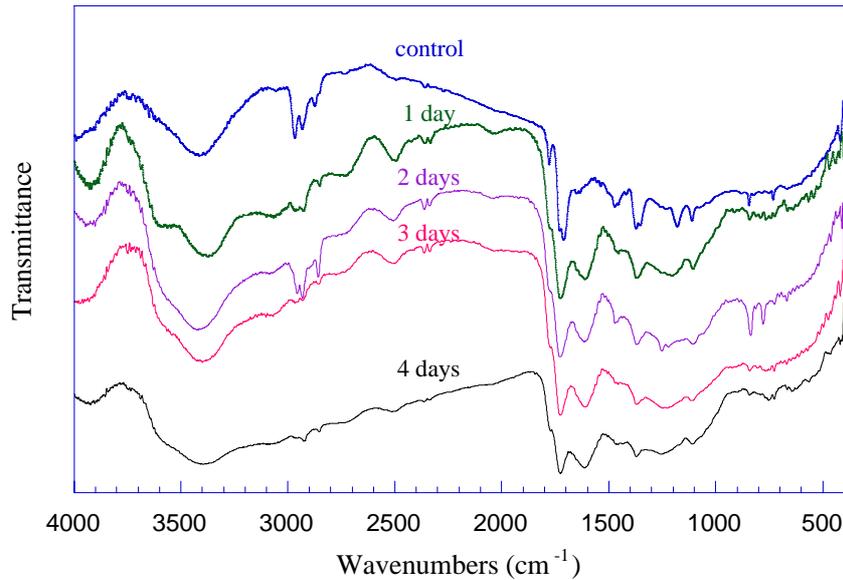


Fig. 4: FTIR spectra of the surface of a CBR 320/328 composite shown after (top to bottom) 0, 1, 2, 3 and 4 days of aging at 250°C

The changes observed in the infrared spectra of the internal surfaces of the specimen proved to be much more interesting as the chemical changes here are highly relevant to the interlaminar fracture toughness of the composite where the crack propagates through this centre region. In the composites made from the CSIRO resin, no chemical changes were observed by FTIR in the specimens after four weeks of aging. However, a completely different trend was observed in the composites made with the commercial resin system. After four weeks of aging, the spectrum of this material had broadened considerably in the carbonyl (C=O) region, with the ingrowth of a large peak at 1602 cm^{-1} , consistent with a substituted aromatic. The imide carbonyl peak has also shifted slightly from 1710 cm^{-1} to 1717 cm^{-1} . In addition to this the relative intensity of the peak at 1512 cm^{-1} which can be assigned to the methylene group in Matrimid A has also diminished, consistent with oxidation of this moiety to form a carbonyl group. These significant chemical changes occur concurrently with the changes observed previously in the interlaminar fracture toughness.

Raman Spectroscopy

As Raman spectroscopy is a light scattering technique, it is extremely versatile and the Raman microscope technique is particularly useful for the analysis of composite materials due to the ability to focus on small ($5\mu\text{m}$) pockets of resin between tows in the laminate. A spectrum can be obtained from this small region which enables the mapping of chemical changes in the Raman spectrum across the width of a sample.

A Raman Imaging Microscope was used to detect extremely degraded regions in the aged specimens. In the Matrimid A/B resin system, it was found that once degraded (after four weeks of aging), the matrix exhibited such a high degree of fluorescence that a spectrum could not be recorded. The same highly fluorescent, highly degraded material was also located at the surfaces of the samples aged for lesser periods of time. For example, a sample which had been aged for a period of one week was found to have a layer of degraded material which had penetrated to a depth of $50\text{ }\mu\text{m}$ from the surface. This can provide a great deal of information as to the physical path of the degradation and is consistent with the work of Bowles [7] who found that in neat resin, polyimide degradation (as seen in SEM micrographs) occurred within a thin surface layer that developed and grew during thermal

aging. The fact that this material is highly fluorescent also assists in determining the chemical structure of the degraded material and current work has concentrated on the use of model compounds to elucidate the types of structures present.

Dynamic Mechanical Thermal Analysis

Dynamic Mechanical Thermal Analysis (DMTA) was performed on composites of both materials that had been aged for up to six weeks. The DMTA of the unaged commercial material showed a rather broad T_g peak at 365°C which indicates that the material was not completely cured. This is consistent with the previous results from mode I fracture toughness tests which indicated that crosslinking of the matrix continued to occur even after two weeks of aging, causing the observed increase in the value of *G_{IC-prop}*. After two weeks of aging, this peak was no longer as broad and the T_g of the matrix had dropped to 347°C. At four and six weeks of aging at 250°C, there was no measurable T_g (a peak in this region was no longer observed), indicating that the matrix had degraded substantially. Composites made with the CSIRO resin again behaved differently and there was no significant change in T_g even after six weeks of aging at 250°C, the T_g was consistently measured to be 280°C.

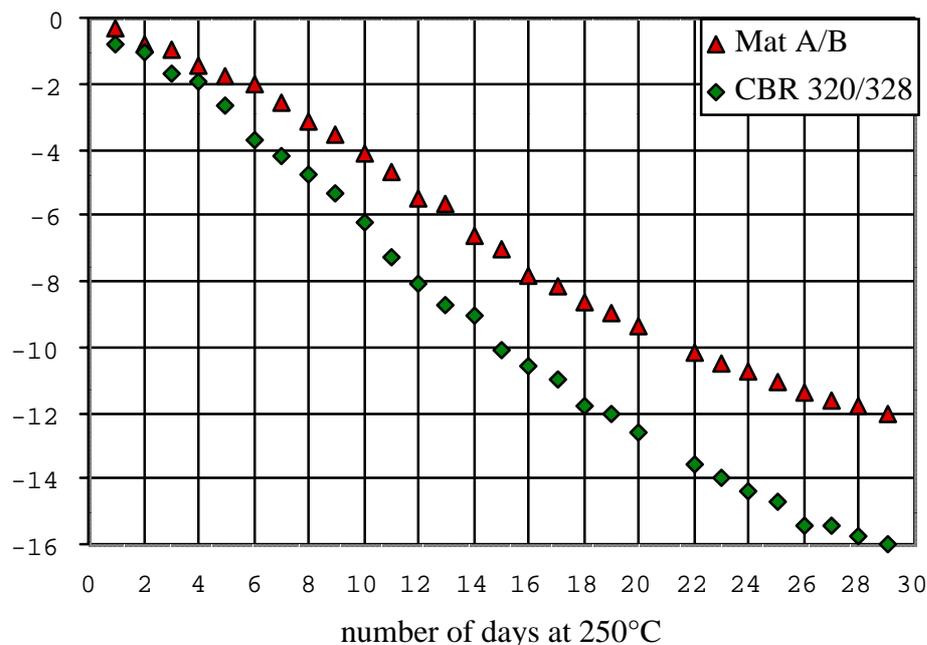


Fig. 5: Plot of the weight losses observed over 29 days at 250°C of the two laminates.

Composite Thermal Stability

There are several methods for evaluating the thermal stability of composite materials including kinetic mapping techniques and thermal gravimetric analysis (TGA). However, one of the most simple techniques, monitoring the weight loss, remains one of the most reliable means of comparing the thermal stability of different composites. [8], [9] Figure 5 (previous page) compares weight loss data over a period of four weeks of aging at 250°C of both CSIRO and commercial composites with samples of the same specimen geometry. Despite all of the previous results which seem to indicate that the CSIRO resin system withstands aging at 250°C better than the commercial system, the thermal stability of the commercial laminates, according to the weight loss data, appears to be superior to the CSIRO laminates.

One explanation for this might be that although the weight loss is slightly greater in the CSIRO system (16% compared to 12%), the chemical changes that occur create the formation of some kind of protective oxidized layer which prevents the centre of the material from deteriorating.

CONCLUSIONS

The critical energy release rate (G_{IC}) during steady crack propagation of composites with a Matrimid A/B matrix was found to initially increase by 100 J/m^2 as the material continued to crosslink during the first two weeks of aging. DMTA confirmed that this was due to incomplete cure of the material, which suggests that the recommended cure cycle should be re-examined. During the following stage in the heat treatment of the material, this value decreases from 400 to 100 J/m^2 after four weeks at 250°C . This coincided with oxidation at the centre of the specimen as detected by FTIR spectroscopy. However, this was not observed in composites of the CSIRO experimental resin. The FTIR spectra of the surface of composites of both materials showed oxidation of the exposed surface of the sample after only four days of aging. No further changes were observed at the surface after this time. A highly degraded surface layer 50μ in thickness was also detected by Raman spectroscopy. Similarly, a DMTA study showed a slight decrease in the glass transition temperature of the commercial composite after two weeks of aging and there was no recordable T_g after four and six weeks of aging. The T_g of the CSIRO composites remained stable at 280°C , even after six weeks of aging. In contrast to these results in which the CSIRO resin seems to be more able to withstand high temperature treatments, the weight loss data measured over four weeks indicates that the commercial resin has slightly better thermal stability. One possible explanation for this is that the oxidized surface layer in the CSIRO resin provides a protective coating for the composite which helps to prevent degradation of the centre of the specimen. This is currently under investigation.

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