Accelerated Ageing Versus Realistic Ageing in Aerospace Composite Materials. III. The Chemistry of Thermal Ageing in Bismaleimide Based Composites

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ABSTRACT: Samples of two Aerospace grade bismaleimide composites (Cytec Fiberite 5250-4/IM7 and 5250-4/RTM) were subject to long-term ($\approx$ 1-year) thermal ageing in air at temperatures of 70, 120, 170, 200, and 250°C. The changes to the chemical and physicochemical structure of the composite were then analyzed by a range of different techniques, including gravimetric analysis, Fourier Transform infrared spectroscopy, and dynamic mechanical analysis, to compare the effects of the different ageing temperatures and to see if much simpler and more fundamental testing techniques could provide more informative forecasting information than the standard mechanical testing methods. The results emphasize the strong variation in chemistry that takes place between the surface and the interior of the composite materials at all temperatures tested. The results also confirmed the significant variations in chemical and physicochemical ageing mechanisms (e.g. glass transition temperature, T_g) that occur between the more realistic ageing temperatures encountered ''in service'' ($\sim$ 120°C) and the accelerated ageing conditions often used for ageing studies ($>$170°C). This article highlights the lack of agreement in scientific literature on the basic chemistry of bismaleimide cure. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2062–2072, 2007

Key words: composite degradation; bismaleimides; chemical changes; gravimetric analysis; FTIR; DMA

INTRODUCTION

This article is the third in a series[1,2] which details the results from an extensive work program which was undertaken in an attempt to develop low-cost, accelerated ageing tests for aerospace composites that could be used to replace some of the expensive and time-consuming mechanical testing protocols now required.[3,4] The study was also designed to determine which type of accelerated ageing regime would give chemical degradation mechanisms most similar to those seen in commercial ''in service'' conditions.

In the previously reported work, the composite materials studied were two commercial epoxy composites with very different chemistries. The current study was concerned with the degradation chemistry of two common commercial bismaleimide (BMI) composite materials with nominally the same resin chemistry. The first type of BMI tested, System A, was a medium/high-temperature cure BMI (5250-4/IM7) with unidirectional, intermediate-modulus, and carbon fiber reinforcement. The second type of BMI tested, System B, was a 5250-4 resin with 728 RTM cloth and an unknown binder (Cytec, 5250-4/IM7, Product data 1997). Both the chemical and mechanical effects of thermal ageing of the resin, and even the composite have been studied previously,[5–16] but the accelerating conditions have generally been short and very severe ($>$200°C) and well above the normal continuous-use limits. Also, some systems studied have been simplified (noncommercial) formulations[17,18] or the techniques used to analyze the chemical changes have not been adequate to understand the changes.

One of the most detailed recent studies of the thermal-oxidation-mechanisms of commercial poly(bismaleimide) resin was by Colin et al.[19] They determined oxygen diffusion rates and reaction mechanism changes through cured resin samples at temperatures between 180 and 240°C. In this study, the initial free radical reactions of oxygen were shown to lead to the formation of peroxide and hydroxyl groups on the resin surface and, as the gas diffused, through the resin. However, no particular (susceptible) hydrocarbon groups in the molecule were considered to be targeted at much lower temperatures. A number of recent review papers have detailed the problems and pitfalls of the use of accelerated test methods for the characterization of advanced composite materials[7,9,10] but most of this information has emphasized the physical and mechanical aspects. The present work attempts to compare the chemistry seen under accelerated temperature conditions (170–250°C) with that found under reasonable ''in service'' conditions (70–120°C) and involves complex, commer-

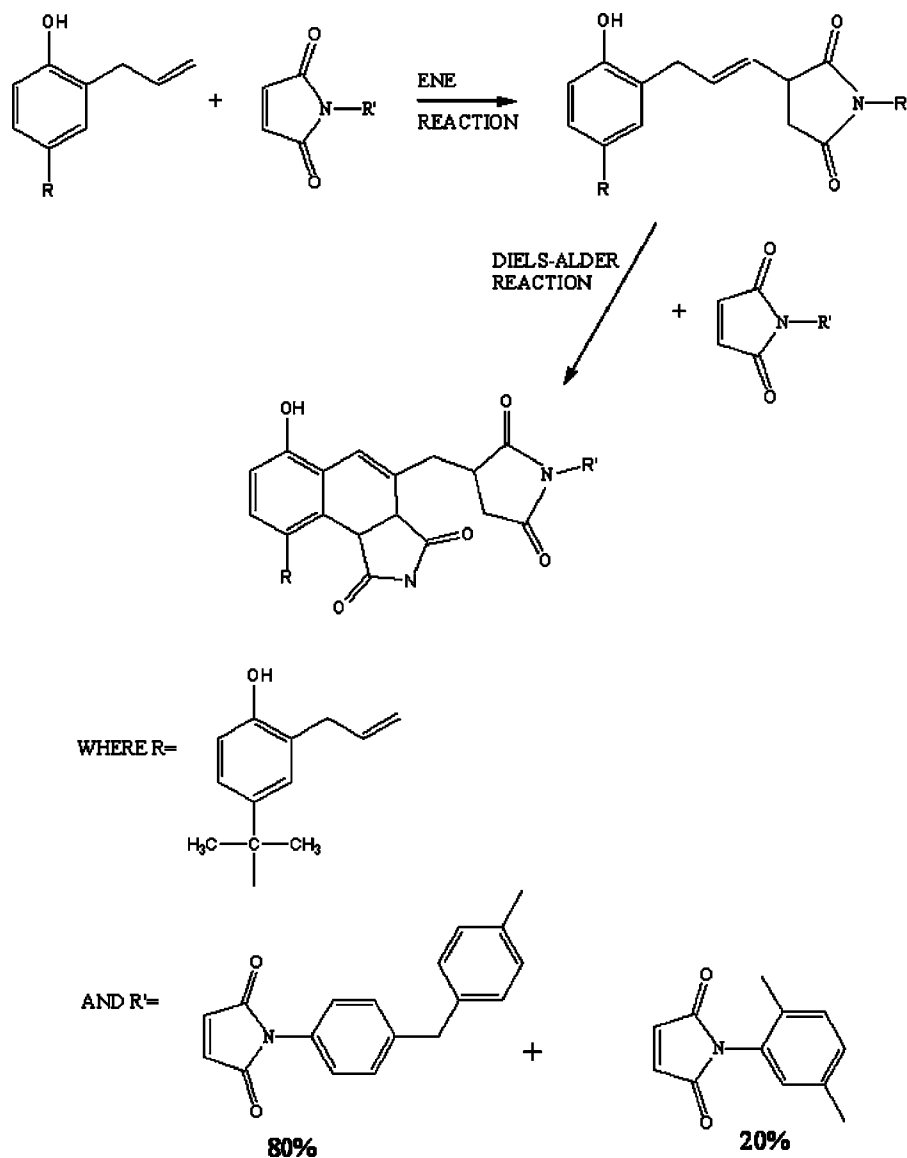*Correspondence to:* J. Hodgkin (jonathan.hodgkin@csiro.au).

Figure 1 A highly idealized structure of the 5250-4 resin system.

cially-produced, and carbon-fiber-composites rather than simplified resin formulations.

This article compares both the different chemical changes and the physicochemical effects observed for the two BMI systems when they are subjected to thermal (only) ageing for up to 7500 h in air at five different temperatures: 70, 120, 170, 200, and 250°C. A subsequent study will report the ageing effects on these materials at 70°C under conditions of high, medium, and low humidity, and also the effects of thermal spiking on the moisture-equilibrated samples. The results will be compared to those of the isothermally aged (dry) materials.

Chemical structure of BMI resins

The chemical structure of the 5250-4 resin system has been described by a large number of earlier

workers[5–16,20–22] and most of the degradation work has assumed the highly idealized chemistry shown in Figure 1.

Previous authors have suggested a range of reactions that can occur depending on the conditions of resin formulation and cure. Of particular interest are some of the free-radical polymerization reactions of Phelan and Sung[23] (Fig. 2), the Michaels reaction[20,24,25] (with free NH_2 and OH groups) and some unusual chemistry suggested by Grenier-Loustalot et al.[26] Even small amounts of specific impurities in the commercial resin formulation can cause the chemistry to vary greatly. For example, some free-radical reactions can be prevented by small amounts of amino compounds or metal impurities and the former are believed to be part of many commercial prepreg formulations[20] along with other unknown additives or materials subject to commercial confidentiality.
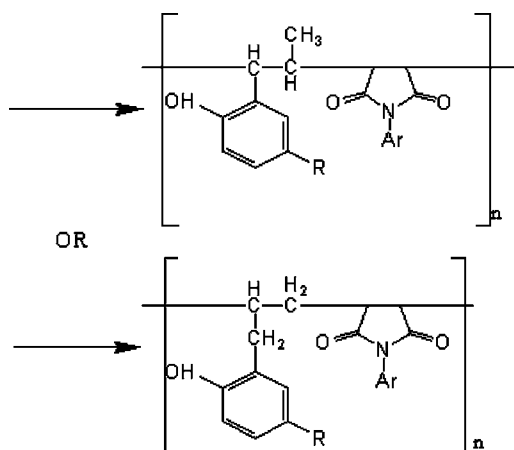
Figure 2 Free-radical polymerization reactions of Phelan and Sung.[23]

In a recent study by Rozenberg et al.,[27] the cure chemistry of BMI was questioned further and it was suggested that the cure mechanism "consists of a unique combination of all known ways of polymer formation." It was also suggested in this study that the second reaction in Figure 1 (Diels–Alder) is unlikely to occur because of steric constraints, and that the major curing and ageing reaction that occurred at higher temperatures was loss of phenolic groups by dehydration, and crosslinking by ether formation. Many of the above complications were suggested for simplified, academic formulations, however, the real chemistry of the complex, commercial formulations is even less certain.

In line with previous work on industrially important epoxy composites, it appears to us that it may be more useful to focus on changes in possible defect structures during the ageing of BMI composites rather than the idealized structures proposed previously. This is especially true when the "in service" ageing conditions are consistently at much lower temperatures than the common, accelerated-ageing, test regimes. This will be the chemical focus of the current article.

The chemical changes in the aged BMI composite samples have been followed by a wide range of different techniques including near infrared spectroscopy (NIR), X-ray photoelectron spectroscopy (XPS), Mass spectroscopy (including time of flight secondary ion MS), and differential scanning calorimetry (DSC) as described in the first article,[1] however, none of these gave reproducible, detailed chemical information which compared to that supplied by Fourier Transform infrared spectroscopy (mid FTIR). Even in this case, reproducible spectra of composite material over extended time and different temperature conditions could only be obtained by one specific sampling technique; as described in the experimen-

tal. The chemical information supplied by FTIR was complemented by the gravimetric and dynamic mechanical analysis (DMA) information.

EXPERIMENTAL

The two BMI materials selected for investigation were medium/high-temperature cure BMI resin systems, 5250-4. One material had a unidirectional, intermediate-modulus, and carbon fiber (5250-4/IM7), and the other had a 728 RTM cloth and binder (5250-4/728RTM). All materials were prepared as laminates with the dimensions of ~ 700 mm by 1000 mm and were 2 mm thick. The laminates were individually cured in an autoclave, utilizing standard aerospace cure cycles. The 5250-4/IM7 was subjected to a cure cycle designed to give good toughness of the BMI, while the 5250-4/728 RTM cloth was cured to give a high glass-transition temperature. The cured laminates were C-scanned and measured for thickness (consolidation) to ensure the quality of the laminate. The large laminate was then cut into a series of 50 mm by 50 mm plaques. These plaques were used in all accelerated-ageing experiments. All plaques were dried at $50°C$ over phosphorous pentoxide (P_2O_5) until a constant weight was achieved, prior to thermal ageing.

Both BMI composite materials were aged in air at five isothermal conditions (70, 120, 170, 200, and $250°C$) although only a limited analysis was carried out on the $200°C$ samples. The lowest ageing temperature, $70°C$, was chosen to represent a typical temperature that an aircraft surface could reach on the ground because of solar heating. Temperatures were chosen thereafter to aid in the definition of accelerated-ageing conditions with the upper temperature of $250°C$ chosen as a sensible limit on the temperature performance of the material.

All ovens were temperature calibrated and an isothermal volume of operation defined. The oven at the $70°C$ temperature had P_2O_5 placed in the bottom to keep the relative humidity at a minimum. Samples were weighed at regular intervals and witness plaques removed after 400, 900, 2025, 3600, 5800, and 7500 h for analysis. Plaques were weighed on a Mettler Toledo AB 204-S four-decimal-place balance (experimental error $< 0.01\%$). At least three plaques at each ageing temperature were removed from the oven, transferred to a desiccator containing P_2O_5, and allowed to cool to room temperature before being weighed. The laminates were then placed back in the oven and used in the collection of the next data point. The whole weighing process was optimized to take less than 30 min.

DMA was conducted on a Rheometrics Scientific IIIe. This instrument was completely computer con-

trolled and the proprietary software used is known as Orchestrator. All samples were run on a large frame in dual cantilever mode. The sample was cut in a jig, with a diamond blade saw, to give a reproducible sample width of ~ 10 mm. The cut, for the unidirectional composite, was made so that the fiber direction ran parallel with the clamps (i.e. the test was conducted in the least stiff direction allowing easier investigation of the resin properties). A multifrequency analysis was undertaken at 1, 10, 50, and 100 Hz, over a temperature range of 50–350°C, at a heating rate of 5°C/min. Glass-transition temperatures were derived from the onset of the decline in the loss modulus (E'_{onset}) and by the tan δ peak position at 1 Hz.

FTIR were obtained in accordance with a standard operating procedure written for this project; as follows. Approximately 1.5 mg of composite was removed from the surface of the aged laminate. This was very finely ground with ~ 50 mg of dry KBr and left in a desiccator over P_2O_5 before being pressed into disc. The disc was analyzed (256 scans) in a Perkin–Elmer 2000 FTIR spectrophotometer, in transmission mode using KBr as the background reference. Analysis was undertaken by direct comparison of spectra, as well as by the use of difference spectra.

RESULTS

Gravimetric analysis

The weight-change measurements carried out during the ageing tests were performed on composite plaques with relatively large surface-to-thickness ratios (50 mm × 50 mm × 2 mm) to better represent real
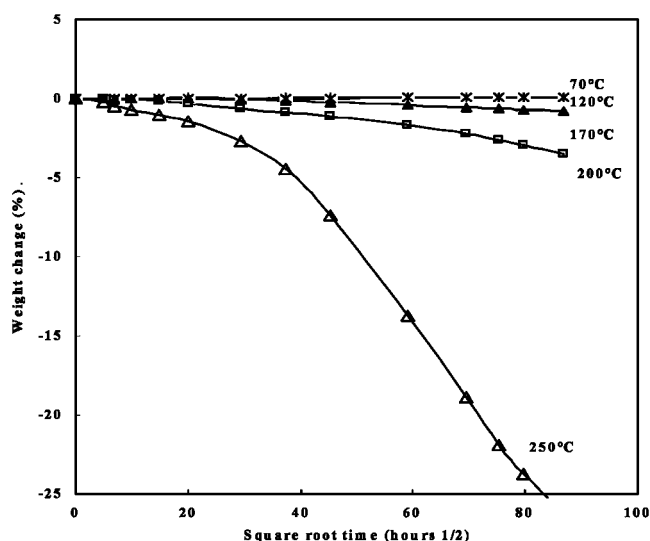
Figure 3 The percentage mass change of the 5250-4/IM7 (System A) resin as a function of the square root of time at all temperatures over the 7500 h.
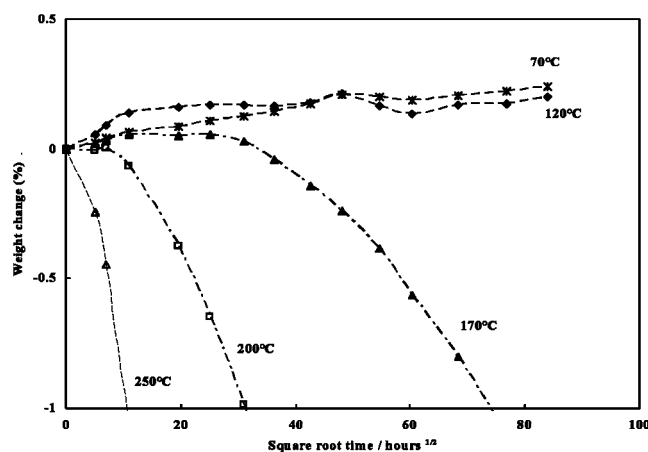
Figure 4 The percentage mass change of the 5250-4/782 RTM (System B) composite as a function of the square root of time (hours$^{[1/2]}$) at all temperatures over the 7500 h.

composite samples. The chemical changes therefore mainly occur on the surface and were almost entirely due to the resin matrix, which was approximately one third to one half of the material bulk. This meant that even quite-low-percentage weight changes in the plaques equate to very significant chemical changes at the composite surface, as previously demonstrated by the work of Nam and Seferis.[13]

Figure 3 displays the percentage mass change of the System A BMI composite as a function of the square root of time (hours$^{[1/2]}$) at all ageing temperatures over the 7500 h of experiment time. If only one mechanism of oxidation/degradation had been involved the lines would have been simple straight lines.[28] As plotted in this figure, only the 250°C line has a significant deviation from a straight line, with a strong change in slope at about 400 h. However, the loss of material is so great after this time that it is obvious that the 250°C ageing temperature is much too high an accelerating temperature for a long-term study. The 200°C line is showing some increase in loss rate at later times also and even this ~4% loss is chemically great if confined to a thin surface layer.

For the 5250-4/728 RTM (System B) the weight change patterns are of similar overall shape; however, at the higher temperatures (200 and 250°C), the weight loss rate is at least double System A (due partly to the higher resin levels) and the total weight loss of >10% at 200°C and 7500 h indicates a complete loss of surface layers. A better indication of the changes in the chemistry of degradation is seen in the expanded version of the System B gravimetric plots in Figure 4. At the lower temperature (70 and 120°C) there is a very significant oxidative increase in weight of the surface layers, even up to 7500 h. At 170°C, there is a small oxidative increase at first but then a sharp oxidative loss of material, simi-
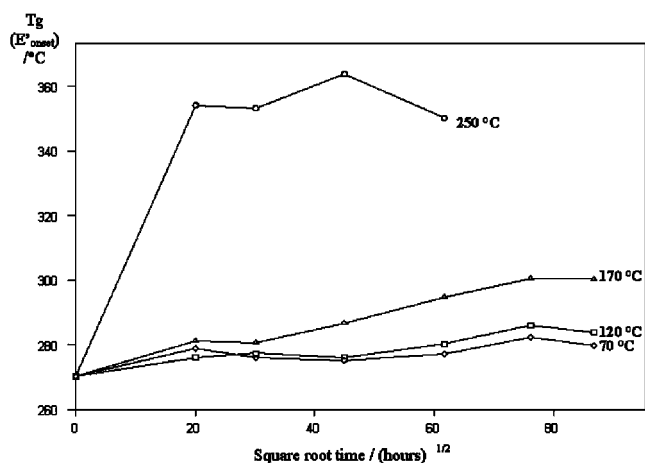
Figure 5 T_g (E'_{onset}) as a function of time and temperature for 5250-4/IM7.

Figure 6 Comparison of the DMA tan δ traces of unaged 5250-4/IM7 at 1 and 100 Hz.

lar to that seen at higher temperatures, indicating that the critical change in the degradation mechanism occurs around this temperature. These results are very much in line with the oxidation mechanisms detailed in the work of Colin et al.,[19] although their initial increases-in-weight were much more fleeting because they studied the oxidation at the higher temperatures.

Dynamic mechanical analysis

The DMA of a composite material can provide a detailed picture of variations in the matrix-resin and molecular motions and hence chemical and mechanical changes in the material over a large temperature range. The aerospace industry is particularly interested in the temperatures at which the loss of modulus commences (T_g, E'_{onset}) and the shape and position of the tan δ peak.[3] However, DMA (as with most mechanical test methods) measures an average result over a relatively thick sample and the chemical ageing changes in a composite generally occur very selectively from the surface.

Figure 5 shows the changes in T_g (E'_{onset}) as a function of time and temperature for the 5250-4/IM7 (System A) composite. The 5250-4/728 RTM cloth composite (System B) showed a very similar pattern (not reported) even though it has been ''cured'' to a higher initial level (T_g, E'_{onset} 304°C). More detailed information on what may be happening can be obtained from the tan δ curves of the unaged System A material at two different frequencies, 1 and 100 Hz (Fig. 6), and the 100 Hz curves at different (250°C) ageing times (Fig. 7). There appears to be two different types of molecular structure present in the unaged material and one of these is changed quickly by ageing at 250°C. The progression of this change can be seen partially in the 170°C aged samples as shown in Figure 8 and even ageing at lower temper-
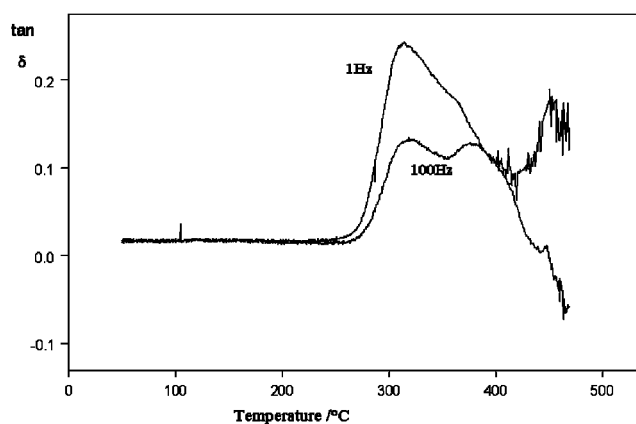
atures shows the beginnings of the change. This type of effect is normally viewed as the material showing further cure, or crosslinking,[28,29] but FTIR evidence presented later, and some literature evidence,[19] indicated significant functional group changes (oxidation) from the surface, but not necessarily extra crosslinking.

Similar DMA studies of the System B material also showed closely related changes in composite structure on high-temperature ageing, although the change in tan δ peak at 100 Hz is not as marked (Fig. 9) because the initial chemical change has been progressed by the much-higher-temperature, cure conditions.

Fourier transform infrared spectroscopy–Introduction

FTIR spectroscopy has been used extensively to study the chemistry of thermal cure and degradation of neat BMI resin systems over many years.[5,12,17–23]
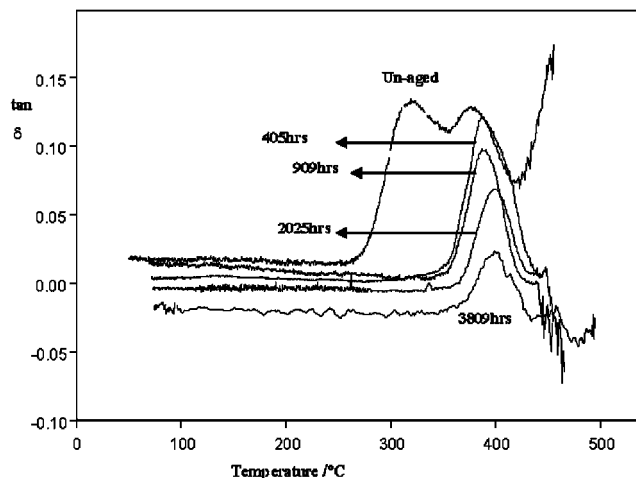

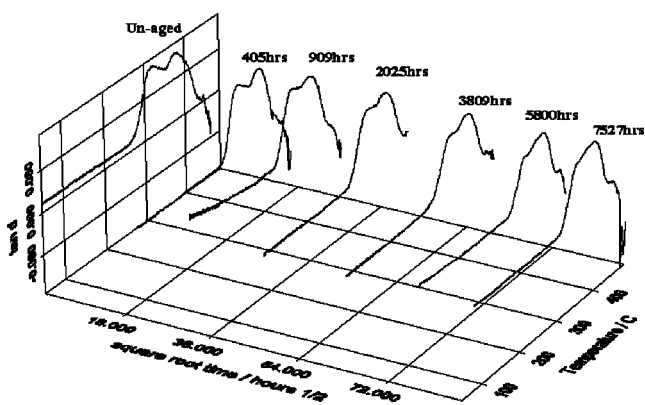**Figure 7** The DMA tan δ plots of the 250°C thermally aged 5250-4/IM7 at 100 Hz.

Figure 8 A 3D plot of the 100 Hz DMA tan δ temperature, square root of time, for 5250-4 IM7 thermally aged 170°C.

Figure 10 Mid-FTIR surface spectra of unaged 5250-4/782 RTM (a) and unaged 5250-4/IM7 (b).

However, very little has been done previously with chemistry of cure and degradation of commercial composites containing large amounts of carbon fiber. Our attempts to use FTIR techniques such as ATR-FTIR (direct contact with the surface), diffuse reflectance or photoacoustic methods were very unsatisfactory. In the first case, it was due to the stiffness and unevenness of the surface, and in the latter techniques because of the variable absorbance of intact carbon fibers. The resulting spectra were broad and very variable: some literature reports have indicated that others have had a similar lack of success.[30] However, recently it has been shown that high quality and reproducible spectra from such materials, even when they are extensively aged,[1,2,17,18] can be obtained by the detailed method described in the experimental section. As the spectra only require small amounts of material (1–2 mg), analysis can be carried out at different depths and different areas of
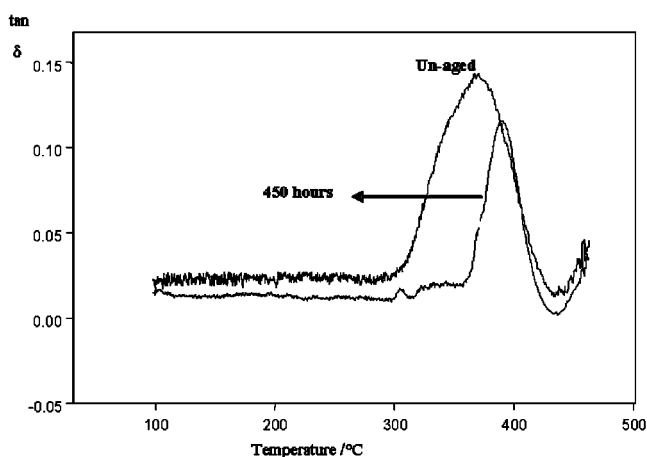

Figure 9 Overlay of the 100 Hz tan δ temperature curves for unaged 5250-4/782 RTM cloth and thermally aged at 250°C and 450 h.
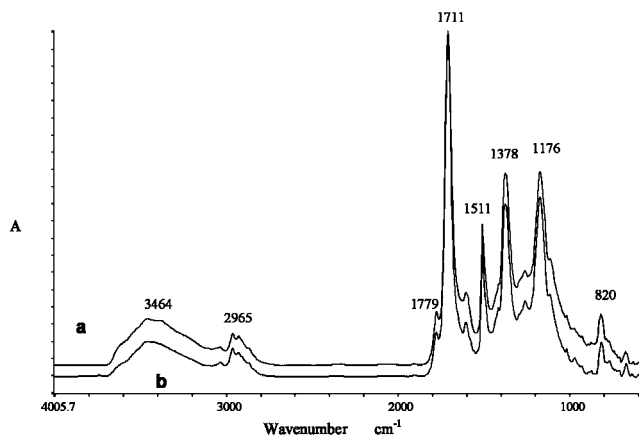
the composite section, for example; the surface of unaged BMI Systems (Fig. 10).

Because of the extensive previous studies on BMI resin chemistry, the FTIR peak-position-correlations with chemical structures are relatively well known[5,6,31] (Table I) although not always agreed upon.[5,19,26,31] However, without further model compound work, minor shifts in peak positions cannot be used to distinguish between structurally similar chemical groups. This particularly applies to the BMI resins, as the various closely related imide structures have significant peak shifts depending on neighboring double bonds or oxidized groups.

FTIR results

The spectra shown in Figure 10 were obtained from the surfaces of unaged 5250-4/IM7 (b) and 5250-4/728 RTM (a) composites, respectively. The spectra appear to be almost identical except for a slightly (but significantly) stronger OH/NH absorption area, and 1606 cm^{-1} peak in the RTM material because of increased surface oxidation caused by the higher cure temperature. The spectra were also very similar to previous spectra of the equivalent neat-resin materials obtained by previous workers.[32] In the thermal ageing studies it was found that, as far as chemical changes were concerned, the two materials of the present study followed a very similar pattern, so they will be discussed together. The only real difference occurred at the higher ageing temperatures (200 and 250°C) where the rate of degradation was considerably faster for the 5250-4/728 RTM material (as expected) because of its much higher resin content and its extra, initial heat treatment.

At 70°C, the chemical changes due to thermal ageing appeared very minor even after 7500 h. At the composite surface, the greatest noticeable spectral changes occurred in the OH/NH region (3500–

TABLE I
Assignment of FTIR Peak Positions in BMI Composites[5,17,31]

Approximate peak position	Tentative assignment	Functional group
3650-3550 (W)	Water, non bonded hydroxyl	—OH
3550-3380 (S)	Hydrogen bonded hydroxyl	—OH
3075 (W)	Aromatic hydrocarbon	Ar—H
3035 (W)	Double bond, allyl	—CH=CH—
2966 (M)	Asymmetric CH_3 stretch	—CH_3
2922 (M)	Asymmetric CH_2 stretch	—CH_2—
2852 (W)	Symmetric CH_3	—CH_3
1780 (M)	Symmetric imide	—C—O
1725-1710 (VS)	Asymmetric imide	—C=O
1605 (W)	Phenyl with C—O conjugation	Ar—C=O
1512 (S)	Phenyl with CH_2 bridge	Ar—CH2—
1380 (S)	Various aliphatic and imide	CH, CH_2, CH_3
1260 (M)	Various carbon oxygen	—C—O—
1175 (S)	Succinimide? ether?	C—N—C, —C—O—C
1120 (W)	ether	—C—O—C—
820 (M)	Maleimide deformation	—C=C—

3200 cm^{-1}), with initial peak increases up to about 3500 h and then decreases, and the decrease in vinyl group peak at 3037 cm^{-1}. However, when these spectra were compared to the initial center spectra (Fig. 11) the changes were marked. The relatively sharp peaks at $\sim$ 3630 cm^{-1} (nonbonded OH), $\sim$ 3470 cm^{-1} (bonded OH), and $\sim$ 3325 cm^{-1} (NH) in the center material were merged into a larger broad peak at $\sim$ 3450 cm^{-1} for the surface indicating that, even on initial curing, the surface had been quite heavily oxidized. This was backed up by general oxidative-broadening in the rest of the spectra between 1770 and 1000 cm^{-1} (not shown). At the center of the composite, small peak-absorption-increases and broadening were found in the OH/NH region (3500–3200 cm^{-1}) after 7000 h air ageing but to only a very minor extent at this temperature.

At 120°C, ageing temperature and chemical changes at the surface became more noticeable (especially late in the ageing program) but these observed changes were still relatively small unless compared to the spectra from the center. The largest peak-absorption-changes (apart from the OH/NH region), occurred at 1603 cm^{-1} (increase) and at $\approx$ 1277 cm^{-1} (a broad increase and shift). However, it was also significant that position shifts started to be noticeable in some of the major peaks (an increase at 1711 cm^{-1}, and a decrease at 1379 cm^{-1}) which provide an analysis problem, as these two peaks are the most stable for peak intensity measurements and hence used for normalization. Difference spectra (Fig. 12) could be used to emphasize these changes and point out other oxidative changes at $\approx$ 1740 cm^{-1} and $\approx$ 1660 cm^{-1} (increase) and 1511 cm^{-1} (decrease) which progress with ageing time. It is unfortunate that double-bond peaks absorb poorly in the FTIR spectrum (unlike the Raman[17,18,31]) as the changes in these groups

may be critical to BMI ageing. The peak changes at 3037, 1645, and 972 cm^{-1} are believed to be associated with such double bonds and decrease significantly at the surface of the material (but not the center) over the 7500 h program at 120°C. These surface changes were similar for both materials although (again) greater for the RTM material. The center of the latter showed much higher (and broader) increases in the OH region than the unidirectional composite because of general oxidation effects.

At 170°C, the chemistry changes occurring in the composite surface were similar to those found at the lower temperatures [Fig. 13(a)] but they started at a much earlier sampling time and they were much
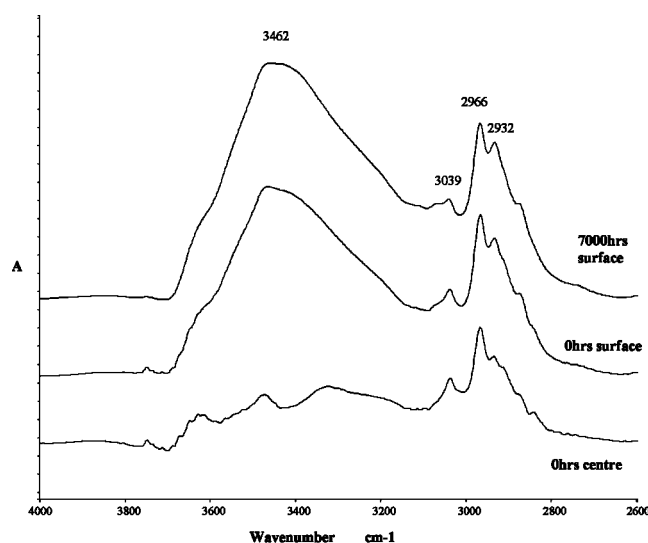

Figure 11 Expanded (4000–2500 cm^{-1}) mid-FTIR surface spectra of unaged 5250-4/IM7 and with 70°C aged 5250-4/IM7 at 7500 h; center spectra unaged 5250-4/IM7.
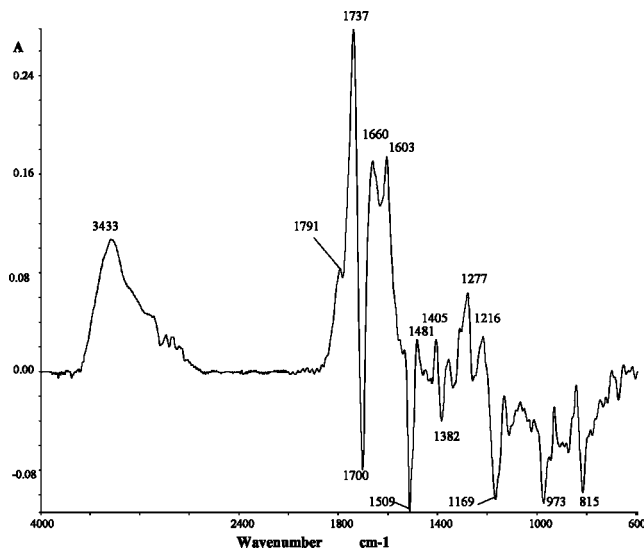
Figure 12 Difference Spectra of 5250-4/IM7 center at 0 h and surface at 7000 h at 120°C.

larger. The oxidative increases were generally broad but quite prominent at ≈ 1740, ≈ 1603, and ≈ 1270 cm^{-1} with the usual small peak position shifts and the decreases at 1711, 1511, and ≈ 1176 cm^{-1}. The actual peak shifts at 170°C were larger than those found at 120°C, with the 1711 cm^{-1} peak shifting to 1718 cm^{-1} by 7500 h of ageing. The changes in the area above 2000 cm^{-1} were difficult to quantify [Fig. 13(b)] as there was no stable peak for normalization, but the various CH peaks (3100–2850 cm^{-1}) disappeared as individual peaks after a few hundred hours of ageing, and the OH/NH ratio (3460–3330 cm^{-1}) varied greatly with ageing time but showed a general decrease and move to lower figures caused by further strong oxidative degradation. The chemical

changes in the surface of the 5250-4/728 RTM material were very similar but initially much faster than those found with the 5250-4/IM7 composite (the lower resin level, unidirectional carbon fiber product). The changes do however appear to slow down after 3000 h of ageing which would indicate that the more oxidatively-sensitive groups had reacted and the new oxidation reactions were occurring deeper in the composite. Both types of composites appeared to be at similar chemical stages at the end of the program. In contrast to the strong surface chemical changes in the spectra, the center of the laminates did not change significantly even at 170°C except for a strong, broad OH region (3440 cm^{-1}) increase in both materials to give a spectrum similar to that of the original surface. This center increase (rather than a decrease) again indicates that the OH decreases at the surface are probably due to extensive oxidative degradation of previously formed alcohols and acids and not crosslinking, as previously suggested.[5,27,28] The surprising result is the low level of change that is seen in the 1770–1100 cm^{-1} region of the spectra at the center of the composite when the surface is so heavily degraded.

The final and highest ageing temperature for the study was 250°C. It was obvious from the FTIR spectra of 5250-4/IM7 [Fig. 14(a,b)] that this temperature is too high for long-term chemical studies. Even at the shortest period of ageing (405 h), all of the major BMI peaks (except the imide) had been heavily changed because of oxidation at the surface. The imide peak, originally at 1711 cm^{-1}, had shifted to 1723 cm^{-1} but remained prominent. The formation of a large new peak at 1600 cm^{-1} indicated the formation of polycyclic aromatics and other oxidized structures. Further, ageing does not change the surface chemistry due to the loss of surface material,
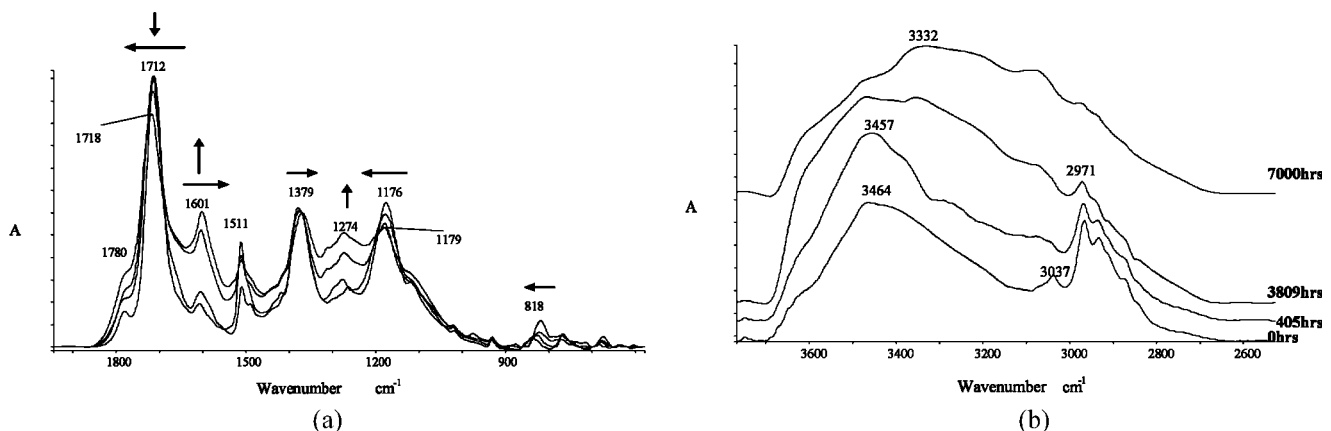

Figure 13 (a) Expanded (1900–600 cm^{-1}) mid-FTIR surface spectra of 5250-4/IM7 isothermally aged at 170°C, the arrows represent the spectral trends observed with increasing ageing time from 0 to 360 h, 3809, and 7000 h (normalized on 1379 cm^{-1}). (b) Expanded (3750–2600 cm^{-1}) mid-FTIR surface spectra of 5250-4/IM7 isothermally aged at 170°C and the trends observed with increasing ageing time from 0 to 405 h, 3809, and 7000 h.
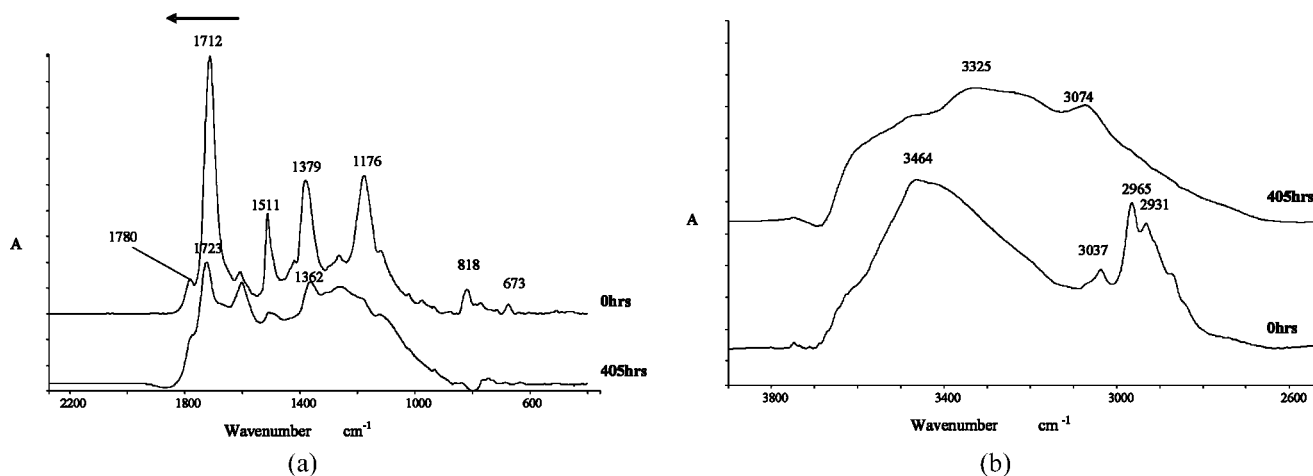
Figure 14 (a) Expanded (2200–500 cm^{-1}) mid-FTIR surface spectra of 5250-4/IM7 isothermally aged at 250°C, the arrow shows the spectral shift observed with increasing ageing time from time zero to 405 h. (b) Expanded (3900–2600 cm^{-1}) mid-FTIR surface spectra of 5250-4/IM7 isothermally aged at 250°C and the trends observed with increasing ageing time from time 0 to 405 h.

and the oxidation of freshly exposed material, as emphasized by the gravimetric analysis results.

In contrast to the composite surface, resin in the interior of the composite laminate remained relatively unchanged until about the 2025 h aged sample point (Fig. 15). The 5250-4/728 RTM material behaved in a very similar fashion except the changes occurred at an earlier time.

DISCUSSION

It is obvious from this and many previous studies of the thermal (and moisture) degradation of carbon fiber composites[5,13,17–19,33,34] that the effects vary greatly from the surface inwards because of the diffusion of oxygen through the material, and these changes will progress at different rates for different temperatures. The FTIR results described earlier have shown that even at quite high temperatures (250°C) for long times (>2000 h) the center of a high quality BMI laminate can be minimally changed and yet the surface will be heavily degraded. However, the results of this study have shown that there has been considerable surface oxidation of both of the commercial BMI laminates, as they were initially produced. This has led to a relatively high level of surface hydroxyl groups (broad aliphatic and acidic signals around 3450 cm^{-1}) when compared with the composite bulk and these increase further and progress deeper on ageing, even at the lower ageing temperatures (70–120°C). This accounts for the weight increases seen. Among the more susceptible groups to be oxidized are the vinyl groups (3037 cm^{-1}); seen as surface absorption decreases on curing and low-temperature ageing. In these commercial composites there would also be many defect

groups, because of additives or minor reaction products which would be similarly affected by oxidation. In comparison, the major peaks in the infrared spectra below 1780 cm^{-1} are mostly due to imide and aromatic structures and are not affected by this low-temperature environment. The only noticeable exception is the increasing aromatic peak at $\sim$ 1605 cm^{-1} which may show the influence of the oxidation of an adjacent aliphatic group.[1]

In contrast to the low-temperature effects, the high-temperature (>170°C) ageing environment leads to degradation and material loss at the surface but, because milder oxidation (including hydroxyl formation) is still occurring below the surface, the measured FTIR hydroxyl loss appears relatively minor and variable. However, the change in peak shape from a strong peak at $\sim$ 3450 cm^{-1} to a broad peak mainly at lower values indicates the formation of more hydrogen bonded acidic OH groups. The
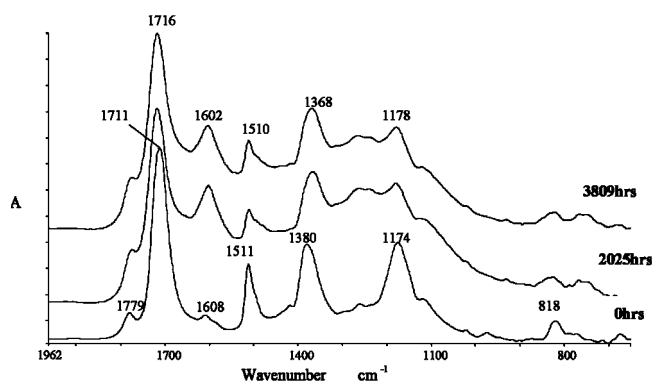

Figure 15 Expanded (1962–760 cm^{-1}) mid-FTIR center spectra of 5250-4/IM7 isothermally aged at 250°C and the trends observed with increasing ageing time from time 0 to 3809 h.

chemical changes are much more noticeable in the aliphatic CH absorption area (3037–2850 cm^{-1}) with strong losses (even at 170°C) over the exposure time. While the main imide peaks below 1780 cm^{-1} are still strong, there is a significant background broadening between 1780 and 1700 cm^{-1} because of carbonyl group formation and the $\sim$ 1605 cm^{-1} peak increases greatly. The imide peak-positions also shift (+8 cm^{-1}) with time indicating adjacent chemical changes.

At 170°C, in the center of the laminate, hydroxyl formation ($\sim$ 3450 cm^{-1}, Fig. 13) increases strongly as ageing progresses but almost all of the other peaks are unchanged, especially below 1780 cm^{-1}. The spectra at the end of the ageing period resemble the original (oxidized) surface spectra.

Above 200°C, the surface chemistry changes were so drastic, even at the early stages, that they are not relevant to any normal ageing situation because of the continual loss of material. However, the central-resin-chemistry of the BMI laminates was still in a mildly oxidized state for a considerable period of time (2000 h at 250°C). The details of all of the above free-radical oxidation reactions of these commercial laminates are very much in line with the results previously obtained for the oxidation-mechanisms proposed for neat, BMI-resins, by Colin et al.[19]

The above results indicate that the relationship between the chemistry of BMI ageing and the mechanical property changes will be complex as most of the common mechanical tests give an average (but varying depending on the type of test) measure of the properties through a laminate. Therefore, mechanical testing may be unable to give a reliable lifetime prediction of composite properties in normal service. However, our DMA results do appear to indicate that the different levels of oxidation throughout the laminate can be seen by changes in the T_g and more particularly in the complex shape of the tan δ curves with multiple peaks at different frequencies. It has been well documented in the literature[8,20,28] that there is a large change in BMI mechanical properties (especially stiffness) and therefore chemical structure, on post curing between 170 and 250°C. This is generally attributed to crosslinking increases such as the dehydration reaction between two phenolic groups, as postulated by Morgan et al.[27] However, our results indicate that the increased level of oxidation and the depth of these changes would account for the loss of hydroxyl groups as well as the higher T_g and the stiffness properties found.

Where micro-cracking is a critical determinant of a composite's useful lifetime, the surface chemical changes seen by FTIR could be a predictor of the composite mechanical property variations as oxidation will greatly stiffen the molecular chains. Micro-

crack formation appears to be a common factor in BMI composite ageing especially in long term fatigue situations[35] or where humidity and thermal spiking take place.[28,29] However, no noticeable micro-cracking was observed in this isothermal ageing study, unlike the results of a hot/wet ageing program with the same composites, which will be reported at a later date.

CONCLUSIONS

The gravimetric and dynamic mechanical experiments indicate that these commercial BMI composite-laminates age in different ways at different temperatures (especially above or below 170°C). The detailed molecular changes, as determined by FTIR, indicate that the chemistry at the lower temperatures is caused by a free-radical oxidation mechanism at susceptible hydrocarbon units, initially at the surface, and then by diffusion further within the composite. These susceptible groups would include vinyl groups, defect amine and hydroxyl groups and tertiary aliphatic CH groups next to aromatic rings. This free-radical attack leads to the addition of oxygen to form peroxide and hydroxyl groups, and to weight increases; as described previously in detail for BMI resins, by Colin et al.[19]

At higher temperatures and longer ageing times, degradative loss of material prevails and further oxidation to carbonyl and acidic structures takes place at the surface. These changes lead to higher T_g and more brittle polymeric layers but, as the changes are uneven, they do not lead directly to consistent mechanical changes in the whole laminate. The chemistry of the particular oxidation susceptible molecular units is not known because of the largely unknown molecular structure of BMI resins[27] and because the commercial materials could also contain many defect groups or additives with active bonds. For example, the FTIR evidence in this work indicates the presence of easily oxidized double bonds in the resin structure such as the double bonds adjacent to the aromatic ring in Figure 1. Previous ageing studies of similar BMI composites using Raman spectroscopy for analysis purposes also showed the presence of double bond changes.[17,18] The surface of both of the composites tested show high concentrations of oxidized (hydroxyl) groups in the as-produced laminates with the greater concentration seen in the more strongly cured (higher temperature and time) laminate. This is not surprising as BMI resins are normally cured well above 170°C for a number of hours. These oxidized groups will not only stiffen the molecular structure but will also provide susceptible sites for further ageing changes, such as hydroxyls changing to aldehydes or ketones

and eventually to acid groups. Further, model compound studies will be required to determine how much of the loss of double bond structures in the resin is due to crosslinking, which is the more generally accepted explanation,[20] or oxidative attack, as suggested in this article.

References

1. Dao, B.; Hodgkin, J. H.; Krstina, J.; Mardel, J.; Tian, W. J Appl Polym Sci 2006, 102, 4291.
2. Dao, B.; Hodgkin, J. H.; Krstina, J.; Mardel, J.; Tian, W. J Appl Polym Sci 2006, 102, 3221.
3. ASTM. The Composite Materials Handbook MIL 17; ASTM International: West Coshohocken, PA, 2002.
4. Joint Aviation Authorities. Am J Chem 1994, 25, 603.
5. Morgan, R. J.; Shin, E. E.; Lincoln, J.; Zhou, J. Proc Int SAMPE Tech Conf 2000, 44, 345 and references therein.
6. Drukker, E.; Green, A. K.; Macrom, G. Compos A 2003, 34, 125.
7. Tsotsis, T. K.; Lee, S. M. Compos Sci Technol 1998, 58, 355.
8. Bechel, V. T.; Kim, R. Y. Proc Int SAMPE Tech Conf 2003, 48, 707.
9. Kerr, J. R.; Haskins, J. F. NASA Langley Research Centre NASA/CR-178272, Hampton, VA, 1987.
10. Boyd, J.; Chang, G. E. C. Proc Int SAMPE Tech Conf 1993, 38, 357.
11. Gates, T. S. NASA Langley Research Centre NASA/TP2003-212407, Hampton, VA, 2003.
12. Morgan, R. J.; Shin, E. E.; Lincoln, J.; Zhou, J.; Drzal, L. T.; Wilenski, M. S.; Lee, A.; Curtis, D. J Proc Int SAMPE Tech Conf 1998, 43, 106.
13. Nam, J. D. Seferis, J. C. SAMPE Q 1992, 24, 10.
14. Salin, I.; Seferis, J. C.; Loechelt, C. L.; Rothschilds, R. Proc Int SAMPE Tech Conf 1992, 37, 1365.
15. Stenzenberger, H. D.; Konig, P.; Herzog, M.; Romer, R.; Pierce, S.; Tear, K.; Canning, M. S. Proc Int SAMPE Tech Conf 1987, 34, 1877.
16. Zhong, Y.; He, Y.; Zhou, J. J Proc Int SAMPE Tech Conf 1999, 44, 741.
17. Fox, B. L.; Lowe, A.; Hodgkin, J. H. Eng Failure Anal 2004, 11, 235.
18. Fox, B. L. Ph.D. Thesis, Australian National University, Canberra 2001.
19. Colin, X.; Marais, J.; Verdu, J. J Appl Polym Sci 2001, 82, 3418.
20. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. Polyimides; Blackie: London, 1990.
21. Barton, J. M.; Hamerton, I.; Jones, R. J.; Stedman, J. C. Polym Bull 1991, 27, 163.
22. Cunningham, I. D.; Brownhill, A.; Hamerton, I.; Howlin, B. J. Tetrahedron 1997, 53, 13473.
23. Phelan, J. C.; Sung, C. S. P. Macromolecules 1996, 29, 239.
24. Hopewell, J. L.; George, G. A.; Hill, D. J. T. Polymer 2000, 41, 8221.
25. Hopewell, J. L.; George, G. A.; Hill, D. J. T. Polymer 2000, 41, 8231.
26. Grenier-Loustalot, M.; Da Cunha, L. Polymer J 1997, 38, 6303.
27. Rozenberg, B. A.; Dzhavadyan, E. A.; Morgan, R. J.; Shin, E. E. Polym Adv Technol 1996, 13, 213.
28. Lincoln, J. E.; Morgan, R. J.; Shin, E. E. Polym Compos 2001, 22, 397 and references therein.
29. Morgan, R. J.; Shin, E. E.; Lincoln, J.; Choi, J.; Lee, A. Proc Int SAMPE Tech Conf 1996, 28, 213.
30. Garton, A. J Macromol Sci Chem 1989, 26, 17.
31. Hummel, D. O.; Scholl, F. Atlas of Polymer and Plastic analysis, Vol. 2b/I; VCH Publishers: New York, 1985.
32. Bao, L.-R.; Yee, A. F. Polymer 2002, 43, 3987.
33. Bowles, K. J.; McCorkle, L.; Ingram, L. J Adv Mater 1998, 30, 27.
34. Bowles, K. J.; Jayne, D.; Leonhardt, T. A. SAMPE Q 1993, 24, 2.
35. Harris, B., Ed. Fatigue in Composites; CRC Press: Boca Raton, 2003.