Accelerated Ageing Versus Realistic Ageing in Aerospace Composite Materials. IV. Hot/Wet Ageing Effects in a Low Temperature Cure Epoxy Composite

B. Dao, J. H. Hodgkin, J. Krstina, J. Mardel, W. Tian

CSIRO Molecular and Health Technologies, Private Bag 10, Clayton South, Melbourne, Victoria 3169, Australia

ABSTRACT: Samples of an aerospace grade carbon fiber epoxy composite (Hexcel, M20/IM7) were subject to long term ($\approx$1 year) hot/wet ageing and thermal spiking under a variety of humidity levels and temperature conditions related to ''in service'' conditions seen by military aircraft. Changes to the chemical and physicochemical structure of the composite were analyzed by a range of different techniques including gravimetric analysis, FTIR, and DMA to compare the effects of the various ageing conditions. The results indicated that the chemical effects of hot/wet and spiking conditions on this incompletely cured type of composite are very complex because of the variations in moisture levels and cure chemistry from the composite surface inwards as the resin ages under the different external environments. Physicochemical changes (such as T_g) and structural effects (such as microcracking) are similarly complex and dependent on composite thickness. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 4264–4276, 2007

Key words: composite degradation; hot/wet ageing; thermal spiking; chemical changes; T_g; microcracking; epoxy resin; FTIR

INTRODUCTION

In the first three articles of this series,[1–3] we reported on the chemistry of isothermal ageing of two commercial epoxy composite materials and two bismaleimide composite systems at a range of temperatures from reasonable ''in service'' conditions to highly accelerated (test) conditions. However, in actual use situations, another critical variable in normal composite ageing is moisture and this will vary considerably with location and exposure times. For instance, commercial aircraft that normally have a very high percentage of time in the air (at very low temperatures, low humidity, and subsonic speeds) generally have a low-average moisture pick-up and with little variation. For military aircraft, different exposure and temperature conditions are experienced in desert, tropical, or arctic environments, so different trends are observed. An early phase of our comprehensive ageing project[4] provided a review of the conditions encountered by these military aircraft under a variety of operational scenarios.[5] From this review, a range of hot/wet ageing conditions relating to the service environments for military aircraft were selected (Table I). Samples of an aerospace-industry-produced, low-temperature-cure, epoxy composite (M20/IM7) were then aged under these selected conditions and the resulting changes were analyzed for chemical and physicochemical effects on the composite. M20/IM7 is a dicyandiamide (DICY) cured epoxy resin formulation on intermediate modulus carbon fiber, supplied as a prepreg by Hexcel Composites, Duxford, UK.[6]

Many other studies of the hot/wet ageing of aerospace composites and neat resin materials have been carried out both as reported in the academic literature[7–15] and as standard testing procedures in the aerospace industry.[16–20] The academic literature has mainly relied on spectroscopic and dynamic mechanical studies to determine the chemistry and physics of moisture interaction with simple (noncommercial) formulations of neat resin. Considerable discussion and disagreement has occurred on the types of molecular environment of adsorbed water (bonded and nonbonded) and the types of absorption kinetics (Fickian or non-Fickian).[21–30] In contrast, the bulk of the industry testing has relied on the mechanical and fatigue (microcracking) effects on composite samples and has often used quite extreme conditions to accelerate changes. For example, the use of full water immersion at 70°C, 90°C, or even boiling water is common. A useful but brief summary of both areas was presented in the review by Hancox,[20] which included both the literature references and the standard test methods.

The emphasis of the current research is on developing more sensitive chemical and physicochemical

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

TABLE I
Ageing Conditions for the M20/IM7 Composite

Humidifying conditions	Spiking temperatures (°C)		
45% RH/70°C	90	120	160
65% RH/70°C	–	–	160
85% RH/70°C	90	120	160

RH, relative humidity.

testing methods for commercial composites, which would include the use of the less extreme environmental conditioning techniques. The eventual aim is to provide a comparison between these simple tests and the mechanical testing information required by industry.

The conditions chosen for this ageing program included constant high (85% RH), medium (65% RH), and low (45% RH) humidity environments, as well as the use of thermal spiking at these humidity levels to mimic some of the effects of short supersonic flight sorties. Previous research[7,9,17,18] has shown that the timing of these thermal spikes is also important. A too short time interval (hours) does not allow sufficient moisture equilibration, while intervals long enough to allow almost complete equilibration (many weeks) will have little impact on composite properties. After some initial testing, an optimized thermal spiking program involving 5-min temperature spikes at intervals of 2–3 days was selected. The 10 environmental conditions used in our study of the M20/IM7 composite are shown in Table I.

Previous research[1,31–33] and manufacturer information[6] has indicated that this composite was produced from a mixture of epoxy resins [tetraglycidyl diaminodiphenylmethane (TGDDM) and triglycidylaminophenol (TGAP)] and cured by DICY hardener. The idealized structure is shown in Figure 1 but, because the material is used as a commercial repair epoxy in a partially cured form, there are considerable quantities of unreacted (and partially reacted) components (DICY and epoxy resins) as well as a number of other additives. One of these, a polyimide-toughening phase, is a prominent contributor to the infrared spectral information. The partially reacted nature of this composite contributes to the complexity of the thermal ageing chemistry,[1] as the thermal and hot/wet ageing environments help to complete the cure chemistry. In contrast, it is also well documented that hot/wet and spiking environments can cause material extraction and composite microcracking in composites with DICY hardeners, even when the cure is believed to be complete.[9,34,35]

EXPERIMENTAL

The composite material selected Hexcel, M20/IM7 was a low temperature cure, repair epoxy matrix on

an intermediate modulus, carbon fiber. The prepreg was laid up by hand to give a unidirectional laminate with the approximate dimensions of 700 mm by 1000 mm and 2 mm in thickness. The laminate was cured in an autoclave utilizing a proprietary, aerospace, cure cycle as used for repair epoxy components, believed to be similar to that described by Hayes et al.[36] Our previously reported differential scanning calorimetry (DSC) analysis results[1] indicated that it was ~ 72% cured. The cured laminate was C-scanned and measured for thickness (consolidation) to ensure the quality of the laminate and then it was cut into a series of 50 mm by 50-mm plaques. These plaques were dried at 50°C over phosphorous pentoxide (P_2O_5) until a constant weight was achieved, before testing. Acid digestion tests indicated a resin weight fraction of 33.6%.

The plaques were conditioned at 70°C at three different humidity levels (45, 65, and 85% RH). The temperature and humidity ovens were calibrated and monitored in accordance with standard operating procedures; however, there was some temperature cycling (±2%) so water condensation occurred at the higher humidity levels. The samples were extracted at appropriate times for weighing, analysis, and/or thermal spiking. In each case, the results were averaged over three sample plaques. Thermal spiking was conducted on samples conditioned at 85 and 45% RH at temperatures of 90, 120, and 160°C, whereas the 65% RH samples were spiked only at 160°C, as indicated in Table I. Thermal spiking was undertaken using a (previously heated) hot press, at minimum pressure to get good contact, for 5 min. This was done in accordance with a standard operating procedure, which included the use of a multiaperture shaped-metal jig designed for good heat transfer and good vapor flow.

The plaques were weighed on a Mettler Toledo AB 204-S four decimal place balance to give a weighing error of 0.01%. At least three plaques at each condition were removed from the humidity cabinets or press and
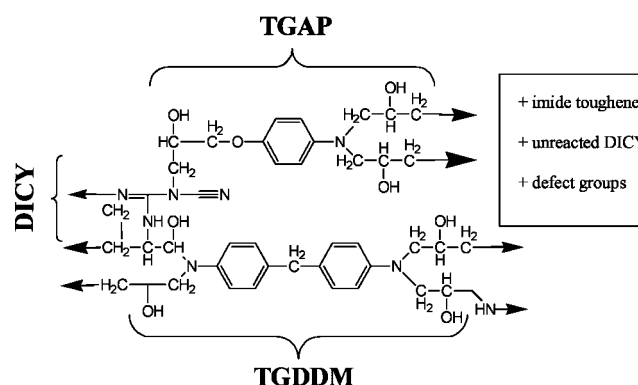

Figure 1 Idealized structure of the M20/IM7 matrix resin.

cooled to room temperature in an enclosed glass container before weighing. The samples retained for Fourier transform infrared spectroscopy (FTIR), DSC, and dynamic mechanical analysis (DMA) experiments were stored at $-4°C$ and wrapped in plastic wrap and then aluminum foil until tested.

All DSC analyses were conducted on a Mettler Toledo 821e with Star Software version 6. Samples were run in alternating DSC mode with an underlying heating rate of 5°C/min. Samples were encapsulated in lightweight aluminum pans. A sample size of between 20 and 30 mg was used. Percentage residual cure was determined by measurement of the enthalpy associated with the unreacted resin and compared with the enthalpy from prepreg, for a similar dynamic scan.

DMA was conducted on a Rheometrics Scientific IIIe. This instrument was completely computer controlled 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 reproducible sample width of ~ 10 mm. The cut 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 storage modulus (E'_{onset}) and by the tan δ peak position at 1 Hz.

FTIR spectra 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 and was finely ground with ~ 50 mg of dry KBr before being pressed into a disc. The disc was analyzed (256 scans) in a Perkin Elmer 2000 FTIR spectrophotometer, in transmission mode using KBr as the background reference. Analysis of wet composite carried out under the same conditions showed significant, but small, water peaks (free and bound) between 3650 and 3450 cm^{-1} for the initial ~ 30–60 scans, but then these were lost by IR heating.

Near infra red (NIR) analysis was conducted on an NIRS Perstorp system in accordance with the appropriate standard operating procedure. Laminate samples (50 mm by 50 mm) were placed directly onto the specimen holder, covering the entire viewing window with the fiber running vertical to the sample holder for the unidirectional material. The sample was scanned for a total of 50 scans and the data saved and transferred to Perkin Elmer spg format for interpretation.

The microscopic examination of the unidirectional composite samples was carried out as follows: the sample was prepared by cutting (by a diamond saw) a small edge section from an aged plaque. The sample was then embedded in epoxy resin to make a solid disc (about 10-mm thick) after curing and polished until a clear microscopic image of the laminate cross-section (fiber ends showing) could be observed.

RESULTS

Introduction

As detailed earlier, the M20/IM7 system has an epoxy resin matrix consisting of a mixture of TGDDM and TGAP cured by DICY hardener and the idealized chemical structure is believed to be as shown in Figure 1. However, the aerospace qualified chemistry has to be significantly different as the material is initially used in a very incompletely cured form ($\approx 72\%$, as determined by DSC[1]) and contains a number of unknown and known additives. The known additives included a polyimide toughening agent and a considerable amount (by extraction) of unreacted DICY and partially reacted DICY.[37] The monomers, oligomers, and the additives are much more likely to be affected by the hot/wet environmental conditions (by hydrolysis reactions and/or extraction) than the cured crosslinked resin and these effects will differ from the plaque surface inwards.

The chemical and physicochemical changes in the composite plaques were followed by a range of techniques (as previously reported in Ref. 1); however, only the gravimetric analysis, DSC, DMA, FTIR, NIR, and microscopic examination results are reported here. DMA and gravimetric analysis, like most mechanical testing methods, provide an average value of a property change over the whole laminate. The other tests, which are microscopic, provide detailed changes occurring at different depths and in different areas of the composite.

Gravimetric analysis

Moisture absorption

The plots of water uptake of the composite (of which 33.6% of total composite weight is resin) over 7500 h at the three different humidity levels are shown in Figure 2. As expected there are large differences in the total amount of water absorbed by the resin under different humidity conditions. While the weighing errors for the three plaques measured at each point were very low ($<0.01\%$) it appears that some of the variations observed in the water absorption curves were due to humidity cabinet control problems (late in the ageing program only) and some water condensation at the highest humidity
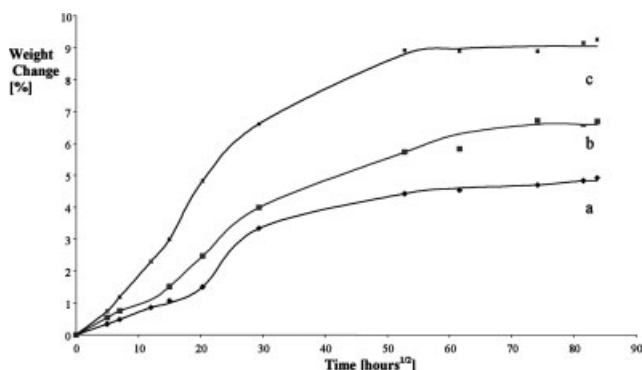
Figure 2 Water uptake curves for M20/IM7 matrix resin during conditioning at 70°C in 45% RH (a), 65% RH (b), and 85% RH (c) environments.

levels. Most previous academic studies (e.g., Ref. 38) have used chemically controlled humidity cabinets (aqueous salt solutions), which are more accurate but possibly less realistic (no condensation) and were more difficult to use for the large number of samples required.

It is noticeable that the curves are different from those seen in the many neat-resin systems previously studied,[13–17,25,27–30] as well as reports documented on some fully cured epoxy composites.[7,21,22] In this complex, reactive system there appears to be an induction period with a slow weight increase; followed by the middle stage with a high absorption rate and then finally a plateau with a very low weight increase rate occurs. This latter area was only reached in the 85% RH conditions after about 4000 h, but even this level was not as evident at the lower humidity levels, until much later. The longer than normal induction period in these curves may be rationalized by considering the various effects of material extraction at the surface of the composite and the defect group (unreacted monomer and oligomer end groups) reactions with water, as mentioned in Introduction. The intermediate, high-absorption rate may relate to the osmotic effects of unreacted DICY as described by Jones[38] for other composite materials with very similar chemical formulations. Moisture absorption experiments carried out at exactly the same time, in the same cabinets, with a fully cured, aerospace epoxy composite (8552/IM7) did not show the induction period and were similar to those seen in the previous literature reports. These latter results will be reported in a later communication.

The rate of composite weight loss on drying after complete saturation was not studied in detail because of time constraints but, for the 85% RH conditioned samples, the materials were monitored as they were dried at 50°C over P_2O_5. Although the initial weight loss was relatively fast, only 50% of the gained weight was lost after $\approx$ 1000 h, and the rate

of weight loss was rapidly approaching zero leaving a residual, resin-weight-gain of nearly 5%. While a common explanation of this in previous work[17,23–30] involved weakly bound and strongly bound water, most of our evidence (see later) was more consistent with a permanent weight gain caused by chemical reactions of defect groups in this commercial material. For example, isolated and initially unreacted epoxy groups could form glycols on reaction with absorbed water over time at the elevated test temperature.

Thermal spiking

The thermal spiking studies were carried out on the M20/IM7 composite equilibrated at 70°C at the three different humidity levels, as shown in Table I. In each case, the water absorption effects caused by thermal spiking were considerably different than those seen by the simple humidity conditioned samples. Figure 3 shows the absorption profile of samples equilibrated at 70°C and 45% RH compared with the spiked data at this humidity level. At the lower two temperatures of spiking (90 and 120°C) the general effect was just a mild delay in parts of the moisture absorption profile. This also appeared to prevent the accelerated absorption period at about 400 h seen in the unspiked samples. For the higher temperature spike regime (160°C), the water absorption was considerably accelerated, but the shape of the curve was similar to the simple conditioning curve.

Figure 4 shows a similar absorption profile of samples equilibrated at 70°C and 65% RH and the spiked sample data at 160°C. In this case, the spiking caused an almost immediate and sharp increase in water absorption over the unspiked sample; however, by the end of the program the two curves
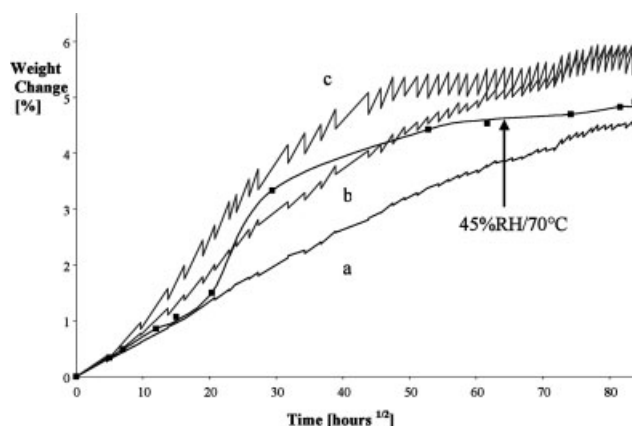

Figure 3 Water uptake curves for M20/IM7 matrix resin during thermal spiking at 90°C (a), 120°C (b), and 160°C (c); samples were conditioned at 70°C and 45% RH environments.
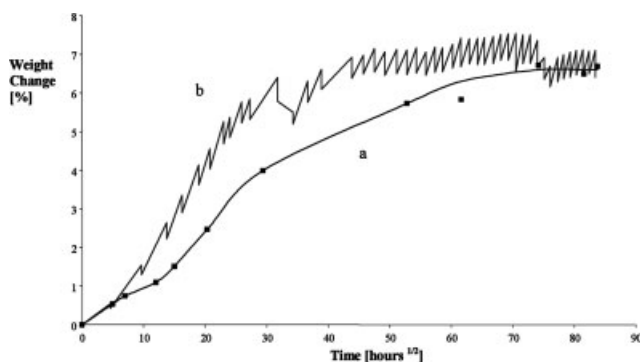
Figure 4 The water uptake curves for M20/IM7 matrix resin conditioned at 70°C and 65% RH (a), and thermally spiked at 160°C (b).

appeared to confirm that a similar equilibrium moisture level had been reached. The two anomalous dips in the spiking curves at about 1500 and 6000 h were caused by a temporary loss of cabinet humidity control over a 24-h-period.

Figure 5 details the absorption curves for samples conditioned at 70°C and 85% RH and those spiked at the three different temperatures. In all cases the absorption of water was significantly accelerated by spiking, but the same equilibrium level of water was reached much earlier than with the unspiked sample. Higher levels of water were lost at higher spiking temperatures but the general absorption level was the same for both spiking temperatures above 100°C. While similar enhanced water absorption (with similar composite samples conditioned at 96% RH) has been noted by Hough et al.,[19] the equilibrium levels of moisture reached by spiked and unspiked materials were very different in this case. The shape of the moisture absorption profiles observed in this work need to be noted when considering the following thermal analysis, DMA and
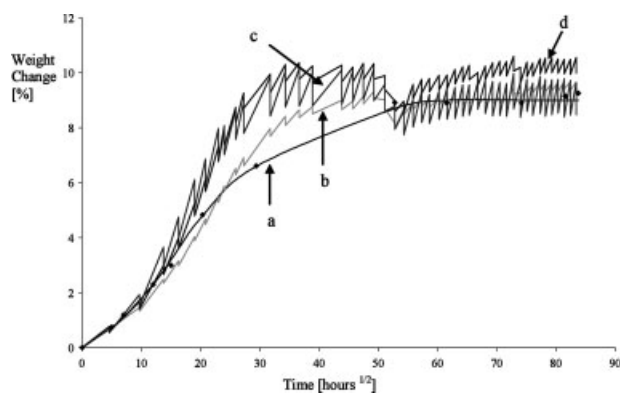

Figure 5 Water uptake curves for M20/IM7 matrix resin during thermal spiking at 90°C (b), 120°C (c), and 160°C (d); samples were conditioned at 70°C and 85% RH (a) environments.

FTIR sections where different water concentrations and/or water reactions could take place across the thickness of the sample and could have a significant influence on the observed behavior.

Thermal analysis

Differential scanning calorimetry

The DSC experiment measures the exothermic energy of any residual reactions present in a composite material as the temperature is increased at a relatively rapid rate (10°C/min in these experiments). The aerospace industry uses this measure of residual exothermic energy, below an arbitrary cut off temperature, as the remaining cure percentage of the composite. However, a DSC analysis sample is relatively small (20–30 mg) and usually taken from the surface or an edge of a material, and in this case may have been subjected to hydrolysis reactions and water extraction effects not seen by the bulk material during its treatment in the hot/wet ageing environment. Such effects have been previously described in the work of Xiao et al.[24]

The DSC determination of degree of cure (72%) of the starting composite material was discussed in a previous article[1] and while this initial measurement error was approximately ±1% the errors for the hydrothermally aged materials will be further increased by the factors discussed earlier. The percentage conversion figures obtained for the unspiked material (as shown in Table II) show relatively consistent increases with increasing humidity levels and ageing time. However, it is very obvious that much more than the simple cure reactions present at 0% RH (straight thermal ageing) take place under high humidity conditions.

The measured DSC conversion figures observed with the spiked materials follow a similar pattern but at a greatly accelerated rate for the higher spiking temperatures and higher humidity levels (i.e., 100% conversion after 925 h at 85% RH and 160°C

TABLE II
Percentage Conversion (±2%) of M20 Resin as a Function of Hot/Wet Conditions and Time at 70°C

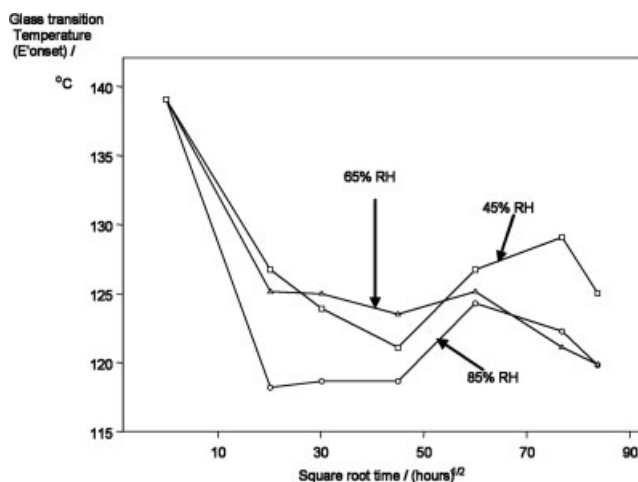| Time (h)	Percentage conversion			
	45% RH	65% RH	85% RH	0% RH
0	72	72	72	72
408	80	82.5	83	76
912	83	82	81	78
2025			98	79
3600	89	95	99	80
5900	94	100	100	80
7012	94	100	100	80

Empty cells indicate sampling problems.

Figure 6 Plot of T_g (E'_{onset}) against square root of time for M20/IM7 conditioned at 70°C and 45, 65, and 85% RH.

spiking). There were, however, a number of significant anomalies which indicated that the exact DSC sampling depth may have been critical because material extraction and/or reaction variations were playing an important part in the results. Because of the variability of these results they have not been reported or analyzed in this publication.

Dynamic mechanical analysis

It is well known that the absorption of water by carbon fiber composite systems normally has the effect of reducing the T_g (E'_{onset}) of the material because of plasticization effects.[28] It is also obvious that this T_g, as measured by a DMA instrument, is an average over the whole thickness of the sample whereas the water absorption will vary greatly over the sample thickness, with time, until equilibrium is reached. Also, T_g (E'_{onset}) is determined as an inflexion point in the modulus curve, so it is generally a less accurate measure than the tan δ T_g point. However, the aerospace industry often prefers the former as it provides the first sign of mechanical property changes; often well before the tan δ T_g.

In a partially equilibrated, partially reacted, commercial material (as used in these experiments and heated at 5°C/min), the T_g changes measured can be difficult to directly relate to molecular and mechanical properties. Figure 6 gives an indication of the complications encountered with the T_g (E'_{onset}) measurement of the M20/IM7 composite as it is aged in a hot/wet environment at different humidity levels. The initial sharp drop in T_g (E'_{onset}) at ≈ 400 hr ageing (at all humidity levels) is directly related to the plasticization effect, which will be particularly greater in an incompletely reacted material. The minimum point at each humidity level was in the area
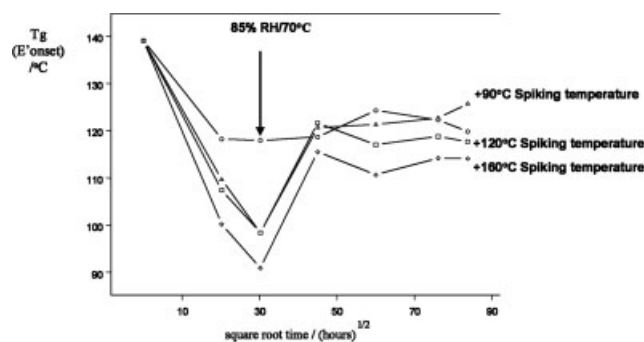

Figure 7 Plot of T_g (E'_{onset}) against square root of time for M20/IM7 conditioned at 70°C and 85% RH and thermally spiked at 90, 120, and 160°C.

where the water absorption figures tended toward equilibrium (Fig. 2). However, at this point the increases in conversion percentages (as seen in Table II) start to have an effect. The rather variable T_g (E'_{onset}) increases and decreases, as seen toward the end of the ageing program, may include extra effects such as microcracking, material extraction, and the reactions of resin functional groups with water.

In the case of the samples that have been hot/wet conditioned and also thermally spiked, the changes in T_g (E'_{onset}) are even more drastic and variable. Figure 7 shows the plot for the 85% RH samples and the initial drop in T_g is as much as 50°C for the 160°C spiked sample, which is in line with the extra amount of water absorbed, as shown in Figure 2. The quick recovery of 25°C in T_g is also in line with the observed increase in cure levels (DSC).

In contrast, the 45% RH samples (Fig. 8) showed an increase in T_g (E'_{onset}) of ≈ 15°C (after an initial drop of similar amounts) as cure increases have counteracted the initial plasticization effects. All curves (85, 65, and 45% RH at the different spiking
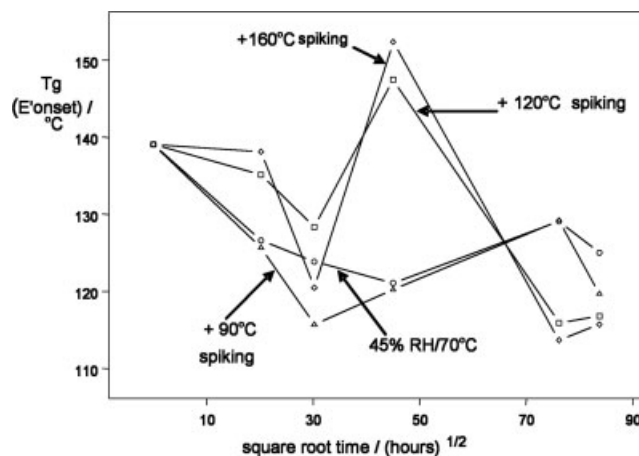

Figure 8 Plot of T_g (E'_{onset}) against square root of time for M20/IM7 conditioned at 70°C and 45% RH, and thermally spiked at 90, 120, and 160°C.
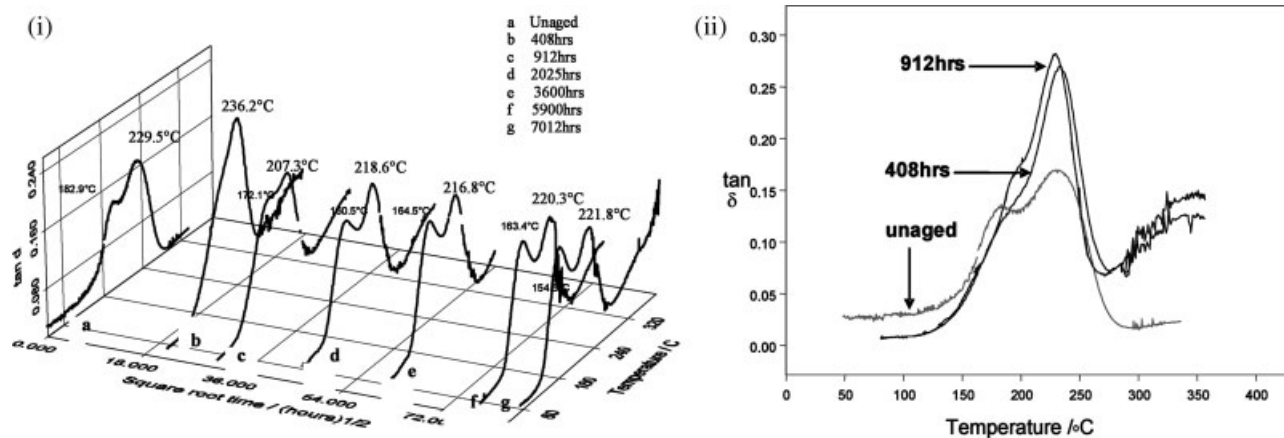
Figure 9 (i) A 3D plot of tan δ against temperature as a function of the square root of time for M20/IM7 conditioned at 85% RH. (ii) A Plot of tan δ verses temperature for unaged M20/IM7 and 70°C and 45% RH conditioned M20/IM7 at 0, 408, and 912 h.

temperatures) were very complex, indicating that a number of independent variables were affecting the measurements over the ageing time, and confirming that this measure of initial loss of modulus is not a very reliable measure of hot/wet ageing in this composite.

A more complete picture of the effects of the molecular complexity of the environmental ageing of this material was shown in the DMA tan δ plots run at 100 Hz (tan δ plots at 1 and 5 Hz were also run but were less informative). The simple hot/wet environment curves show two different molecular domains in the composite, which vary in amount and influence as water absorption and further cure reactions progress through the sample. Figure 9(i) shows a 3D plot of the tan δ temperature changes over time of ageing at 70°C and 85% RH, and while the lower tan δ peak shows a consistent fall in peak temperature with ageing time, the higher temperature peak is somewhat more variable with both increases and decreases with time. Similar complex behavior is seen at 65 and 45% RH, although the latter tended back toward a single tan δ peak (at 212°C) after about 900 h [Fig. 9(ii)]. As expected thermal spiking accelerated the changes but the final curves for the three different humidity levels ended up very similar to their final unspiked tan δ curves. The tan δ curves at intermediate times showed quite complex patterns of behavior, which defied simple analysis.

These experimental DMA results indicate that mechanical test results on hot/wet and spiked composites of the M20/IM7 type (commercially cured) can bear little relation to reality, if the environmental conditions chosen for testing are not very closely related to conditions encountered ''in service.'' This is especially the case if the test type is too simplified [e.g., T_g (E'_{onset}) compared with a full tan δ curve]. It

is also obvious that the molecular environment of the final hot/wet aged material is quite different from the starting matrix resin, and the chemistry of this material at different ageing times will vary with depth in the composite plaque.

FTIR analysis

Introduction

FTIR spectroscopy has been used extensively to study the absorption and reactions of water with various epoxy resins, including aerospace formulations and a very good library of peak positions for each molecular structure has been built up. Table III is a modification of the tables produced by Musto et al.[35] to emphasize the DICY hardener used in M20 resin rather than the DDS used in their work. The FTIR data were obtained using the commercially produced carbon fiber composite and not experimental neat resin systems utilized in previous studies. The FTIR spectra were obtained from small amounts

TABLE III
FTIR Peak Assignments for M20/IM7 ([35])

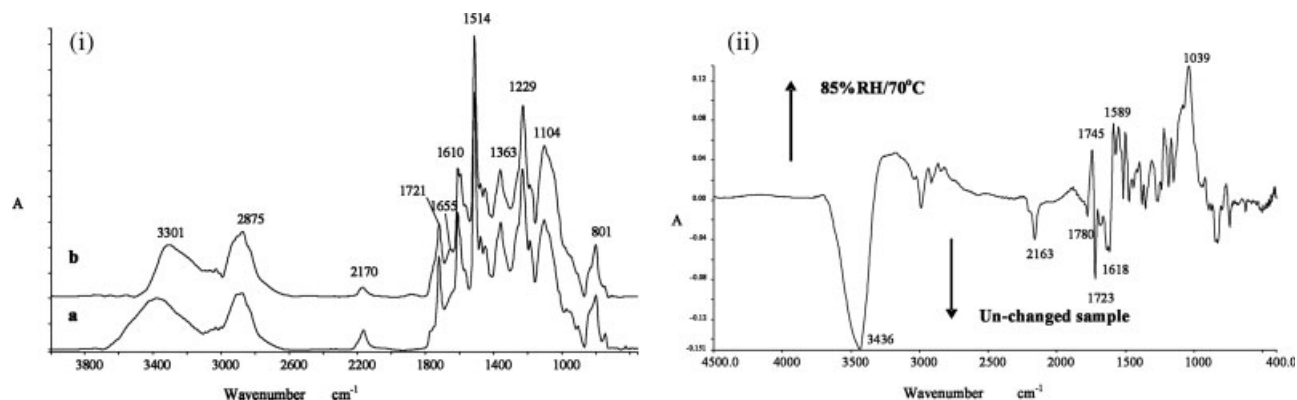| Wavenumber (cm^{-1})	Peak assignment
3600–3400	OH/NH$_2$
3400–3200	NH
3060–2800	Various CH
2170	DICY C≡N etc.
1780, 1720	Imide C=O
1670–1650	Amide C=O
1610–1590	Aromatic ring
1514	Aromatic ring
∼ 1360	DDS, S=O
1229	Ar—C—Ar[35]
1120–1040	—C—O— and Ar—S—[35]
801	Aromatic

Figure 10 (i) Mid-FTIR surface spectra of M20/IM7 aged at 70°C and 85% RH for 7500 h (b) with the unaged, time zero sample (a). (ii) Differential spectra of the mid-FTIR surface spectra of M20 aged at 70°C and 85% RH for 7500 h and the unaged, time zero sample.

of composite (~ 2 mg including fiber) finely ground and dried at 50°C and then mixed with very dry KBr. This technique eliminates the effects of any absorbed water (even "so called" strongly bound water) and only shows the effect of reacted water or the results of water extraction from the composite surface. To test this, wet composite (~ 2 mg) was finely ground, briefly allowed to air dry before the KBr was added and then quickly analyzed. A small signal for water (~ 3650 cm^{-1}) and bound water (increases at 3550–3400 cm^{-1}) was seen for the first 30–60 scans but these were soon lost. This contrasts strongly with most of the recent FTIR analysis work on the interaction of water and bulk epoxy resins, where the exact state of water binding has been a topic of intensive discussion.[23–30] The KBr technique also tends to produce much narrower FTIR peaks and more reproducible spectra than other methods, especially with composites. The final spectra displayed are the Fourier transform of 256 co-added interferograms.

Results

The FTIR spectra of both the hot/wet conditioned and the conditioned plus spiked samples of M20/IM7 show much smaller changes over time than the previous high temperature treated composite samples.[1] All of the samples were followed at seven or more intervals during ageing and the changes seen were very consistent but because of the detail supplied by all of these spectra only a short overview is possible in this article.

Figure 10(i) shows an example of the larger chemical changes that can be seen, even within the broad spectra, and it is a comparison of the surface of the unaged M20/IM7 sample with the surface of the same material aged for 7500 h at 70°C and 85% RH.

Figure 10(ii) is a differential spectrum of the two traces, which emphasizes exactly where the changes have occurred. These major changes have occurred in the following regions: ≈ 3440 cm^{-1} (OH/NH$_2$ decrease), 2162 cm^{-1} (C≡N decrease, DICY), 1745 cm^{-1} (carbonyl increase), 1780 cm^{-1}, 1723 cm^{-1} (imide decrease), 1611 cm^{-1}, 1514 cm^{-1} (aromatic decrease), 1595 cm^{-1} (aromatic increase), 1038 cm^{-1} (C—O increase). Similar changes are seen in the M20/IM7 material conditioned at the high humidity level (85% RH) and then spiked, but even with the high spiking temperatures the effects were less than those seen in the simple conditioned (85% RH/70°C) sample.

Of particular interest is the large changes in the hydroxyl/primary amine area, in contrast to the adjacent secondary amine (≈ 3300 cm^{-1}, reacted DICY) area. At first glance, the large decrease in hydroxyl at the surface under high humidity conditioning (compared with the low humidity and simple thermal ageing gains[1]) is counterintuitive. It is also the inverse of the total moisture uptake levels seen in the gravimetric data. However, it has to be noted that the FTIR samples were from the immediate surface (from which DICY and partially reacted DICY must have been extracted by water condensation) and all free water has been removed in the analysis process so "only chemical changes remain."

A much closer look at the composite spectra of this area (Fig. 11) provides further information on what has taken place. In this case, all the materials have been aged at 85% RH/70°C for 7500 h, but three of the materials have also been spiked at regular intervals at different temperatures. As discussed earlier, the unspiked material (spectrum "a") has lost the most hydroxyl/amine product (3436 cm^{-1} and DICY at 2172 cm^{-1}) when compared with the starting composite because of material extraction [Fig. 10(i,ii)]: the starting composite spectra was not
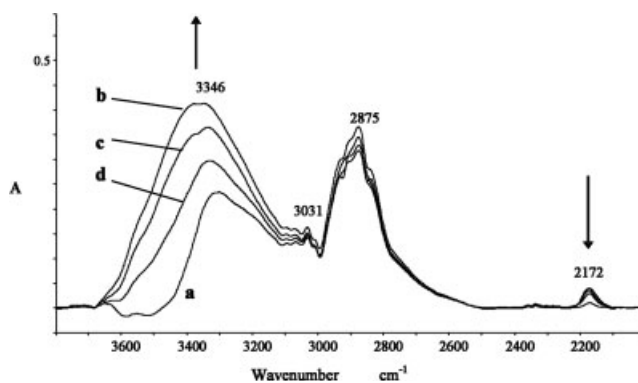
Figure 11 The expanded (3800–2000 cm^{-1}) mid-FTIR surface spectra of M20/IM7 aged at 85% RH/70°C and 7500 h (a) with some of the changes observed with increasing spiking temperature from 90°C (b), 120°C (c), and 160°C (d) over 7500 h.

reincluded at Figure 11 as it overlaps (spectra ''c''). In the material spiked at 90°C (spectra ''b'') the hydroxyl/amine peak has increased with time, probably due to hydrolysis reactions with the unused epoxy groups. After 120°C spiking (spectra ''c'') there is probably a competition between further cure, extraction, and the hydrolysis reactions, which causes some hydroxyl decreases balanced by various gains. After 160°C spiking (spectra ''d'') further cure would occur but so would decomposition reactions of glycol groups, so there is considerable hydroxyl loss compared with the starting material.

Similar OH/NH peak (3436 cm^{-1}) absorption variations were found at the surface of the composite during the humidity ageing, without spiking. The OH/NH peak increased (compared with the starting material) at 45% RH because of oxidation and epoxy/water reactions with no water extraction but decreased slightly at 65% RH and further at 85% RH because of the extraction of surface material. The changes occurred smoothly over the seven analysis intervals.

Very detailed examination of the changes in other areas of the spectra, especially with the use of differential spectra as seen in Figure 10(ii), were possible and showed the progression of the oxidation effects (amide formation, at ~ 1660 cm^{-1} and aromatic changes, at 1596 cm^{-1}) similar to those seen in isothermal ageing test results,[1] as well as continuing cure reactions (loss of epoxy at ~ 915 cm^{-1} and NH$_2$ at ~ 3400 cm^{-1}) within the composite.

The above FTIR results mainly concerned the dried, immediate-surface material; however, the NIR results (Fig. 12) showed the expected increase in hydroxyl/water peaks (at 5219 cm^{-1}) with increases in the ageing humidity conditions. For the NIR analyses, the composite samples used were the undried composite plaques, and the depth of penetration of NIR (~ 30 μm) is much greater than for the mid-IR

spectra so the results are a reflection of the bulk composite properties. Further details of the NIR data are not included in this report as the interpretation of the spectra is much less reliable than the mid-IR data, because the peaks are combination peaks and there is some interference from the carbon fiber in the composite. However, it does appear to confirm that there are minor changes in the aliphatic CH overtone region (4350 cm^{-1}) at deeper levels for the ageing under different humidity conditions.

Unlike the surface chemistry effects of hot/wet ageing, the internal chemical changes seen in the FTIR spectra under most of these ageing conditions were very minor and just indicated further cure progression with temperature, time, and spiking and could only be interpreted from differential spectra.

Physical effects of hot/wet ageing

The M20/IM7 composite (hot/wet aged and spiked) samples were examined microscopically after being removed from the conditioning and spiking environments, then dried and embedded in a clear epoxy. The samples were polished to display the fiber end sections of this unidirectional composite. As seen in Figure 13 (samples a–d), even the samples removed at the first analysis point (424 h) after only a few spike excursions were significantly microcracked near the surface. The microcracking was more pronounced at the higher humidity levels and the higher spike temperatures, but could be seen even in the 45% RH/70°C with 160°C spike at 424 h. As spiking continued, the extent of microcracking increased and progressed inward. In contrast, the simple conditioned samples did not show microcracking until late in the program. Even at the final ageing time (7500 h) at 85% RH/70°C, the extent of microcracking, and the crack size was minor compared with that found in the spiked samples.
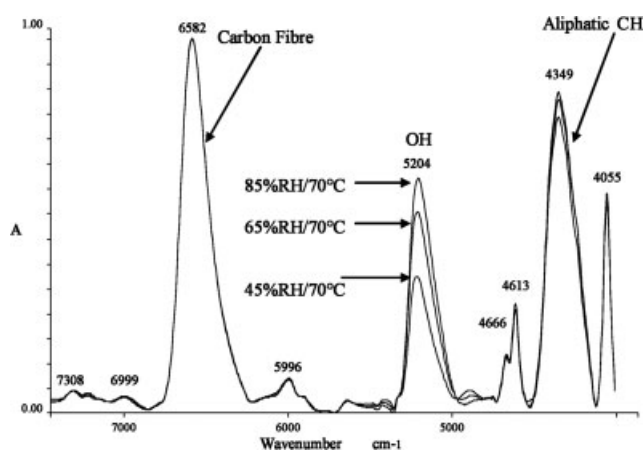

Figure 12 The NIR spectra of M20/IM7 conditioned at 70°C for 7500 h (45, 65, and 85% RH).
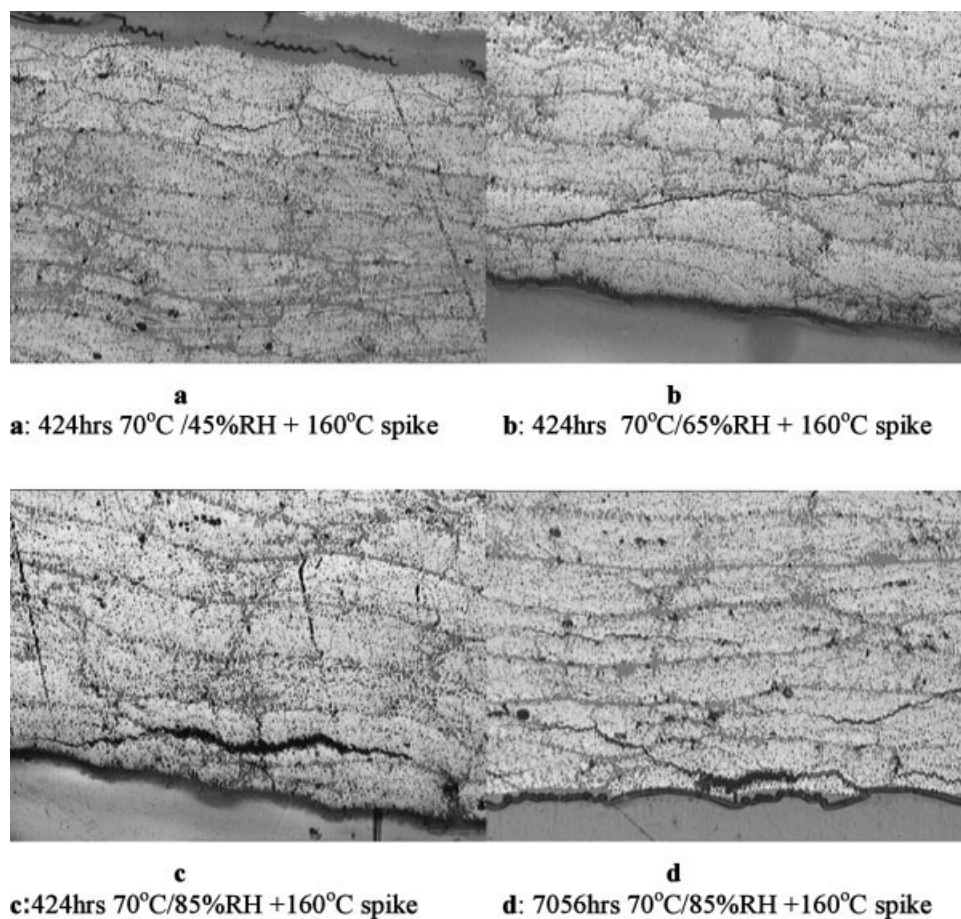
a: 424hrs 70°C /45%RH + 160°C spike

b: 424hrs 70°C/65%RH + 160°C spike

c: 424hrs 70°C/85%RH +160°C spike

d: 7056hrs 70°C/85%RH +160°C spike

Figure 13 The magnified surface (×20) of M20/IM7 laminate aged under a range of spiking conditions.

Discussion of results

The chemistry of the commercial M20/IM7 composite (as outlined also in our isothermal studies[1]) is highly complex because of the number of different monomers and additives present, and because of its partially cured state. The idealized structure is as shown in Figure 1, but the "defect" chemistry, which would be modified by hot/wet ageing, may be very different from that shown. The chemical changes also differ from those seen during isothermal ageing, where further curing and surface oxidation occurs, but will also vary considerably over the thickness of the composite. Many research studies have been carried out on the absorption of water into epoxy resins and epoxy composite systems, especially those cured by DICY, with different research groups favoring various strong and weakly bound water states.[20–27] This current research, on a commercially produced composite sample, indicates that the complexity of the results obtained might be better explained by variations in some chemical reactions and material extraction as well as simple water absorption in this matrix resin as the moisture progresses through the sample. The article of Xiao

et al.[24] on a DICY-cured, neat-epoxy-resin immersed in hot water proposed both hydrolysis reactions and material-extraction-effects in a similar situation except that their material was supposed to be fully cured and our experimental conditions allowed only moisture condensation not full immersion.

In our gravimetric studies of the M20/IM7 composite, the increases in weight with time and humidity were as expected but the shape of the curves were different from the standard Fickian absorption curves. The initial slower-than-expected increase in weight in all curves (including the spiked conditions) combined with the changes in the surface FTIR spectra and separate extraction studies, indicated an initial loss of material from the surface as well as water absorption. This initial loss of material would be expected to be much higher, and could lead to critical changes in physical properties, when some of the more extreme (but commonly used) hot/wet accelerated ageing conditions are used, e.g., full immersion in water at 90°C. However, a noticeable inflection was even seen in the 45% RH curve where condensation was a minimum may indicate not all of the weight loss was by extraction.

After the initial, relatively slow weight increases, large increases in water absorption rates were seen for the composites spiked at the higher humidity levels and higher spike temperatures even though the spiking test tended to remove significant quantities (>15%) of water during each thermal spike. Although the equilibrium moisture level was reached in these samples much earlier in the ageing program, almost the same final equilibrium water content (EWC) was obtained as with the simple conditioned samples. However, even though the EWCs reached in the spiked and unspiked samples (conditioned at the same humidity levels) reached similar values, the chemistry in the composites appeared to be significantly different, as determined by the surface hydroxyl levels (not water) in the FTIR (Figs. 10 and 11), and the DSC percentage conversions and DMA curves.

A first consideration was the surface chemistry as seen by FTIR. Since a small sample size was used for these analyses (and the sample could be comprehensively dried) only the matrix chemistry was evaluated and the results were not affected by the absorbed water levels, such as seen in many previous resin studies. The spectra were very repeatable and, as they were followed on at least seven occasions during each ageing program, even small changes could be analyzed reliably by differential spectra. The large loss of hydroxyl peaks on high humidity ageing was accompanied by losses of CH, C≡N and selected aromatic peaks [Fig. 10(ii)], and indicated loss of DICY and low-molecular-weight oligomers. This was accompanied by small peak gains in the carbonyl regions (1745 and 1655 cm^{-1}) because of oxidation of the type seen on isothermal ageing.[1] Under lower humidity conditions and with spiking treatment, similar but milder chemical changes took place.

These larger chemical changes were shown by FTIR to be only at the surface and probably would have a very small effect on the mechanical property measurements that are averaged over the whole composite thickness. These, however, could have had a much greater influence on the surface microcracking results seen on the spiked samples (Fig. 13). In contrast, the NIR results (Fig. 12) combine the changes in the chemistry of the resin with a measurement of the absorbed water because the samples were analyzed wet and to a greater depth (∼30 μm). The major changing peak (at ∼ 5205 cm^{-1}) is a combination of water and hydroxyl peaks and increased greatly with both the humidity levels and time as expected.

The lower level of absorption in the 3400 cm^{-1} region of the 85% RH/70°C sample at 7500 h (Fig. 11), when compared with the unaged sample, would indicate this area of FTIR absorption is due to the

formation of hydroxyl peaks by monomer reaction and not by strongly bound water peaks proposed by other groups.[15,17] The other changes seen in Figure 11 can be rationalized by invoking high surface extraction levels of uncrosslinked material (for the simple conditioned sample) versus increases in cure levels (formation of more OH, NH$_2$, and crosslinking) at the higher spiking temperature. Other areas of the spectra, and hence the chemistry of the aged matrix resin surface, also change significantly on spiking but only when the spectral details are examined closely or in differential spectra [Fig. 10(i,ii)]. Model compound work would need to be carried out to determine the reasons for the changes.

The above chemical group changes are obviously not just of academic importance as seen in the DMA data changes with ageing time, humidity levels, and spiking temperature effects. In this case, the T_g (E'_{onset}) curves (Fig. 6) initially drop drastically with moisture absorption levels (in both the conditioned and spiked samples), but after the initial large drop (up to 50°C) caused by plasticization, other factors such as ''cure level'' variations and material extraction at the surface cause more minor variations including T_g increases in the spiked samples. The tan δ curves are similarly complex and indicate the presence of at least two different areas or phases in the composite with large variations in the tan δ maxima with increases in humidity and ageing times.[38] Such variations would cause significant problems in reconciling many of the standard mechanical tests carried out on aerospace parts that have not been aged to equilibrium under very standard conditions.

The final effect noted in this research has been the effect of the large spikes in composite temperature on the internal physical structure of this composite material. While simple hot/wet conditioning did not cause significant microcracking of the samples until late in the ageing program, thermal spiking (especially for the high humidity conditions and high spike temperatures) caused significant surface microcracking very early into the program and considerably deeper and more extensive microcracking by 7500 h, Figure 13. This result would also have an effect in many of the possible mechanical property test results.

CONCLUSIONS

The results of this study indicate that the chemistry of the hot/wet ageing of the commercial M20/IM7 carbon fiber composite can be very complex because of variations in moisture absorption levels and moisture reactions as well as cure chemistry, from the surface inwards, as the resin ages with time, humidity/spiking variations, and the specific test

conditions. Because this commercially produced composite was incompletely cured, the ageing chemistry was also very different from that previously described in a simple isothermal ageing study.[1] This is due to the fact the material extraction effects can remove unreacted monomers and oligomers from the surface areas and moisture reactions can deactivate monomers, such as DICY and epoxy groups (as suggested by earlier work of Xiao et al.[24] and others) but not break completed chains, further in the body of the composite. This type of ageing result would be expected from any commercial composite that was incompletely cured to a significant degree. In the isothermal ageing environments previously studied[1] further cure reactions would be relatively unaffected by the test conditions.

The complexity of the ageing chemistry was indicated both by the FTIR analysis results and the non-Fickian, moisture-absorption-profiles seen under different ageing-conditions. Also in the case of the DMA results complex tan δ curves with multiple peaks indicated variations in molecular structure within the composite that could not be explained by simple moisture plasticizing changes over time.[38,39] The results did show that reliance on simple T_g (E'_{onset}) measurements in such mixed-structure materials can be unhelpful, because they are obtained from small directional changes in complex curve shapes.

The DMA results on this particular composite also indicate that standard mechanical test methods, which supply an average result over the whole composite thickness, could be greatly influenced by the exact conditions of composite ageing. This shows that highly accelerated ageing conditions used to test any partly cured composite could produce material with very different properties to those seen in "in-service" conditions. Such variations were observed in the microcracking levels seen in the spiked and unspiked samples of these composite materials.

The present results have suggested that the chemistry of realistic, hot/wet ageing of commercially produced composites, such as M20/IM7, may be better explained by changes in "defect" structures (especially at fiber and material surfaces) in the molecular chains of the matrix resin and not by changes in the major molecular units such as seen in Figure 1, or the effect of various types of absorbed water.

RECOMMENDATIONS

Future studies concerned with the long term ageing effects in advanced composites under different environments could benefit from using much less drastic accelerating conditions and instead look at ways of enhancing the analysis of small changes at the surface of a composite with more advanced analytical methods. In particular, new techniques of advanced FTIR spectroscopy (including appropriate computer techniques) appear to be able to deliver realistic information on small changes in the chemistry, which occurs during ageing. The exact nature of these chemical changes can be further elucidated by careful model compound work.[40]

Long-term chemical changes in matrix resins with many active defect groups (e.g., incompletely cured monomers) may be a more important factor in the decrease in composite properties than simple physical effects (e.g., plasticization, polymer crystallization) in some commercial materials.

However, even composite mechanical changes at aged surfaces can be studied by standard microtechniques, such as atomic force microscopy, micro-indentation, etc., and then related to larger scale mechanical test results.

An expected large cost savings for both the chemical and the physical and micromechanical tests mentioned earlier compared with the standard mechanical testing protocols was the original purpose of the project reported in this and previous articles of this series.

References

1. Dao, B.; Hodgkin, J.; Krstina, J.; Mardel, J.; Tian, W. J Appl Polym Sci 2006, 102, 4291.
2. Dao, B.; Hodgkin, J.; Krstina, J.; Mardel, J.; Tian, W. J Appl Polym Sci 2006, 102, 3221.
3. Dao, B.; Hodgkin, J.; Krstina, J.; Mardel, J.; Tian, W. J Appl Polym Sci 2007, 105, 2062.
4. Attwood, D.; Hodgkin, J.; Mardel, J.; St. John, H. In Proc ACUN-3, "Technology Convergence in Composite Applications"; Bandyopadhyay, S.; Gowripalan, N.; Heslehurst, R., Eds.; UNSW: Sydney, Australia, 2001; p 416.
5. Attwood, D. Conditions Encountered by Modern Aircraft, CSIRO Internal Report DEGAS/1311/001 May 2000.
6. M20/IM7, Hexcel Composite Materials, Product Data. 1998.
7. McKague, E. L.; Halkias, J. E.; Reynolds, J. D. J Compos Mater 1975, 9, 2.
8. Springer, G. S. In Developments in Reinforced Plastics; Pritchard, G., Ed.; Applied Science: London, 1982; Vol. 2.
9. Collings, T. A.; Stone, D. E. Compos Struct 1985, 3, 341.
10. Luoma, G. A.; Rowland, R. D. J Appl Polym Sci 1986, 32, 5777.
11. Morgan, R. J.; O'Neal, J. E. Polym Plast Tech Eng 1978, 10, 49.
12. Apicella, A.; Nicolias, L. Makromol Chem Macromol Symp 1987, 7, 97.
13. Xiao, G. Z.; Shanahan, M. E. R. J Polym Sci Part B: Polym Phys 1997, 35, 2659.
14. Merdas, I.; Thominette, F.; Tcharkhtchi, A.; Verdu, J. Compos Sci Technol 2002, 62, 487.
15. Ivanova, K. I.; Pethrick, R. A.; Affrossman S. J Appl Polym Sci 2001, 82, 3477.
16. Lin, Y. C. J Polym Res 2006, 13, 369.
17. Apicella, A.; Nicolias, L. Prod Res Dev, 1984, 23, 288.
18. Clark, G.; Saunders, D. S.; van Blaricum, T. J.; Richmond, M. Compos Sci Technol 1990, 39, 355.
19. Hough, J. A.; Xiang, Z. D.; Jones, F. R. Key Eng Mater 1998, 144, 27.

20. Hancox, N. L. Plastics Rubber Compos Process Appl 1984, 27, 97.
21. Bueller, F. U.; Seferis, J. C. Composites: Part A 2000, 31, 741.
22. Patel, S. R.; Case, S. W. Int J Fatig 2002, 24, 1295.
23. Jelinski, L. W.; Dumais, J. J.; Chiolli, A. L.; Ellis, T. S.; Karasz, F. E. Macromolecules 1985, 18, 1091.
24. Xiao, G. Z.; Delamar, M.; Shanahan, M. E. R. J Appl Polym Sci 1997, 65, 449.
25. Zhou, J.; Lucas, J. P. Polymer 1999, 40, 5505.
26. Ngono, Y.; Marechal, Y.; Mermilliod, N. J Phys Chem B 1999, 103, 4979.
27. Musto, P.; Ragosta, G.; Muscia, L. Chem Mater 2000, 12, 1331.
28. Musto, P.; Ragosta, G.; Scarinzi, G.; Muscia, L. J Polym Sci Part B: Polym Phys 2002, 40, 922.
29. Liu, M.; Wu, P.; Ding, Y.; Chen, G.; Li, S. Macromolecules 2002, 35, 5500.
30. Bockenhiemer, C.; Tata, D.; Possart, W. J Appl Polym Sci 2004, 91, 369.
31. Gumen, V. R.; Jones, F. R.; Attwood, D. Polymer 2000, 42, 5717.
32. Jones, F. R. In Fatigue in Composites; Harris, B., Ed.; CRC Press: Boca Rata, 2003; Chapter 4, p 117.
33. Adams, R. D.; Singh, M. M. Composites Part A 2001, 32, 797.
34. Walker, L.; Hu, X. Z. Compos Sci Technol 2003, 63, 531.
35. Musto, P.; Ragosta, G.; Russo, P.; Muscia, L. Macromol Chem Phys 2001, 202, 3445.
36. Hayes, B. S.; Gilbert, E. N.; Seferis, J. C. Composites Part A 2000, 31, 717.
37. Grenier-Loustalot, M.-F.; Metras, F.; Grenier, P. Eur Polym J 1990, 26, 83.
38. Jones, F. R. Proceedings of Conference on Designing Cost Effective Composites I. Mechanical Engineering; London 1998, 65.
39. Karad, S. K.; Jones, F. R.; Attwood, D. Polymer 2002, 43, 5209.
40. Bondzic, S.; Hodgkin, J.; Krstina, J.; Mardel, J. J Appl Polym Sci 2006, 100, 2210.