Accelerated Aging Versus Realistic Aging in Aerospace Composite Materials. V. The Effects of Hot/Wet Aging in a Structural Epoxy Composite

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ABSTRACT: Samples of an aerospace-grade, carbon-fiber epoxy composite (Hexcell 8552/IM7) were subject to long-term ($\approx$ 1 year) hot/wet aging and thermal spiking under different humidity levels and temperature conditions related to the "in-service" conditions seen in military aircraft. Changes to the chemical and physico-chemical structure of the composite were analyzed by a range of experimental techniques including gravimetric analysis, FTIR, and DMA, to compare the effects of the various aging conditions. The results indicated that, while the chemical changes (as seen by FTIR) in this well cured composite appeared to be only significant at the surface, they did appear to have a deeper influence on some of the major physical property changes observed, such as microcracking, glass-transition-temperature (T_g) variations, and Tan δ curves. These physical changes could not be fully explained by standard water-absorption effects alone but could also be influenced by chemical changes similar to those seen at the surface. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 901–910, 2010

Key words: aging; composites; FTIR

INTRODUCTION

In the earlier articles of this series,[1–3] we have reported on the chemistry of isothermal (only) aging of a number of different aerospace composite materials, including the Hexcell 8552/IM7 carbon-fiber structural composite. In these studies,[1–3] the composite materials were aged under a range of temperatures, from reasonable "in-service" conditions to highly accelerated (test) temperature environments, and the chemical and physical effects on the composite were investigated. In actual use situations, the other critical variable in normal composite aging is moisture, and this will vary considerably with the use environment.[4] For commercial aircraft, which typically spend a very high percentage of their time in flight (at very low temperatures, low humidity levels, and subsonic speeds), a low average moisture pick-up with little variation is generally seen. For military aircraft, however, their "in-use" conditions are very different. Military aircraft typically spend greater times on the ground, in extreme weather conditions, followed by short supersonic flight sorties that can cause significant thermal spiking at the composite surfaces.[5]

The current article details the chemical and physico-chemical effects on 8552/IM7 unidirectional, carbon-fiber composite of hot/wet aging combined with thermal spiking under the conditions of temperature and humidity detailed in Table I. These conditions, except possibly for the highest spiking temperatures, are comparable to those experienced during military "in-service" conditions, as determined by a previous literature study.[5]

Many other studies of the hot/wet aging and thermal spiking of neat epoxy resins and aerospace composites have been carried out both as reported in the academic literature[6–13] and as standard testing procedures in the aerospace industry.[14–20] These have even included research on the 8552/IM7 composite.[21,22] However, in these studies, most of the accelerated aging conditions have been severe and only the mechanical property changes have been investigated. The possible chemical and physico-chemical changes found under realistic aging conditions in the composite were not reported. It has been demonstrated by others,[20,23,24] as well as ourselves,[1–4] that aging effects in composites generally occur very unevenly from the surface and edges into the bulk of the material. The mechanical property testing methods are, therefore, a very crude way of measuring the physico-chemical changes that are occurring. These tests generally measure an average property value throughout the composite; some (such as DCB) measure the property value at the least affected point—the center.

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

Previous research[2,21,22] and manufacturers' product information, has indicated that this particular type of composite matrix resin (Hexcell, 8552) was produced by the reaction of a mixture of commercial grade tetraglycidyldiaminodiphenylmethane (TGDDM) and triglycidyl-aminophenol (TGAP) epoxy resins, with a mixture of diaminodiphenylsulfone (DDS) isomers.[25] The idealized structure of the cured resin is shown in Figure 1. However, since the monomers used

(Fig. 1) have high functionality in a relatively compact structure, and the commercial TGDDM monomer in particular is very impure,[26] there has to be a significant quantity of unreacted (or partially reacted) monomer groups and other chemical defect structures that are likely to be more susceptible to hot/wet aging than these idealized chemical structures. The commercial composite also has a thermoplastic toughening phase, and other possible additives present that may be available for extraction, especially under the more extreme humidity conditions. For these reasons, the chemistry of hot/wet aging of a commercial sample of this carbon-fiber composite is likely to be very different from that of a neat resin mixture of the main (pure) ingredients.

EXPERIMENTAL

The structural composite material selected for this study, 8552/IM7, was a high temperature epoxy matrix material on a unidirectional, intermediate-modulus, carbon-fiber, supplied as a pre-preg by Hexcell Composites (Duxford, UK). The pre-preg was laid up by hand to give a laminate with the approximate dimensions of 700 mm by 100 mm and 2 mm in thickness. The laminate was cured in an autoclave utilizing a propriety aerospace-cure-cycle with a maximum processing temperature of 180°C. Differential scanning calorimetry (DSC) indicated that it was greater than 97% cured. The cured laminate was C-scanned and measured for thickness (consolidation) to ensure the quality of the laminate, and then cut into a series of 50 mm by 50 mm plaques. These plaques, after drying at 50°C over phosphorous pentoxide (P_2O_5) to constant weight, were used in all accelerated aging experiments. Acid digestion tests indicated a resin weight fraction of 27.4%.

The plaques were conditioned at three different humidity levels at 70°C as indicated in Table I. The temperature and humidity ovens were calibrated and monitored in accordance with standard operating procedures; however, there was some temperature cycling ($\pm 2\%$) 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% RH and 45% RH, at temperatures of 90°C, 120°C, and 160°C, whereas the 65% RH samples were only spiked at 160°C. The thermal spiking was undertaken using a previously heated hot press, at minimum pressure to obtain good contact, for 5 min. This was done in accordance with a standard operating procedure which included the use of a multi-aperture, 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 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.

DMA experiments were 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 saw, to give a 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
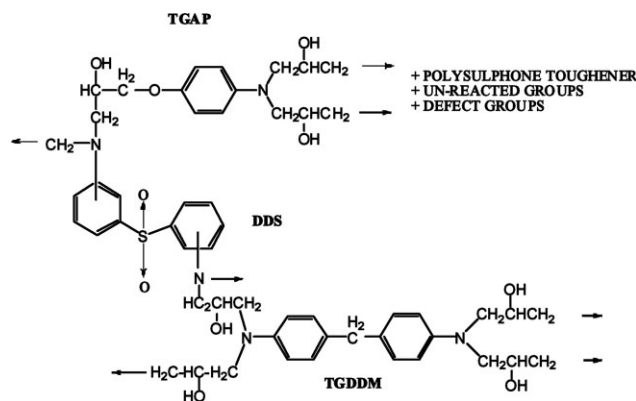

Figure 1 Idealized structure of the 8552/IM7 composite matrix.

least stiff direction allowing easier investigation of the resin properties). A multi-frequency analysis was undertaken at 1, 10, 50, and 100 Hz, over a temperature range of 50°C to 350°C, at a heating rate of 5°C/min. Glass-transition temperatures (T_gs) 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 and dried over P_2O_5 before being ground with $\sim$ 50 mg of dry KBr and pressed into a disk. The disk 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 cm^{-1} and 3450 cm^{-1} for the initial $\sim$ 30–60 scans but then these were lost by IR heating.

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 disk (about 10 mm thick), which after curing and polishing gave a clear microscopic image of the laminate cross section (fiber end showing).

RESULTS

Introduction

Although the chemical and physico-chemical changes in the composite plaques were followed by a broad range of techniques (as previously reported), only the significantly informative techniques of gravimetric analysis, DMA, FTIR, and microscopic examination are reported here. Of these, DMA and gravimetric analysis, like most mechanical testing, provide an average value of a property change over the whole laminate thickness, while the other (microscopic and FTIR) tests can be more informative of the detailed changes occurring in different areas.

Gravimetric analysis

Moisture absorption—simple humidity conditioning

The plots of water uptake of the resin in the composite (of which $\approx$ 27.4% by weight, is resin) over 7500 h at three different humidity levels are shown in Figure 2, and there are large differences between the total amounts of water absorbed by the resin under the different conditions, as is expected. The higher relative humidity (RH) levels and even full
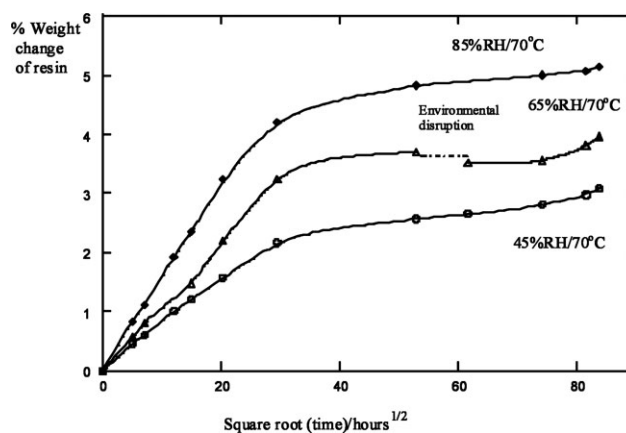

Figure 2 Water uptake curves for 8552/IM7 during conditioning at 70°C in 45% RH, 65% RH, and 85% RH environments.

immersion conditions often used in accelerated aging tests would be expected to lead to even higher absorption levels, but such results may be further complicated by material extraction variables not seen in-service. The Figure 2 moisture absorption curves are relatively simple and, in the case of the 85% RH curve, almost Fickian[24] but, even after aging for 1 year, the moisture levels have not reached a full equilibrium position. In the case of the 65% RH and 45% RH plots, the curves may even be showing signs of accelerating moisture intake after almost leveling off after the first 1000 h. The break and drop in the 65% RH curve resulted from a temporary breakdown in the 65% RH cabinet. These results are, very different to the complex curves obtained from the less completely cured M20/IM7 composite system reported on previously.[4]

Thermal spiking

The thermal spiking studies were carried out on materials that were being equilibrated at 70°C at the three different humidity levels shown in Table I. In each case, the water-absorption effects caused by spiking were considerably different to those seen by the simple humidity conditioned samples; except for the 45% RH case (Fig. 3). At the higher humidity levels, 65% and 85% RH (Figs. 4 and 5), the increase in with spiking over simple conditioning was very large (up to $\approx$ 100%). Similar results were obtained by Jones and coworkers[11,16,27] for other systems at higher humidity levels. These type of results, however, were again in strong contrast to our previous reported results for the M20/IM7 composite system, where the increase in moisture absorption level was only seen at intermediate times ($\approx$ 3000 h), and was almost gone by the end of the program (7500 h).[4] In this current work, the plateau level of water-

Figure 3 Comparison of the thermal spiking performance of 8552/IM7 samples conditioned at 45% RH and spiked at 90°C, 120°C, and 160°C.
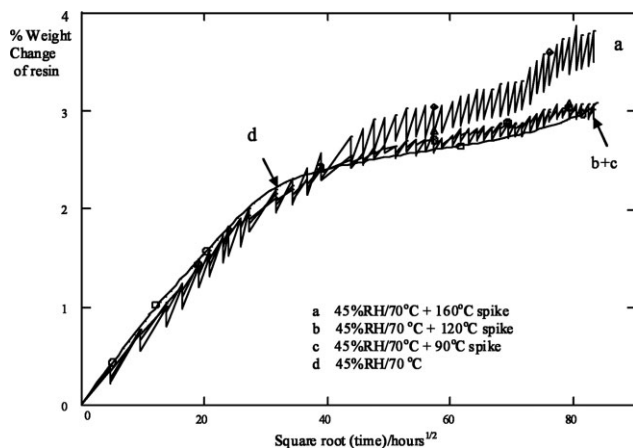

Figure 5 Comparison of the thermal spiking performance of 8552/IM7 samples conditioned at 85% RH and spiked at 90°C, 120°C, and 160°C.

absorption was reached at a similar time ($\approx$ 3000 h) but not a similar level, for both the spiked and unspiked samples, again in contrast to the M20/IM7 material. It was also noted in this program that when a temporary loss (16 h) of humidity cabinet conditions occurred (at about 3000 h, 85% RH), a large drop in the moisture level followed, but this was recovered relatively quickly. The high levels of surface microcracking seen in the thermally spiked samples of this composite (refer below) may have had a considerable effect on these absorption characteristics of the material, but the work of Jones and others has also involved a number of other possible explanations including strongly and weakly bound water states.[27–29]

Dynamic mechanical analysis

Moisture conditioned samples

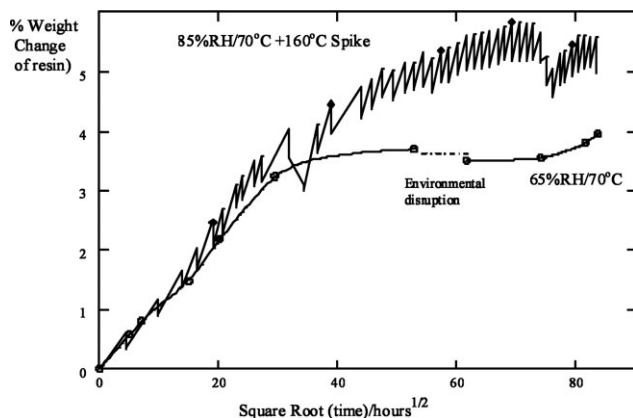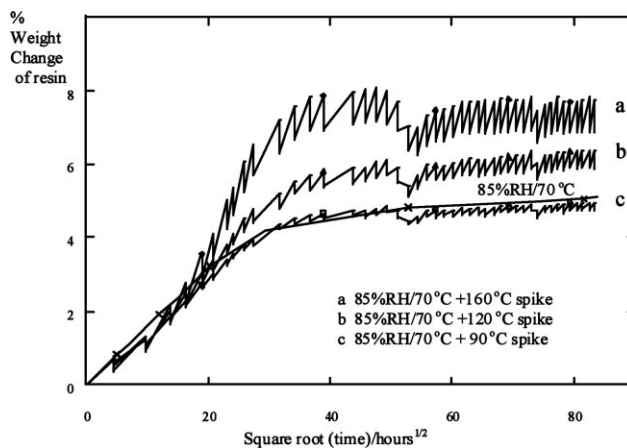It is well understood that the absorption of water by carbon-fiber composite systems has the effect of

reducing the T_g (E'onset-initial loss of modulus, temperature) of a material due to plasticization effects, but it is also obvious that this T_g, as measured by a DMA instrument, is a weighted average over the whole thickness of the sample. In contrast, water-absorption levels will vary over the sample thickness with time, at least, until equilibrium is reached. The curves obtained from the plots of T_g (E'onset) with time for the 8552/IM7 material at the three different humidity levels (Fig. 6) were relatively simple with a sharp initial drop whose magnitude increased greatly at the high humidity levels ($\approx$ 50°C at 85% RH). The T_g (E'onset) position then appeared to almost level out (especially at 85% RH) at the time of the large drop in the water-absorption rate (Fig. 2). Although the T_g (E'onset) point is of interest to the aerospace industry it is both difficult to measure accurately as it is a point of change in slope of the
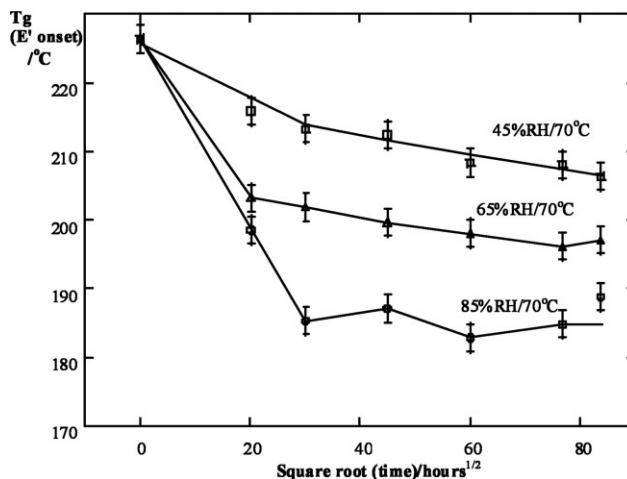

Figure 4 The thermal spiking performance of 8552/IM7 samples conditioned at 65% RH and spiked at 160°C.

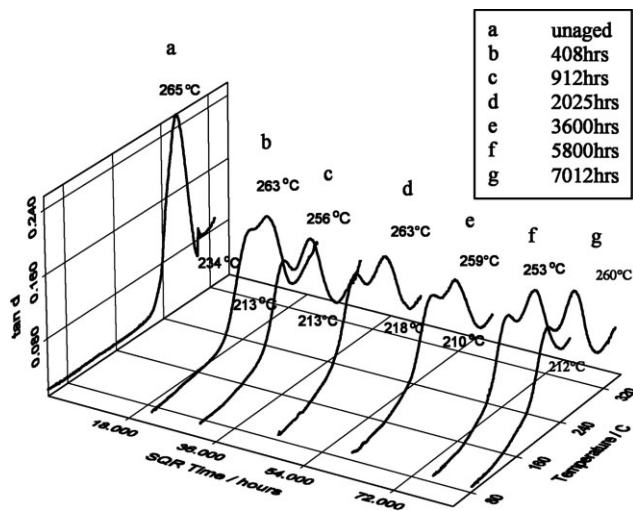**Figure 6** Plot of T_g (E'onset) against square root of time for conditioned 8552/IM7.

Figure 7 A 3D plot of Tan δ against temperature as a function of the square root of time for 8552/IM7 conditioned at 85% RH at the various aging times.

modulus curve and of less fundamental value than the Tan δ curve.

A much more complex pattern of physico-chemical property changes was seen when the Tan δ (100 Hz) peaks were observed over the aging time at 85% RH (Fig. 7). In this case, the Tan δ peak separated into two distinct peaks at conditioning times greater than 400 h but only at the higher test frequencies. The research of Hough et al.[16] on similar epoxy composites with thermoplastic modifiers yielded a similar, but smaller, peak separation result when tested at 1 Hz. While the high temperature peak (at ≈ 260°C) showed little change with aging, the low temperature peak developed with increasing time reaching a steady state around 900 h, at ∼ 215°C.

The separation at high moisture content of the Tan δ signal into two separate peaks would suggest a two-phase resin system and, as it did not change at later aging times, it would not indicate that it was due to differences in moisture level between the surface and the center. It may instead be an effect of the plasticisation of only one of the components of this multi-phase system, as suggested previously.[16]

The Tan δ peak separation was also found at the 65% RH level. However, this Tan δ peak separation occurred later than that found with the 85% RH sample (> 900 h for initial separation and ≈ 2000 h for complete separation) and the lower peak reached equilibrium at 225°C while the upper peak again remained at about 260°C. At the lowest studied humidity level, 45% RH, the Tan δ peak broadened after ∼ 3600 h and formed a consistent shoulder, but it never fully separated into two peaks. The changes were obviously affected by the very different equilibrium moisture levels at the different humidity levels.

DMA of thermally spiked composite

Figure 8 displays the effect of thermal spiking (at 90°C, 120°C, and 160°C) upon the T_g (E'onset) of the 8552/IM7 composite compared with the conditioned-only material at 85% RH. Although the error in this T_g measurement was significant (up to ± 2°C), it was noticed that the thermal spiking conditions led to greater drops in T_g when compared to the results of simple conditioning. After thermal spiking at 90°C, the final T_g was found to be ∼ 20°C lower than that of the conditioned material. Thermal spiking at 120°C and 160°C had an even greater effect upon the T_g leading to values which were ∼ 30°C lower than the conditioned material and almost 70°C lower than the starting composite. The effect of thermal spiking on T_g appeared to level out at ∼ 1000 h.

Similar effects, but not such drastic effects, were noted for the 65% RH and 45% RH conditioned and spiked samples with the initial sharp drop in T_g to 1000 h and then a leveling out at about 55°C and 35°C below the T_g of the initial composite.

The molecular effects of thermal spiking can differ from simple humidity conditioning (as seen in Fig. 9) where composite samples with the same total moisture level (1.38%) showed very different Tan δ plots. For the thermally spiked material, both peaks were moved to lower temperatures. It appeared that the water was more effectively plasticizing or hydrolysing defect groups in the thermally spiked samples, but it was also noted that the spiked sample was much more heavily microcracked on the surface (Section "Physical effects of hot/wet aging"). Similar effects on the physico-chemical properties could be seen at all moisture levels and spiking conditions. Spiking increased the total moisture levels, but even at the same moisture levels spiking caused a greater knockdown to the T_g (E'onset) and Tan δ
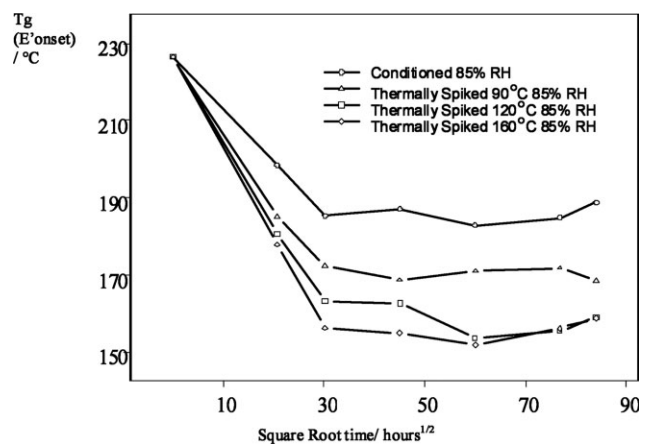

Figure 8 Plot of T_g (E'onset) against square root of time for 8552/IM7 conditioned at 85% RH and thermally spiked at 90°C, 120°C, and 160°C.
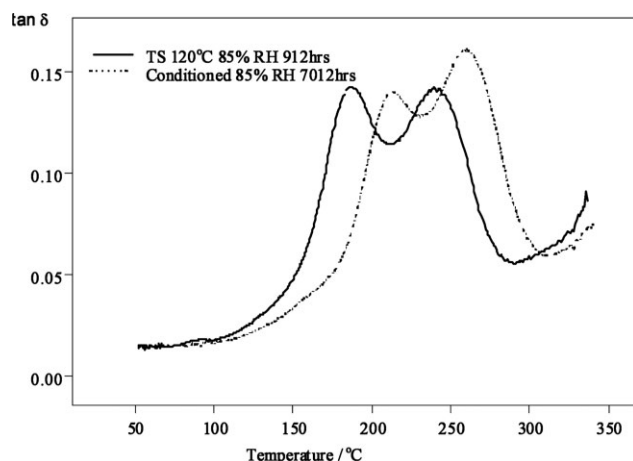
Figure 9 Comparison of thermally spiked and conditioned Tan δ temperature plots for 8552/IM7 laminates containing 1.38% moisture.

peak positions. In contrast to the previously reported results for M20/IM7 composites, an equilibrium position for the effects of spiking and moisture was reached quite early in the aging program (≈ 2000 h) and the changes after this were relatively slight.

FTIR analysis

Introduction

FTIR spectroscopy has been used extensively to study the absorption and reactions of water with various epoxy resin matrix systems, including aerospace formulations very similar to the 8552 resin.[28–30] The major difference between the current FTIR work and previous results has been the use of commercially-produced, carbon-fiber composites instead of experimental neat resin samples. Also, the spectra were obtained from small amounts of composite (including fiber), finely ground with very dry KBr. This technique eliminates the effects of any absorbed water even "so called," strongly bound water and only shows the effects of reacted water or the results of water extraction from the composite surface. These results contrast strongly with most of the recent work on the interaction of water and epoxy resins, where the exact state of water binding has been a topic of intensive discussion.[30–35] The KBr technique also tends to produce much narrower FTIR peaks and more reproducible spectra than other methods, especially with composites.[36,37] The final spectra displayed are the Fourier Transform of 256 co-added interferograms and surface samples from each treatment condition were run at a minimum of seven times during the aging program. Spectra from the center of the samples were generally only obtained at the beginning and end of the aging program as the changes were so small.

Peak assignments were obtained from previous work[3] on this material and are shown in Table II.

Results

As expected, the surface FTIR spectra of the conditioned and the conditioned plus spiked samples of 8552/IM7 showed smaller changes over time than the previous high temperature treated composite samples of the same material.[2] Also, the spectra of the current aged material were less changed than those from our previous studies of the hot/wet-aged, M20/IM7 composite.[4] This latter result was also to be expected as the 8552/IM7 structural composite had been almost completely cured (180°C for a number of hours) before environmental aging in contrast to the incomplete cure of the repair epoxy composite. However, there was one major change in the surface spectrum (and therefore the chemistry) in the OH/NH region (≈ 3430 cm^{-1}) where large decreases in absorption were observed, particularly late in the aging program (> 3600 h) under high humidity conditions [Fig. 10(a)]. This may appear counter-intuitive for a material that has adsorbed water with aging and contrasts strongly with most previous FTIR work on such epoxy resins. However, because the FTIR sample preparation technique used in this research has resulted in the removal of any adsorbed water, the results indicate that the high humidity and spiking environments have extracted uncrosslinked, polar materials from the surface of the composite. A similar effect was seen with the hot/wet aging of the M20/IM7 composite under identical conditions[4] except that in this case the changes took much longer to develop, and the small quantities of material extracted were too degraded to characterize even by FTIR.

Although the major difference in the chemistry of the surface under these relatively mild hot/wet aging conditions was in the hydroxyl group area of the spectra, there are other minor changes which can be easily highlighted by utilizing differential spectra. Figure 10(b) shows a computer-generated differential spectrum where these chemical changes are enhanced. As well as the major hydroxyl/amine differences, there are noticeable differences around

TABLE II
FTIR Peak Assignments for 8552/IM7 Composite

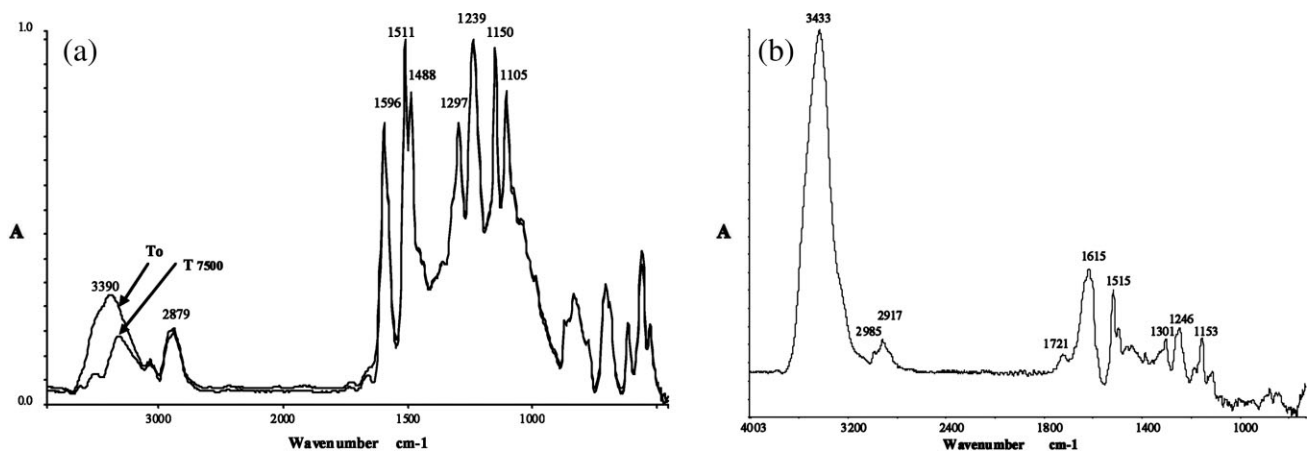| Wave number	Functional group
3660–3400 cm^{-1}	Hydroxyl, —OH
3400–3200 cm^{-1}	Amine, —NH$_2$, NH
3100–2850 cm^{-1}	Hydrocarbon, —CH, CH$_2$, CH$_3$
1665 cm^{-1}	Amide, —C=O
1596, 1511, 1488 cm^{-1}	Aromatic ring
1295, 1150, 1105 cm^{-1}	Sulphone SO$_2$

Figure 10 (a) Mid-FTIR surface spectra of 8552/IM7 aged at 70°C and 85% RH for 7500 h and the unaged, time zero sample. (b) Differential spectrum of the mid-FTIR spectra of 8552/IM7 aged at 70°C and 85% RH for 7500 h and the unaged, time zero sample.

2980 cm^{-1} (loss of CH$_2$ groups) and around 1615 cm^{-1} (aromatic amine loss), and some shifting in various aromatic peaks between 1600 cm^{-1} and 1400 cm^{-1} and loss of sulphone and ether peaks between 1300 cm^{-1} and 1100 cm^{-1} was apparent. Below 1000 cm^{-1}, the spectral differences tend to be very slight and are influenced by random noise. In contrast to the surface changes noted earlier, there were only very minor chemical changes in all of the FTIR spectra, towards the center of the composite plaques. This result appears to indicate that hot/wet aging, and also spiking under these conditions, has little chemical effect within the composite and yet the DMA results indicate the opposite. However, changes in molecular weight between cross-links and degree of cross-linking (caused by hydrolysis of defect groups) would not be expected to show very significant changes in the FTIR spectra if the breakdown products remained within the matrix. In contrast, such changes would greatly influence the DMA results.

As mentioned earlier, in this study, FTIR spectra were taken for all samples at seven intervals over the full aging time, not just at the beginning and end. In the case of the samples aged at 70°C and 85% RH, the initial drop in the broad absorption peak at ∼ 3400 cm^{-1} was quite slow but the major change was seen between 3600 and 5800 h, as shown in Figure 11. At lower humidity levels (45 and 65% RH), the loss of this peak followed a similar pattern but to a lesser extent. Again, the spiked samples showed similar patterns of behavior with minor variations in peak heights, both with the 3400 cm^{-1} area peak and other peaks in the spectra. Unlike the chemistry which occurred in this hot/wet environment, the chemical changes shown in our previous work on dry thermal aging at 70°C showed a much lower loss of OH/NH groups but more oxidative

losses of CH$_2$ groups (2980 cm^{-1}) and the formation of carbonyl compounds (1719 cm^{-1}). As the aging temperature was only 70°C in both cases, the differences were not great, however, they were obvious in the spectra (Fig. 12) after 7500 h of aging. Such small changes would not be significant alone but they were consistent when followed over the duration of the aging study with both the isothermal 85% RH samples and the various spiked 85% RH samples.

Physical effects of hot/wet aging

As part of this study of the hot/wet aging of the unidirectional 8552/IM7 composite, the aged samples were examined microscopically after removal from the conditioning and spiking environments and after embedding in epoxy resin. As seen in
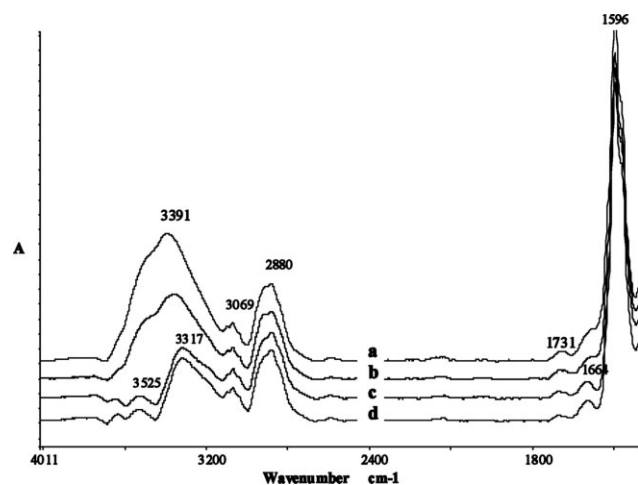

Figure 11 The expanded (4000–1500 cm^{-1}) mid-FTIR surface spectra of 8552/IM7 aged at 85% RH/70°C and (a) time zero, (b) 5600 h, (c) 6500 h, and (d) 7500 h.
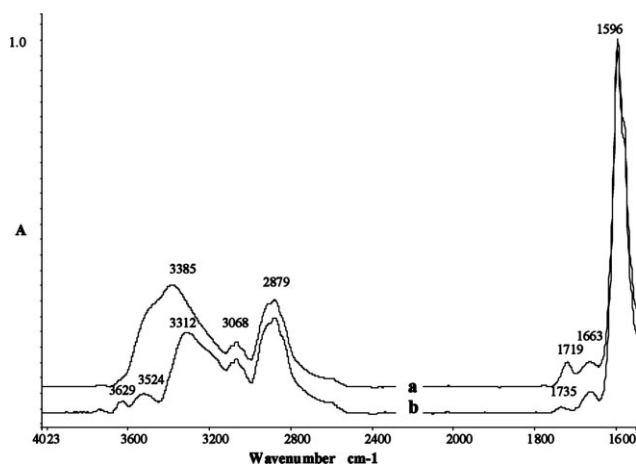
Figure 12   The expanded (4000–1500 cm^{-1}) mid-FTIR surface spectra of 8552/IM7 aged at 70°C and 7500 h (a) dry, (b) 85% RH.

Figure 13(a–d) in a view into the polished ends of the fibers, even the spiked samples removed at the first analysis point (424 h) were very significantly microcracked near the surface after only a few spike excursions. The microcracking was much more pronounced at the higher humidity levels, higher spike temperatures and longer aging times, but could be seen even after the early 45% RH conditioning and

spiking exposures. A surprising development was the much more extensive microcracking of this relatively completely cured composite to that seen for the partially cured M20/IM7 system. Again, the simple conditioned samples did not show significant microcracking until much later (> 3600 h) in the aging program.

DISCUSSION

The hot/wet aging environments used in this research were relatively mild and, except for the 160°C spike, would probably not exceed conditions seen by military aircraft "in-service." A significant difference between the current research and much of the previous work has been the use of environmental chambers rather than chemically controlled moisture environments (aqueous salt solutions). The latter give a much more controlled relative humidity condition whereas the chambers used had some temperature variability (±2°C) and allowed moisture condensation to occur on the samples at the higher humidity conditions. Moisture presence at the composite surface provides a more realistic (if variable) environment and can allow material extraction from the resin surface. As the composite samples tested (8552/IM7) are identical to the materials used in

a   70°C/45%RH +90°C spike at 424hrs

b   70°C/45%RH +160°C spike at 424hrs

c   70°C/65%RH + 160°C spike at 424hrs

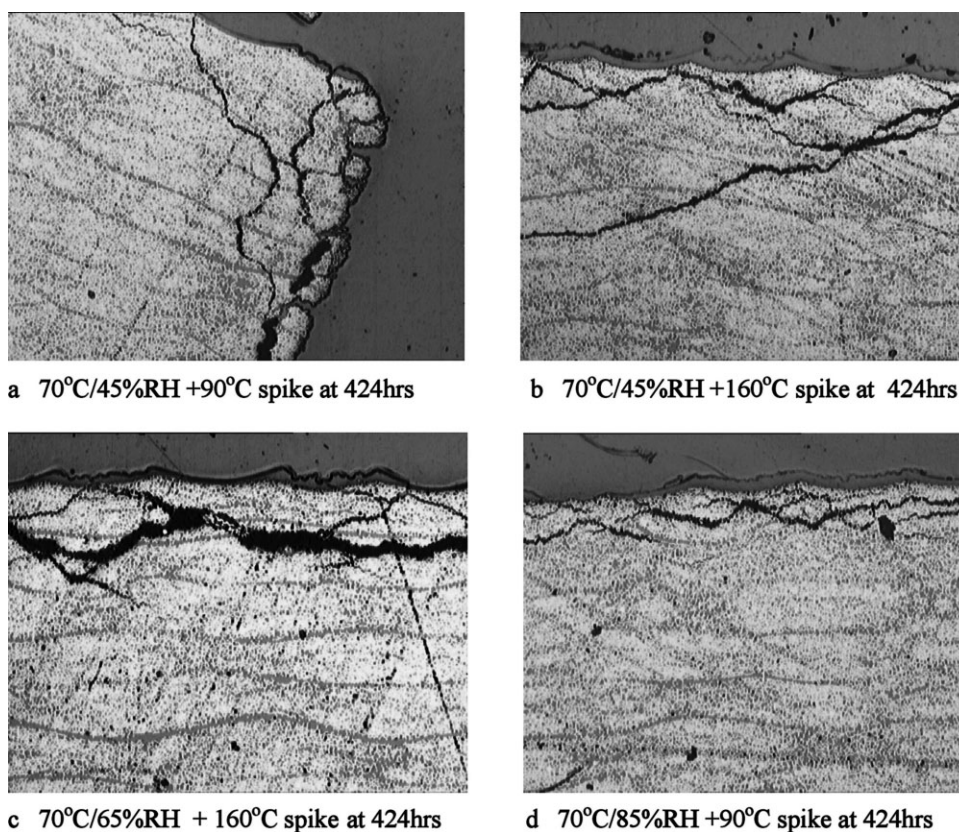d   70°C/85%RH +90°C spike at 424hrs

Figure 13   The magnified surface (X20) of 8552/IM7 laminate aged at different humidity levels and spike temperatures.

current military aircraft, the changes observed should be in line with the lifetime changes seen in the field. The short test duration (1 year), however, means that some of these changes are confined to the surface layers only.

The water-absorption curves of both conditioned and spiked 8552/IM7 composites (Figs. 2–7) are of similar non-Fickian shape to those obtained by other workers for similar composites.[8,16,27] A closely related example was the work of Hough et al. on Fibredux 927(Ciba Geigy), a high temperature, modified epoxy blend and Fibredux 924 (Ciba Geigy), a thermoplastic blend.[16] This work included a detailed explanation of the effects that they and previous workers observed including the possibilities for plasticization of various components, hydrolytic degradation, and free volume changes. In this particular article, a much higher humidity condition (96% RH) was used with a thinner sample so the large drop in moisture uptake rate was reached earlier in the aging program ($\sim$ 500 h) than in the current work (1500 h). However, in both studies the spiking treatment caused an almost doubling of the water-absorption levels at the higher humidity levels (80% and 96% RH) and higher spiking temperatures (120–160°C). In neither case was an equilibrium level of water-absorption seen after nearly a year of conditioning, although (as expected) the higher the humidity the earlier the sharp drop in absorption rate took place.

These results contrast significantly with our previous results with a much less completely cured commercial composite (M20/IM7) under identical conditions. Here, total water-absorption was generally the same by the end of the program for both spiked and non-spiked samples, although equilibrium was approached much faster in the former. Also, the shape of the absorption curves were very different (and even further from Fickian), especially early in the aging program. It is probable that much higher levels of material extraction and water-caused reactions had affected this material even in the non-spiked composite. Similar results have been reported for "low-cross-linked" neat resin materials by others.[12,29]

As far as the physical effects of hot/wet aging in the 8552/IM7 composite, as studied by DMA, the drop in T_g (E'onset) followed the increase in water-absorption curve to a large extent for both the spiked and non-spiked samples. This result was similar to that obtained by Hough et al.[16] for related composites and, as in their work, spiking greatly decreased T_g (E'onset) and hence showed the plasticizing effect of absorbed moisture. However, there was not a close correlation between the exact moisture level in a composite sample and its T_g (E'onset) when comparing spiked and non-spiked samples or even samples spiked at different temperatures (espe-

cially at the higher water levels), indicating that there were effects other than plasticization.

T_g (E'onset), which is the point of change in slope of the DMA modulus curve, is often considered to be less reliable as a measure of physical change compared to the Tan δ plot, which details changes in molecular motion as temperature increases. In the current work, moisture absorption in both the spiked and non-spiked samples led to a split in the Tan δ peak at higher moisture levels, as shown in Figure 7. Again this result was similar to that obtained in the earlier work[23] although the behavior of the two peaks was somewhat different in experiments with the 8552/IM7 composite. The high temperature peak shifted only slightly lower (between 2°C and 9°C) as water was absorbed, in the conditioned samples, and the low temperature peak shift was much larger due to the higher frequency of the test curve shown. Hough et al.[16] suggested that the lower T_g peak reflected the plasticization and separation of a thermoplastic component in the composite but probably included some hydrolytic degradation reactions, particularly in the spiked samples. The latter would help explain the lack of correlation between moisture level and the various T_gs under the different treatment conditions found in both this and the previous study.

In contrast to the large physical changes seen by DMA under different aging conditions, the chemical effects noted by FTIR (hydrolysis and material extraction) appear to apply only to the surface. However, it is probable that the same hydrolysis reactions are occurring within the composite and are reducing the molecular weight between cross-links and breaking chains, but the broken fragments cannot diffuse away as they do on the surface. It appears likely that the chemical changes that occur are due to the hydrolysis of polar defect groups as the changes are greatest after a period of time (so not just changes in additives or unreacted monomers) and the expected epoxy structures (shown in Fig. 1) would not hydrolyse easily even under the spiking conditions used in this study. The likely products of defect group breakage would be materials with excess hydroxyl and amino groups, as shown from changes in the surface FTIR spectra, and would include partially reacted linear polymer units. As suggested by the work of Karad et al.,[12] for similar highly-cross-linked and commercially-produced polymers, a high level of defect groups would be expected. Because commercial composites are usually stoichiometrically low in the amino monomers the major defect structures would include unreacted epoxy groups in the TGDDM unit.[25] These would readily hydrolyse to glycols, which could oxidize further to aldehydes, ketones, acids, and amides.

CONCLUSIONS

A detailed hot/wet aging study of a fully-cured aerospace-qualified, 8552/IM7 composite has been carried out over ∼ 1 year at three different humidity levels, 45, 65, and 85% RH. The overall aging temperature used was only 70°C but some samples were also regularly spiked (5 min) at temperatures of 90, 120, or 160°C to simulate supersonic flight excursions in military aircraft. Changes in water-absorption levels were measured by gravimetric analysis, basic physical property changes by DMA, chemical changes by FTIR, and material structural changes by microscopy.

The water-absorption characterization of this composite under simple isothermal conditions differed only slightly from previous literature results with this and related composites.[16,21,22]

The main difference was a lack of a significant absorption plateau and even an absorption rate increase late in the aging studies. Much higher water-absorption levels and the late rate-acceleration was particularly significant with some of the heavily spiked samples and is a result of the resin chemical changes and the increased microcracking of the composite observed under these conditions.

The chemical changes that occur in the matrix resin during hot/wet aging have been determined from the FTIR spectra of the surface layers of the composite. It appears that hydrolysis of "defect" groups in the epoxy matrix causes the formation of low-molecular weight, polar oligomers, which are extracted from the surface by condensing moisture. Although similar defect groups are hydrolysed within the composite and break polymer chains and cross-links, they can not be extracted so the internal FTIR spectra do not change significantly. However, the molecular breaks do cause major changes in the physical properties of the composite, as evidenced by the DMA results, especially the Tan δ curves. This combined with moisture plasticization of the matrix resin greatly lower the polymer T_gs and the composite mechanical properties.

The combination of surface material extraction and the thermal shock of spiking a moisture-saturated, heavily-crosslinked, matrix resin has greatly enhanced the surface microcracking in this composite, compared to that shown with the previous results obtained on a partially cured, and therefore less cross linked, composite system (M20/IM7).[1]

The current work, combined with previous studies of fully-commercial composite systems, confirm the variability of aging effects (chemical and physical) between different types of composite under different conditions. It suggests that the mechanical testing of either non-commercial resins or commercial composites under unrealistic accelerated aging conditions may provide errors in the understanding of long-term aging effects in actual aerospace composite items.

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