

Accelerated Aging Versus Realistic Aging in Aerospace Composite Materials. I. The Chemistry of Thermal Aging in a Low-Temperature-Cure Epoxy Composite

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ABSTRACT: Samples of an aerospace-grade epoxy composite (M20/IM7) are subject to long-term (~ 1 year) thermal aging at temperatures of 70°C, 120°C, 170°C, and 200°C (in air) and the changes to the chemical and physicochemical structure of the composite are analyzed by a range of different techniques, including gravimetric analysis, FTIR, DSC, and DMA to compare the effects of different severities of degradation treatment. The results show that at the lower temperatures, the oxidative degradation changes are very selective for chemical defect groups, par-

ticularly near the sample surfaces. However, at the higher temperatures, combinations of further cure reactions and generalized oxidative degradation changes (again from the surface inwards) make for a highly complex ageing pattern for this particular composite material. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4291–4303, 2006

Key words: composite degradation; aerospace epoxy; thermal aging; chemical analysis; gravimetric; FTIR; DSC; DMA

INTRODUCTION

Historically, epoxy resins have been used on military aircraft for over 30 years with few discernible ageing problems. However, in recent years there has been a movement to use new epoxy formulations, often with multiphase toughening systems in place, and for the materials to encounter more severe environments for longer periods of time. For example, the F-111s used by the Royal Australian Air Force (RAAF) have already been in service for over 30 years, while traditional analyses for aircraft performance generally estimate 25 years of use.¹ New aircraft either in service or under consideration are designed for increased time at supersonic speeds, giving rise to aerodynamic heating of surfaces for much longer than has previously been the case.^{2,3}

All materials used in aerospace structures must undergo rigorous testing before use and very strict requirements are placed on proof of fitness for purpose.⁴ The process is known as “qualification.” In the case of modern composite materials, where there is not a long history of use (especially in flight-critical areas), the testing regimes imposed are costly in both time and money. Both civil and military certification requirements address composites and the

effect of the environment upon their structure performance.^{4,5}

For all of the above reasons it was considered relevant to re-examine the area of environmental ageing of some of the newer composite types with the intention of establishing chemical analysis as a measure of ageing. An early phase of the project provided a review of the conditions encountered by aircraft under a variety of operational scenarios. From this study, 14 accelerated ageing conditions that related to these service environments were selected, and the materials were aged under these conditions.⁶ The conditions chosen for this program were selected to differentiate out thermal effects, from moisture ingress (plasticization) effects, from thermal spiking effects. Four different composite materials were selected for chemical and physicochemical testing with a view to relating the results to mechanical testing^{5,7} and the extensive literature on microcracking^{8–11} and fatigue,¹² at a later date. An important consideration in the selection of the thermal ageing conditions was to use a range of temperatures from reasonable “in service” temperatures to the highly accelerated conditions often used in aerospace testing protocols and in most academic ageing studies. It was of interest to see whether the fundamental chemical degradation mechanisms remained the same, or similar, throughout.

This particular article reports the chemical changes and physicochemical effects observed for one of the epoxy composite materials chosen, M20/IM7, sub-

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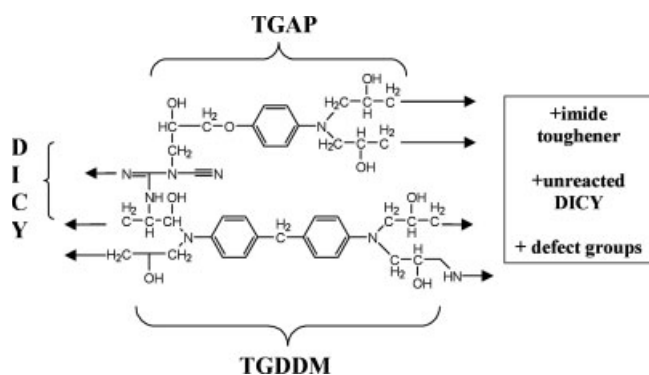


Figure 1 Idealized structure of the DICY containing M20/IM7.

jected to thermal ageing for up to 7500 h in air at four different temperatures 70°C, 120°C, 170°C, and 200°C. A number of the mechanical property changes under some of the similar cure and ageing conditions have been reported previously.^{13,14} This material is believed to be used in an incompletely cured form, and so it was expected to show continuing cure type behavior as well as degradation chemistry.

Future articles will report the effects of the exposures of the other three composites under the same thermal ageing regime and also all four materials under variations in relative humidity at 70°C and thermal spiking effects on moisture equilibrated samples.

EXPERIMENTAL

The material selected, M20/IM7 carbon/epoxy prepreg, was from Hexcel Composites, Duxford, UK. It was laid up by hand to give a unidirectional laminate with the dimensions of $\sim 2 \times 700 \times 1000 \text{ mm}^3$. It was cured according to the aerospace standard operating procedures for repair panels. The cured laminates were C-scanned and measured for thickness (consolidation) to ensure the quality of the laminate. The large laminate was cut into a series of $50 \times 50 \text{ mm}^2$ plaques. These plaques were used in all accelerated ageing experiments. All plaques were dried at 50°C over phosphorus pentoxide (P_2O_5) until a constant weight was achieved prior to isothermal ageing.

The plaques were aged under four isothermal conditions, 70°C, 120°C, 170°C, and 200°C. The lowest ageing temperature (70°C) was set to be representative of a typical temperature that an aircraft surface could reach on the ground due to solar heating. Temperatures were chosen thereafter to aid in the definition of accelerated ageing conditions with the upper temperature of 200°C chosen as a limit on the temperature performance of the material, and well above the initial glass-transition temperature (T_g).

All ovens were temperature calibrated and an isothermal volume of operation defined. The oven at

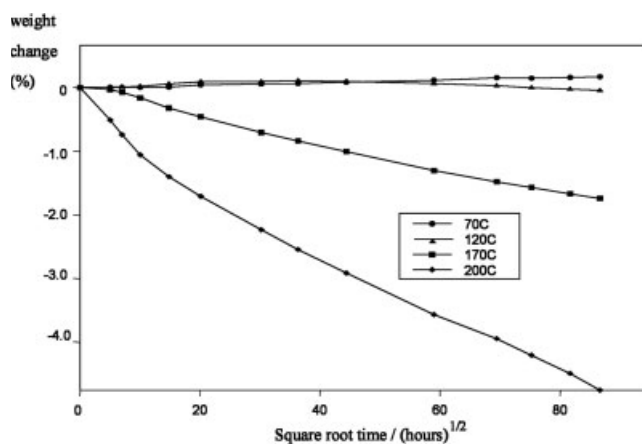


Figure 2 %Mass change for M20/IM7 matrix (at 70°C, 120°C, 170°C, and 200°C ageing temperature) versus square root of time ($\text{h}^{1/2}$).

70°C had P_2O_5 placed in the bottom to minimize the relative humidity. Samples were weighed at regular intervals ($\sim 50 \text{ h}$) and witness plaques removed after 400, 900, 2025, 3600, 5800, and 7500 h for analysis. The plaques were weighed on a Mettler Toledo AB 204-S four decimal place balance. At least three plaques at each ageing temperature were removed from the oven and transferred to a desiccator containing silicate, and allowed to cool to room temperature before being weighed. The laminates were then placed back in the oven and used in the collection of the next data point. The whole weighing process was optimized to take less than 30 min.

Dynamic mechanical analysis (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 dia-

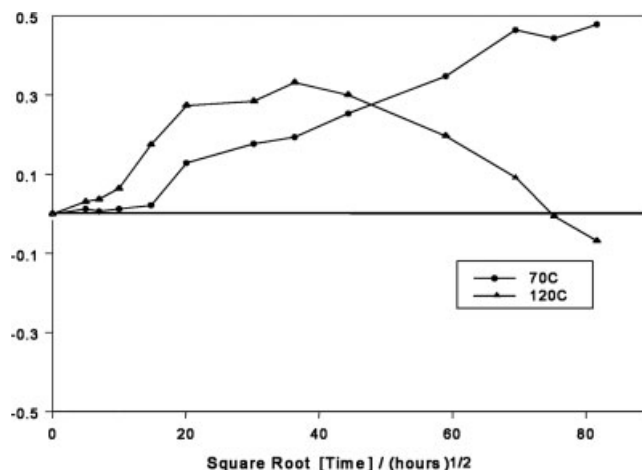


Figure 3 Plot of weight change against square root of time for M20/IM7 matrix at 70°C and 120°C; expanded from Figure 2.

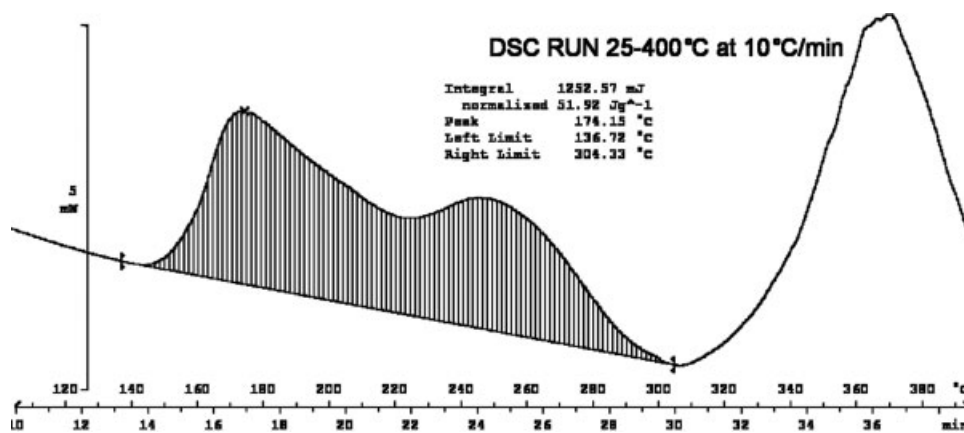


Figure 4 Dynamic DSC of unaged, cured M20/IM7 laminate.

mond blade 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 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 -150°C to 350°C , at a heating rate of $5^{\circ}\text{C}/\text{min}$. Glass-transition temperatures were derived from the onset of the decline in the loss modulus (E'_{onset}) and by the $\tan \delta$ peak position at 1 Hz.

All differential scanning calorimetry (DSC) analyses were conducted on a Mettler Toledo 821 with Star Software version 6. Samples were run in alternating DSC mode with an underlying heating rate of $5^{\circ}\text{C}/\text{min}$. Samples were encapsulated in lightweight aluminum pans (13 mg). A sample size of between 10 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.

To obtain a Fourier transform infrared spectrum (FTIR), ~ 1.5 mg of previously dried composite was cut from the surface of the aged laminate. This was ground up with ~ 50 mg of anhydrous KBr and subsequently pressed into a disk. The disk was analyzed in a Perkin-Elmer 2000 FT-IR spectrophotometer, in transmission mode using KBr as the background reference. Analysis was undertaken by direct comparison of original spectra and by computer-enhanced difference spectra. Chemometric analysis programs were carried out on the spectra but due to the broadness of the various oxidation peaks the method produced anomalous results and was not further investigated.

RESULTS

The M20/IM7 system has been described by previous workers as consisting of an epoxy matrix of both

tetraglycidyl diamino-diphenylmethane (TGDDM) and a triglycidyl *para*-aminophenol (TGAP) cured by dicyandiamide (DICY). A highly idealized structure would be as shown in Figure 1 and is similar to that proposed by Gumen et al. and others.¹⁴⁻¹⁶ However, the aerospace qualified chemistry would be significantly different as it is obviously incompletely cured (thermal analysis results). Also, the strong FTIR peaks in the unaged starting laminate, at positions 1775 , 1722 , and 1360 cm^{-1} , would indicate the presence of a considerable quantity of polyimide structure¹⁷ (probably a thermoplastic toughening agent) that does not appear to change significantly on ageing except at high temperatures.

The chemical changes in the composite plaques were followed by a range of different techniques, including weight changes, FTIR, and near infra-red (NIR) spectroscopy, mass spectrometry (MS), positron annihilation lifetime spectroscopy (PALS), X-ray photoelectron spectroscopy (XPS) as well as various thermal analysis methods such as DSC, thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and DMA. Only the chemically more informative techniques are reported here.

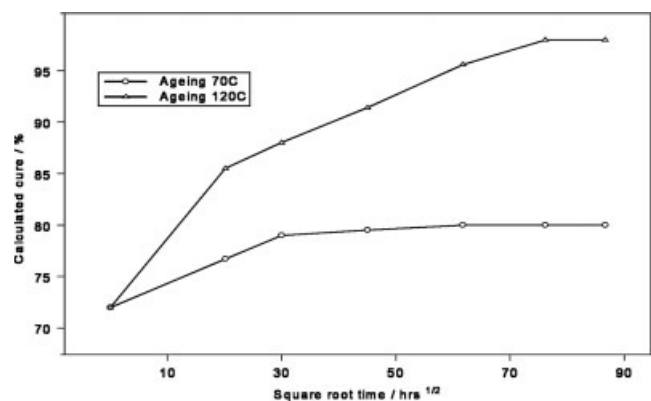


Figure 5 Plot of percentage cure against time for M20/IM7 aged at 70°C and 120°C .

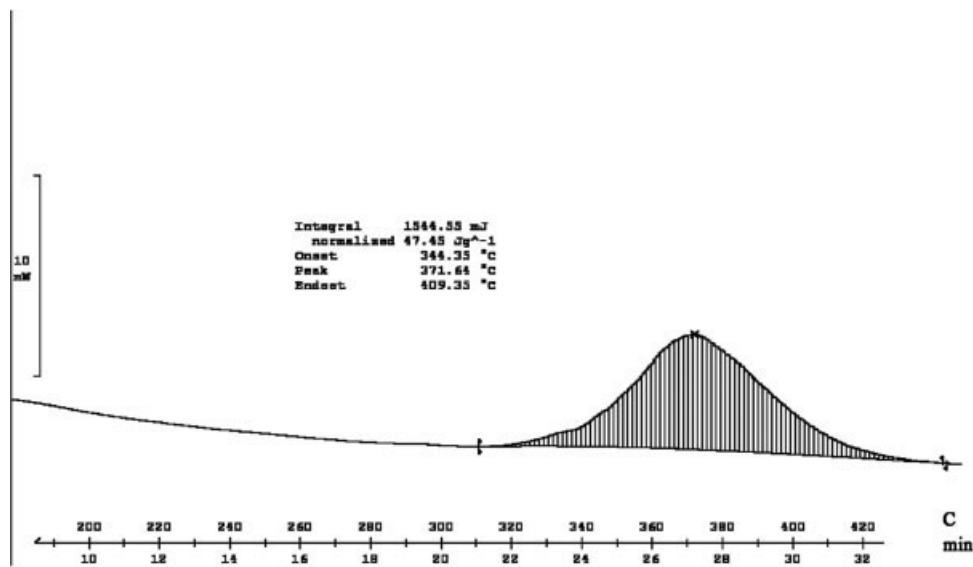


Figure 6 DSC trace for M20/IM7 aged at 200°C for 720 h.

Weight changes

While the weight change measurements carried out during the ageing tests were performed on the whole plaque, the chemical changes and hence the real weight changes were largely confined to the resin matrix itself, which consists one-third of the composite material by weight. Furthermore, in simple thermo-oxidative ageing of dry composites, the bulk of the chemical changes occur from the surface inwards and do not penetrate very deeply, except at higher temperatures and long times.^{18,19} This means that even small weight-change figures can translate to significant chemical changes at the composite surface.

Figure 2 displays the percentage mass change of the M20 matrix as a function of the square root of time ($h^{1/2}$) at all temperatures during the 7500-h experimental ageing time. At the higher temperatures (170°C and 200°C) weight loss started immediately and progressed strongly, although not at an even rate. The changes at 200°C, in particular, show a significant rate change (slow down) at about 150 h, and another possible rate change later in the process. This could indicate changes in the ageing mechanism, although the latter one, in particular, may just have been due to the oxidation protection of the bare carbon fibers and char layer left at the surface after the large resin losses (15% total).

Figure 3 displays an expanded version of the weight loss curves for the two lower temperatures and indicates the presence of two very different ageing mechanisms under these conditions. The 70°C curve shows an oxidative, addition mechanism with no indication of slowing down even after 7500 h. The 120°C plot shows similar oxidative increase competing with the strong oxidative loss mechanism later in the ageing.

The slight unevenness of the expanded curves gives an indication of the total experimental errors involved in the drying and weighing process.

Thermal analysis

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 cutoff temperature, as the remaining cure percentage of the composite. Figure 4 shows the typical DSC trace for the unaged M20/IM7 laminate (as provided by the aerospace supplier). It is obvious from this curve that a number of different matrix reactions are occurring over this highly accelerated time/tempera-

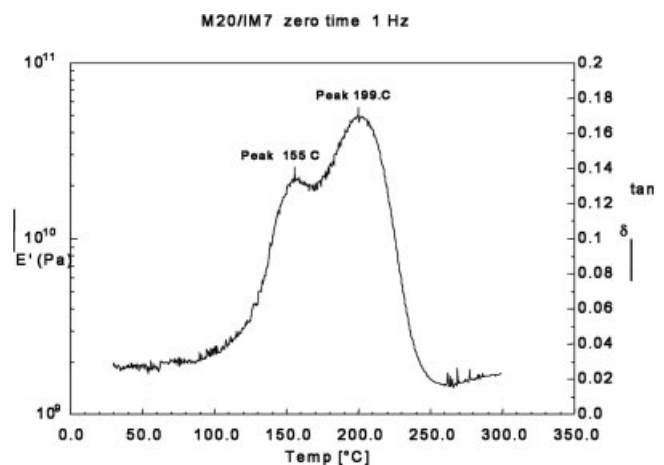


Figure 7 DMA spectra of unaged M20/IM7.

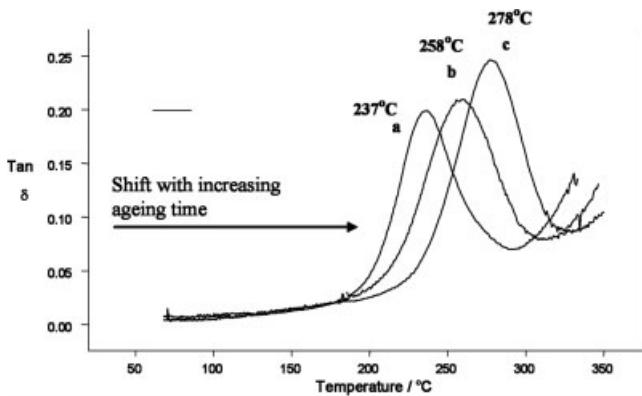


Figure 8 DMA spectra of M20/IM7 aged at 200°C (a: 360 h, b: 3809 h, and c: 5499 h).

ture profile. It is generally assumed that the reactions below $\sim 300^\circ\text{C}$ are "cure" reactions and above this are oxidative degradation reactions. Comparison of the exothermic energy of this trace with the original prepreg indicated a "cure" level of 72%. The plots of changes in this "cure" level for the 120°C and 70°C aged composites are shown in Figure 5.

The curves confirm that there are many partially- or unreacted chemical groups present in the composite over its whole ageing lifetime at these temperatures. In contrast, the M20/IM7 aged at 200°C and 170°C reached a full "cure" very early in the ageing program. The DSC trace for M20/IM7, aged at 200°C for 720 h, (Fig. 6) shows only oxidative degradation reactions occurring. In effect the matrix resin would have behaved as two different types of material under the two different sets of ageing environments.

Dynamic mechanical analysis

The DMA of a composite material can provide a detailed picture of the molecular motions and hence chemical/mechanical changes in a material over a large temperature range. Of particular importance to the aerospace industry is the temperature of loss of modulus (T_g , E'_{onset}) and the shape and position of the $\tan \delta$ peak. However, it is important to realize with these measurements (as with most mechanical testing) that the results reflect an average figure over a relatively thick sample. Figure 7 shows the shape of the DMA trace for the unaged M20/IM7 sample and the two peaks in the $\tan \delta$ curve reflect the partially cured nature of the system.

Even the long-term aged samples at 70°C have a broad main peak with some of the remaining lower peak in the $\tan \delta$ curve. The $\tan \delta$ curves at all other temperatures are also complex: for example at 200°C (Fig. 8) and together with the very broad ranging T_g , E'_{onset} figures (Fig. 9) indicate a reactive system with significantly different (average) chemical structures

throughout the testing regime, and not a single cured chemical structure.

Fourier transform infrared spectroscopy

FTIR spectroscopy has been used extensively to study the thermal and photochemical oxidation of epoxy resin systems over many years.^{20–27} Many of these systems have been aerospace type formulations (although generally highly simplified) and a very good library of peak positions for each molecular structure has been built up. The table produced by Musto et al.²¹ for M20/IM7 resin systems with DDS hardener has been modified to emphasize the chemistry of the DICY hardener used in this study (Table I). It has generally been assumed that the presence of a large amount of carbon fiber would prevent a similar analysis of commercial aerospace composites.²² We have found that this is not the case with mid IR spectroscopy but it does appear to cause difficulties with NIR due to a major (and variable) carbon peak at 6170 cm^{-1} .

As shown in Figure 10, the quality of the spectra obtained from a carbon fiber composite can be as good as that of the neat resin and it is such that detailed chemical analyses can be readily undertaken. Also, because only a very small amount of material is required (1–2 mg), analysis at the composite surface or at various levels throughout a composite can be obtained. To compare the FTIR spectral changes in a polymer or composite material during the ageing process, the use of an unchanging spectral peak for normalization purposes (or by the use of differential spectra, as seen in Ref. 21) is desired. Owing to the very reactive nature of the M20/IM7 composite it has been difficult to find a peak that does not change substantially with time and temperature, even with the most commonly used peak for normalization, the aromatic $-\text{CH}-$ peak at 1512 cm^{-1} . In this study, for spectral

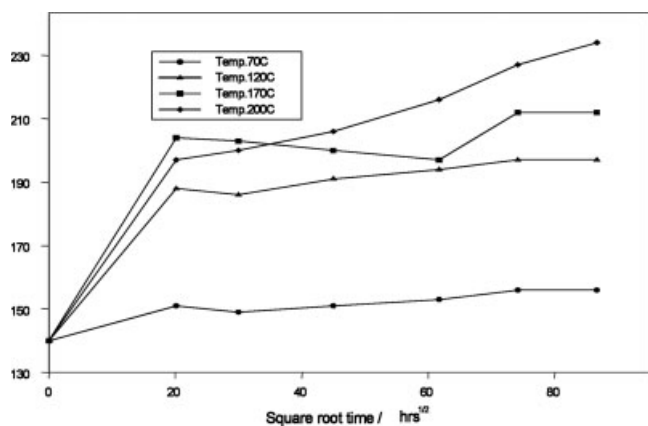


Figure 9 T_g (E'_{onset}) as a function of time and temperature for M20/IM7.

TABLE I
Mid-FTIR Peak Position Assignments Above 1000 cm^{-1}

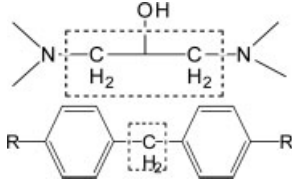
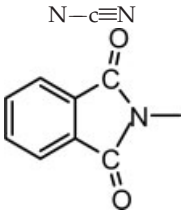
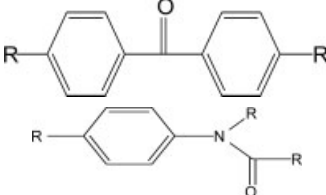
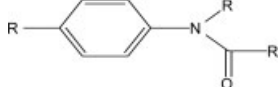


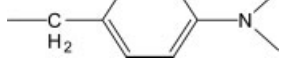
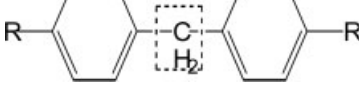
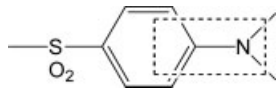
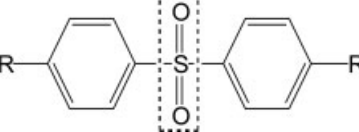
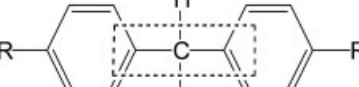
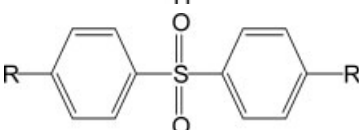
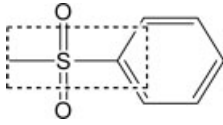
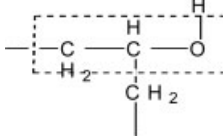
Approximate peak position (cm^{-1})	Tentative assignment	Functional group
3600–3550 3400 broad 3380–3200 3040, 3028–3006 2980–2780	Water $\nu(\text{O}-\text{H})$; hydrogen bonded $\nu(\text{N}-\text{H})$ $\nu(\text{Ar}-\text{H})$ $\nu(\text{C}-\text{H})$ and $\nu(\text{CH}_2)$ TGDDM, DDS	H_2O $\text{R}-\text{O}-\text{H}$ $\text{R}-\text{N}-\text{H}$ 
2165 1778 1723	$\nu(\text{CN})$ $\nu(\text{C}=\text{O})$ imide $\nu(\text{C}=\text{O})$ imide	$\text{N}-\text{C}\equiv\text{N}$ 
1725 1710 1695 1685	$\nu(\text{C}=\text{O})$ aldehyde or ketone $\nu(\text{C}=\text{O})$ aliphatic carboxylic acid $\nu(\text{C}=\text{O})$ aromatic carboxylic acid $\nu(\text{C}=\text{O})$ ketone	
1667	$\nu(\text{C}=\text{O})$ amide	
1611	Ring quadrant stretching I, TGDDM	
1594	Ring quadrant stretching I, DDS	
1514	Ring semi-circle stretching I, TGDDM	
1453	$\delta(\text{CH}_2)$ TGDDM	
1359–1341	$\nu(\text{Ar}-\text{N})$, TGDDM, DDS	
1289	$\nu_{\text{as}}(\text{SO}_2)$	
1232, 1188	$\nu(\text{Ar}-\text{C}-\text{Ar})$	
1144	$\nu_{\text{s}}(\text{SO}_2)$	

TABLE I
Continued

Approximate peak position (cm^{-1})	Tentative assignment	Functional group
1105	$\nu(\text{Ar}-\text{S})$	
1075	$\nu(\text{C}-\text{C}-\text{O})$, secondary alcohol	

comparison purposes, normalization was carried out using two separate peaks each in different spectral regions. The least variable peak for normalization below 2000 cm^{-1} appears to be the 1361 cm^{-1} peak, probably due to the imide toughener additive. Above 2000 cm^{-1} , peaks for aromatic $-\text{CH}-$ in the 3060 cm^{-1} region appear to be the least variable peaks for most of the ageing temperatures employed. Differential spectroscopy is not particularly helpful for this system because of its reactivity and also because it is slightly heterogeneous due to pockets of unreacted or partially reacted DICY and the imide toughener particles.

The spectrum shown in Figure 10 is of the dried starting composite and indicates that the structure contains both TGDDM and TGAP epoxy resin²⁷ and that it is cured by DICY¹⁶ hardener ($\text{C}\equiv\text{N}$ peak at 2165 cm^{-1}) as confirmed in the literature.^{14,26} Solvent extractions of the initial composite have also confirmed that large amounts of the DICY are still in an unreacted form even in the "cured" structure. This also would imply that a considerable number of the epoxy groups in the matrix are unreacted, and a small but sharp FTIR peak at 907 cm^{-1} that

decreases on heating confirms this. The distinctive carbonyl peaks at 1723 and 1773 cm^{-1} also indicate the presence of the imide toughener in the composite matrix, as mentioned above.

70°C thermal ageing changes

The changes in the FTIR spectra of the composite surface with time at 70°C are shown in Figure 11.

The changes are mostly small (as expected for such a low temperature) and only the unaged and final 7500-h aged spectra are shown for clarity. A differential spectrum (Fig. 12) can be used to emphasize the small differences between the initial and final spectra. The major consistent changes seen in the spectra include a decrease in the hydroxyl peak area of the spectra (3420 cm^{-1}) and the $\text{C}\equiv\text{N}$ area (2165 cm^{-1}). The latter is particularly large on a percentage basis but does not decrease to zero even after 7500 h. Decreases in the 1612 and 1513 cm^{-1} peaks are also evident and these are considered to be aromatic peaks connected with TGDDM and TGAP and have been used in the past^{21,23} for normalization standards in

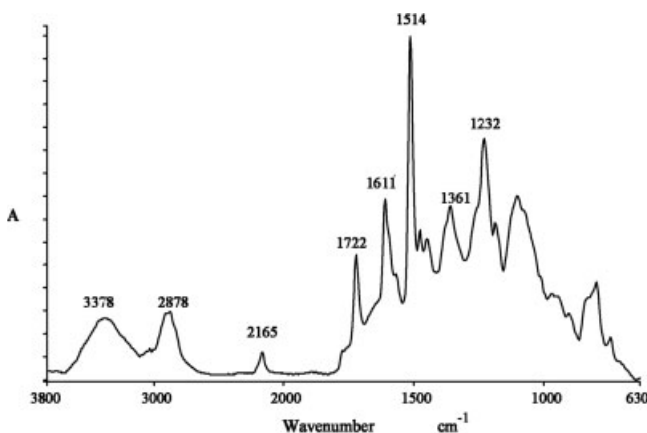


Figure 10 Mid-FTIR surface spectrum of unaged M20/IM7.

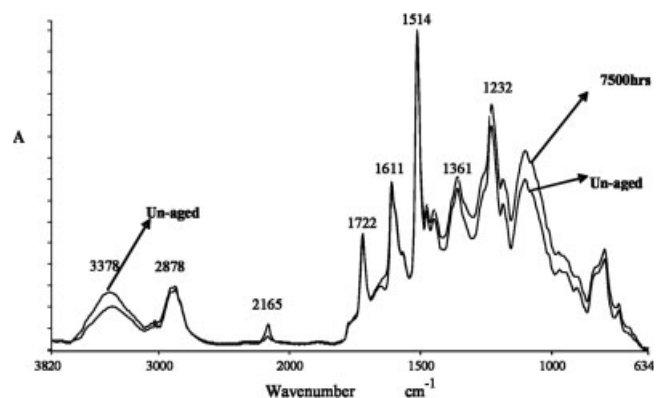


Figure 11 Mid-FTIR surface spectra of the M20/IM7 laminate aged at 70°C for 7500 h and the unaged sample.

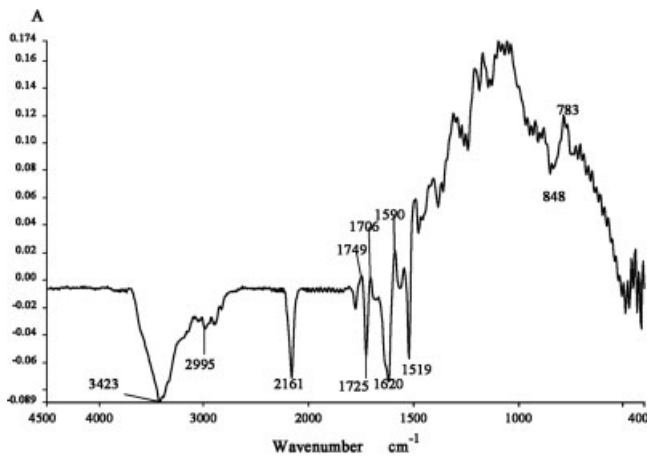


Figure 12 Differential spectrum of M20/IM7 aged at 7500 h at 70°C and the time zero sample.

studies of epoxy degradation. The small epoxy peak at 907 cm^{-1} decreases late in the ageing program.

In contrast to the surface spectral changes, the changes in the center of the laminate are very much smaller and only noticeable in the differential spectra. There are hydroxyl, nitrile, and aromatic losses as well as increases at $\sim 1750 \text{ cm}^{-1}$ (carbonyl) and a relatively strong increase around 1080 cm^{-1} , which may indicate changes in C—O bonds.

Although all changes at 70°C are small, they are highly significant because this is the most realistic temperature for long-term “in service” conditions seen for military aircraft. The changes are somewhat different to those seen in the other accelerated ageing environments (described later).

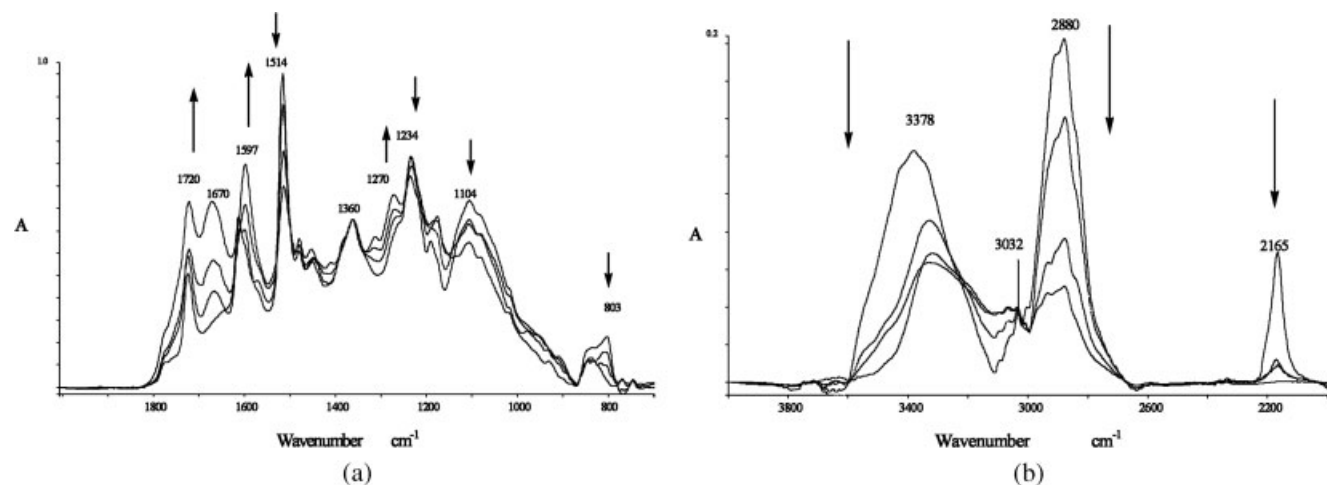


Figure 13 (a) Expanded ($2000\text{--}700 \text{ cm}^{-1}$) mid-FTIR surface spectra of M20/IM7 aged isothermally at 120°C over 7500 h (the arrows indicate the increasing or decreasing spectral changes observed with increasing ageing times from 0 to 400, 5800, and 7500 h at 120°C). (b) Expanded ($4000\text{--}2000 \text{ cm}^{-1}$) mid-FTIR surface spectra of M20/IM7 aged isothermally at 120°C over 7500 h (shown are the spectral changes observed with increasing ageing time from 0 to 400, 5800, and 7500 h at 120°C).

120°C thermal ageing changes

As seen in Figure 13(a,b) the changes at the surface of the 120°C aged samples are noticeably different from those seen at 70°C even at very early stages in the ageing program. At this temperature in particular, there are many changes (throughout the spectrum) which vary with ageing time, and so the choice of a normalization peak is difficult. For the range below 2000 cm^{-1} , the 1361 cm^{-1} imide peak appears to be the most reliable [Fig. 13(b)]. For the range above 2000 cm^{-1} all of the peaks vary to some extent, but the 3060 cm^{-1} peak (aromatic CH) appears to be the most reasonable normalization peak [Fig. 13(a)]. The most noticeable changes are the very fast formation of a relatively sharp amide peak at 1670 cm^{-1} and strong decreases in the C \equiv N (2165 cm^{-1}), CH ($\sim 3000\text{--}2800 \text{ cm}^{-1}$), aromatic (1513 cm^{-1}), and hydroxyl areas ($3500\text{--}3300 \text{ cm}^{-1}$). While the C \equiv N and amide areas change immediately (400 h) and then partially stabilize, the other peaks continue to change with time. Also underlying the general carbonyl area ($1770\text{--}1650 \text{ cm}^{-1}$) is a broad general increase in oxidized structures, which is partly disguised by the sharp, imide and amide peaks.

Another more gradual group of changes which may be connected are the aromatic peaks at 1612 and 801 cm^{-1} which appear to move to 1597 and 835 cm^{-1} respectively, over the test period, and are either due to changes in ring substitution patterns or large changes in polarity of the attached groups.

A number of other significant but small changes also occur during the 120°C ageing at the composite surface. These include 768 cm^{-1} (aromatic, increase), 906 cm^{-1} (epoxy, loss), 1105 cm^{-1} (unknown, change),

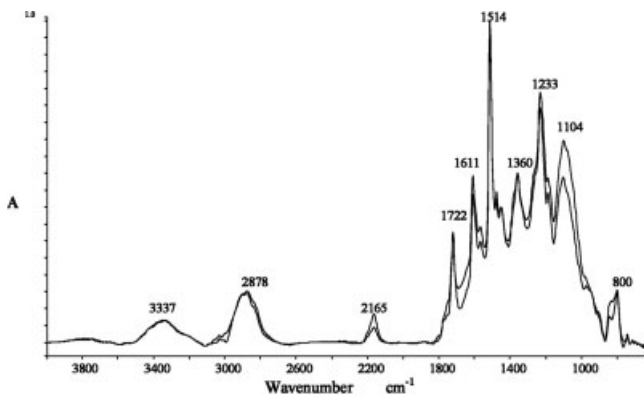


Figure 14 Mid-FTIR center spectra of M20/IM7 aged at 120°C for 7500 h and unaged M20/IM7.

1175 cm^{-1} (C—O, change from 1188 cm^{-1}), 1270 cm^{-1} , (increase), 1310 cm^{-1} (unknown, increase) and some of these continue to increase greatly at higher temperatures, indicating further oxidation.

The changes observed in the center of the laminate with ageing at 120°C is significantly less than that found at the surface. There is still significant loss of the C≡N and CH groups to be found, but there are no increases in the OH or amide group regions to be seen (Fig. 14). Some broad oxidative changes in the 1750–1650 and the 1250–1000 cm^{-1} regions are appearing, but nothing specific and certainly nothing indicating cure changes can be seen.

170°C thermal ageing changes

As seen in Figure 15(a,b), the FTIR ageing changes seen at 170°C are considerably different from those

seen at the lower temperatures. This is not surprising considering the greater state of “cure” of the composite after ageing above its initial T_g for 400 h before the first analysis point. The complete loss of the C≡N peak (2165 cm^{-1}) in this first sampling point (at 400 h) on the surface and in the center (at 2000 h) would suggest that the cure mechanism is very different to that previously suggested in the literature^{13,14} or the proposed product is highly oxidation sensitive, or both.

Perhaps the most noticeable degradation change (that is different from the 120°C ageing) is in the carbonyl area with a drop in oxidation peaks in the 1750 cm^{-1} area, the broad general increase from this point down to 1650 cm^{-1} and the absence of the sharp amide peak at 1670 cm^{-1} (except for a small indication at 400 h). Most of the broad oxidation peaks both here and around 1200 cm^{-1} occurred quite quickly (between 400 and 900 h) and become broader with time. Also, unlike the slow 120°C ageing changes in aromatic peaks (1611–1397 and 801–835 cm^{-1}), the changes at 170°C were accomplished within the first 400 h at the surface and 2000 h in the center of the composite material. Similarly, the losses of OH peaks (3400 cm^{-1}) and aliphatic CH and CH₂ areas (3000–2800 cm^{-1}) were strong and quite fast but the changes were so great that it is difficult to find a peak for normalization and hence obtain a quantification of the changes with time.

Except for the fast C≡N group changes, the changes in the FTIR spectra in the center of the laminate were slow and relatively small (Fig. 16). Even at 7500 h the increase in the broad carbonyl bands between 1770 and 1700 cm^{-1} (but no amide formation) is one of the few noticeable changes below

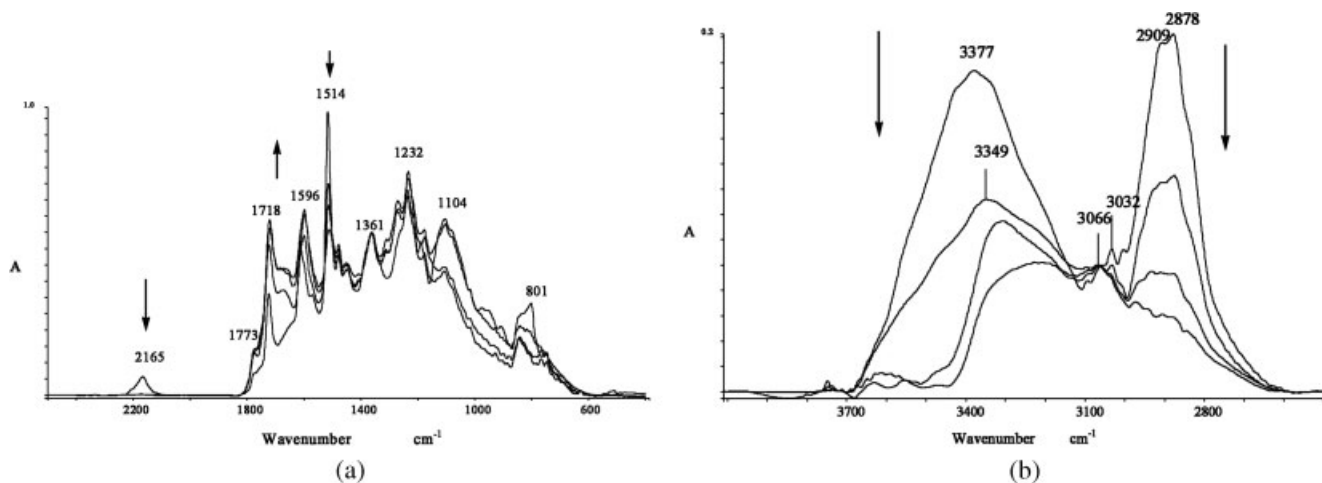


Figure 15 (a) Expanded (2500–400 cm^{-1}) region of the mid-FTIR surface spectra of unaged M20/IM7 and M20/IM7 thermally aged at 170°C for 900, 3600, and 7500 h (and some of the spectral changes observed with increasing ageing time from time zero to 900, 3600, and 7500 h). (b) Expanded (4000–2500 cm^{-1}) region of the Mid-FTIR surface spectra of unaged M20/IM7 and M20/IM7 thermally aged at 170°C for 900, 3600, and 7500 h (shown are some of the spectral changes observed with increasing ageing time from time zero to 900, 3600, and 7500 h).

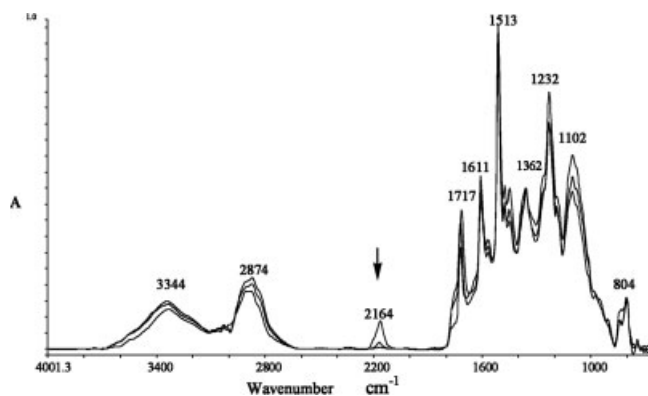


Figure 16 Mid-FTIR center spectra for M20/IM7 aged at 170°C for 400 h, 7500 h, and at time zero (shown are some of the spectral changes observed with increasing ageing time from time zero to 400 and 7500 h).

2000 cm^{-1} . The OH, NH area between 3500 and 3200 cm^{-1} broadens and decreases as well as the general aliphatic CH areas; but again normalization difficulties make this hard to quantitate and the changes are not great. Surprisingly, even at this temperature, the aromatic peaks at 1612 and 805 cm^{-1} , which change quickly at the surface and were thought to indicate cure, do not change.

200°C thermal ageing changes

As seen in Figure 17(a,b), and unlike previous temperature profile changes, there is no significant difference in the FTIR spectra, and hence surface chemistry, from the 170°C ageing study. At 200°C broader oxidation peaks occur very early in the ageing program (before 400 h) and heavy losses of the OH,

NH, and CH groups occur along with the loss of the $\text{C}\equiv\text{N}$ peak.

The laminate weight loss at 200°C is significant with $\sim 50\%$ of the resin oxidized completely away by 7500 h. The resulting spectra are therefore no longer truly surface spectra, but are more representative of the bulk of the composite material.

Even the center spectra (Fig. 18) at the 200°C ageing temperature are showing quite strong changes by 400 h, and many broad changes by 7500 h, which indicate heavy chemical degradation throughout the composite material. This amount of chemical degradation would at last affect the general mechanical properties. It is interesting that the center spectrum at 400 h shows a significant shift in the imide peaks at 1774 cm^{-1} (to 1768 cm^{-1}) and 1723 cm^{-1} (to 1713 cm^{-1}). These trends are also observed in the highly expanded spectra (Fig. 19) and evidence of the beginnings of the spectral chemical shift can be seen at the 170°C ageing temperature (7500 h) as well as the differential spectrum (not shown). It is obvious that the data obtained from the 200°C ageing tests are not very meaningful for the longer times used in this highly reactive matrix resin system. Most other research has been done for shorter ageing times.

DISCUSSION

As outlined in the introduction, the M20/IM7 commercial composite (repair type) system studied in this article is unusual in that it has a very complex chemical structure. It has at least two epoxy resins, at least one (partially dissolved) hardener molecule, plus a (phase separated) polyimide toughening phase and the resin system has been only partially reacted (72%). However, it has been possible to

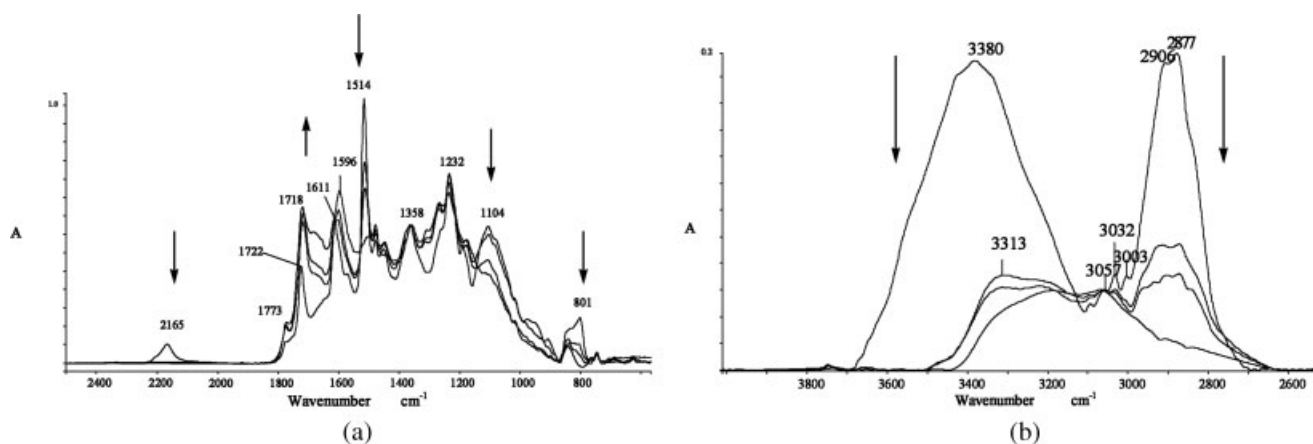


Figure 17 (a) Expanded (2500–570 cm^{-1}) region of the Mid-FTIR surface spectra of unaged M20/IM7 and M20/IM7 thermally aged at 200°C for 400, 2025, and 7500 h (shown are some of the observed changes with increasing ageing time from the time zero sample to 400, 2025, and 7500 h). (b) Expanded (4000–2500 cm^{-1}) region of the Mid-FTIR surface spectra of unaged M20/IM7 and M20/IM7 thermally aged at 200°C for 400, 2025, and 7500 h (shown are some of the observed changes with increasing ageing time from the time zero sample to 400, 2025, and 7500 h).

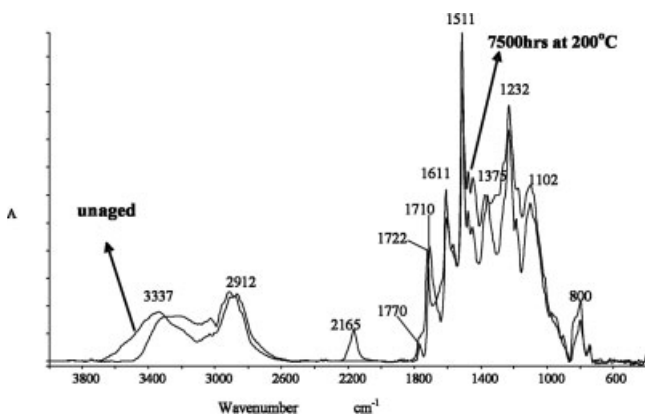


Figure 18 Mid-FTIR center spectra of unaged M20/IM7 and M20/IM7 aged at 200°C.

study the isothermal degradation chemistry of this material at a number of different temperatures ranging from a reasonable “in use” temperature (70°C) to a highly accelerated condition of the type often used in academic or qualification studies (200°C). The complexity of the system means that although the resin chemistry can be partly described by the idealized structure (Fig. 1), the real chemistry has to include the unreacted and defect groups present (Fig. 20). These groups are more reactive and property-affecting than the proposed (cured) resin structures, especially at lower temperatures. For qualification purposes it is essential to understand this real chemistry under all conditions, and how such chemistry could affect the composite mechanical properties over time. Morgan and Mones²⁰ have detailed such defect chemistry for relatively simple TGDDM-DDS systems.

One of the most important defect structures present in this composite, as commercially produced, is the unreacted hardener (DICY), which can be extracted in quite large amounts from the unaged composite. The gradual loss of this unbound hardener has been well known to cause ageing problems (such as micro cracking) in commercial aerospace composites²⁸ and the noticeable loss of the $C\equiv N$ groups in the surface FTIR spectra at all temperatures (even 70°C) may partially indicate DICY loss (not cure) in this composite. However, $C\equiv N$ loss in the center of the laminate at 120°C and above must indicate a different type of reaction (but still not normal cure). The weight increases in the composite during 70°C and 120°C also suggest chemical changes rather than the physical loss, which is seen in the hot/wet ageing of this composite.²⁹ Grenier-Loustalot et al.²⁵ have suggested a number of chemical changes in DICY and its reaction products that could explain the loss of $C\equiv N$; these include melamine formation and reactions with various hydroxyl groups (Fig. 21) but most do not include

weight gains, although the latter could explain some of the $-OH$ losses at all ageing temperatures.

The other major type of defect structure present in this partially cured composite is concerned with both the unreacted epoxy portion of the resin and the original defect structures in the epoxy monomers used. In the latter case it is well known that commercial TGDDM monomer contains up to 25% of a range of defect groups,^{25,26} and these have been shown to degrade selectively at relatively low ageing temperatures in other commercial epoxy materials.^{15,16} Most of these defect structures contain active aliphatic CH and OH groups which can oxidize to aldehyde and ketone groups, and hence may account for the weight gains found at the 70°C ageing temperature. This again would account for the $-OH$ loss seen in the FTIR, but the expected carbonyl group increases, appears to be partially masked by the large imide band at 1720 cm^{-1} . The long-term thermal degradation of unreacted groups would predominantly be oxidation to hydroxyaldehydes and hydroxy acids (as shown in Fig. 22) and would again give weight increases. However, at this temperature only particular susceptible (defect) epoxy groups should react; for example isomerization to aldehydes.

During isothermal ageing at 120°C, the greatest chemical change observed on the surface of the M20/IM7 composite is the formation of an amide at 1670 cm^{-1} . Previous work^{13,23} has indicated that this amide structure is most likely to be the oxidation product of the $-CH_2-$ group next to the nitrogen on TGDDM (Fig. 22). This oxidation is initially fast at 120°C but it slows down once the particular, susceptible (defect?) group is used up, and then the spectral peak broadens due to more general amide formation. These types of oxidation reaction mechanisms are not seen at the center of the laminate even at the highest temperatures.

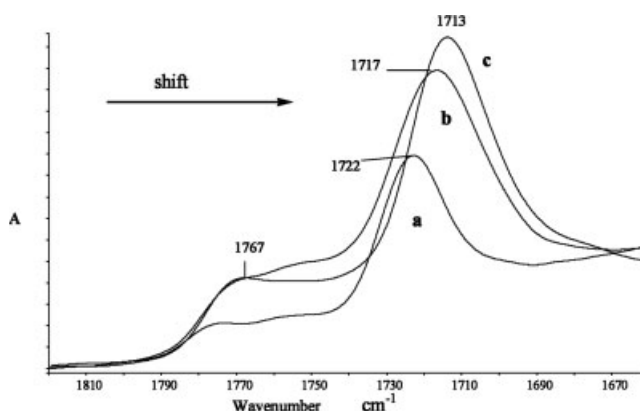


Figure 19 Expanded (1800–1660 cm^{-1}) Mid-FTIR center spectra of unaged M20/IM7 (a), M20/IM7 aged at 170°C for 7500 h (b), and at 200°C for 400 h (c).

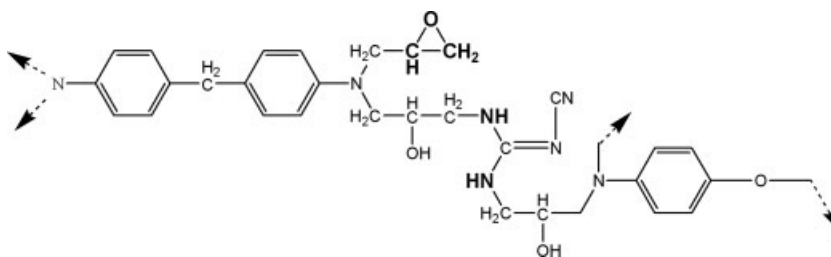


Figure 20 An example of the unreacted groups and the defect groups present in the M20/IM7 composite.

Possibly connected to the above oxidation, because of its timing and also because it does not occur in the center of the sample, is a sharp switch of an aromatic peak at $1612\text{--}1597\text{ cm}^{-1}$. The initial peak is a major peak in unreacted TGDDM but converts to the latter area in fully cured TGDDM/4,4'DDS epoxy matrix systems.²³ A similar type, and possibly connected change, is the sharp absorption drop in the 1512 cm^{-1} aromatic peak, although this is more complex as this peak decreases somewhat in the center as well, whereas the 1612 cm^{-1} peak largely remains unchanged. Both of these peaks are considered to be aromatic —CH— peaks²¹ associated with the various *para*-substituted ring movements, which should be oxidation stable at these lower ageing temperatures. However, the changes seen in this work do not necessarily show that the —CH— itself was oxidized. It is more likely that the change from an amine substituent to an amide was sufficient enough to change the FTIR pattern significantly without affecting the ring itself.

As mentioned above, the chemistry of degradation at the higher ageing temperatures of 170°C and 200°C is very different from those seen at the lower temperatures, and this is emphasized by the weight loss profiles and the various thermal analysis results. It is obvious that a lot of general oxidative changes on many aliphatic groups have occurred before the first FTIR analysis measurement at 400 h. While it is often suggested that there should be some time/temperature correlation, and the 70°C and 120°C type mechanisms should occur very early in the high-temperature ageing conditions, preliminary experiments at early times did not show this, in these or previous studies.²³ Instead, the broad general oxidation started early and just progressed further on the outside of the laminate, and minor but different

changes (except for $\text{C}\equiv\text{N}$ loss) occurred in center of the laminate at 170°C . At 200°C the broad oxidation was similar but worse on the surface of the material and even started to occur in the center of the material later in the ageing profile.

Owing to the large differences in chemistry between the center and the surface of the composite, the correlations of mechanical properties with ageing time and temperature are liable to be very poor (as evidenced in the DMA data) and will depend greatly on the type of mechanical testing carried out.

CONCLUSIONS

The overall finding for the range of analytical testing techniques used in this study is that the thermochemical ageing changes in this partially reacted M20/IM7 commercial system are very complex but dominated by surface oxidation. It is also evident that this surface chemistry varies greatly depending on the ageing temperature. The 70°C thermal ageing appears to be dominated by the oxidative changes in various defect groups (mainly OH and $\text{C}\equiv\text{N}$) at the surface with very minor changes in the bulk of the composite. In contrast, the early 120°C thermal ageing chemistry appeared to be a competition between some normal reaction completion (i.e., epoxy loss) and oxidation of less-susceptible but very specific groups (CH_2 next to a nitrogen, $\text{C}\equiv\text{N}$, OH, etc.). After the early specific oxidation, more general changes start to occur and even some internal loss of $\text{C}\equiv\text{N}$ is seen. For the 170°C and 200°C thermal ageing temperatures, the composite structure has changed very greatly by the first analysis point to give a composite very different from the starting material. Ageing of this new material is dominated at the surface by a great variety of oxidation mechanisms on aliphatic

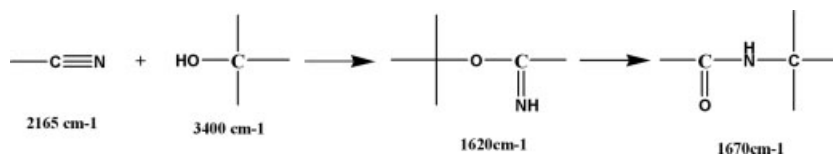


Figure 21 Some of the reactions of the cyano and melamine.

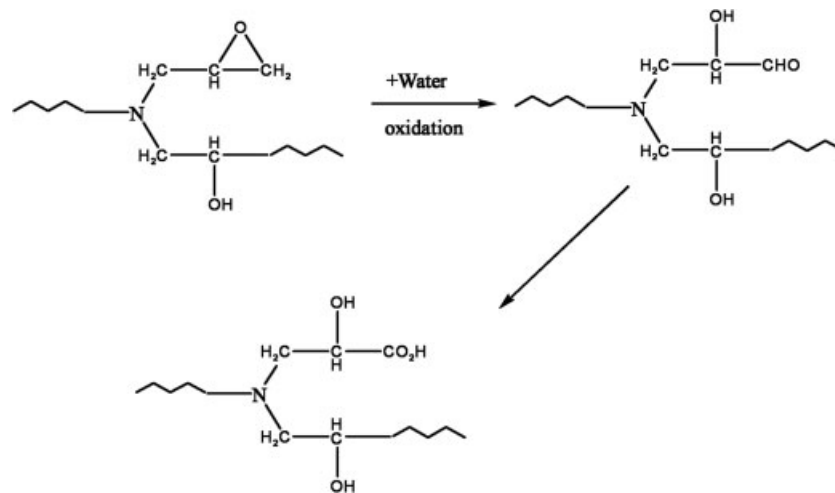


Figure 22 Some oxidation products of TGDDM.

CH₂, OH, and nitrogen containing groups. Only quite late during ageing at 200°C is the center of the laminate affected.

What this work emphasizes is that the exact temperature of ageing can have a great effect on the chemistry of degradation of the composite matrix. However, because this occurs mainly at the surface, the changes may not correlate with many of the important mechanical properties. In summary, accelerated, mechanical property, and ageing studies of such a reactive material without knowledge of the chemical changes taking place would be of little benefit.

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