Chemistry of Thermal Ageing in Aerospace Epoxy Composites

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ABSTRACT: The detailed chemical reactions involved in the thermal ageing (at 120°C) of a typical aerospace epoxy composite have been studied by the mid-Fourier transform infrared spectroscopy (FTIR) spectral characterization of selected model compounds. The FTIR spectra indicate that at this particular temperature, the major reaction in the resin structure is probably an oxidation of a CH_2 group adjacent to the nitrogen atom of the tetraglycidyldiaminodiphenyl methane unit of the molecular structure, particularly where it is attached to one isomer of the diaminodiphenylsulfone hardener unit. The FTIR changes indicate that the major product is an amide group but other minor changes are also detailed and differences in the chemical changes seen at other ageing temperatures highlighted. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2210–2219, 2006

Key words: epoxy composites; thermal ageing; Fourier transform infrared spectroscopy; model compounds

INTRODUCTION

Epoxy resin formulations are widely used as the matrix materials for structural composites employed in the aerospace industry, and a large amount of both basic research[1–8] and routine testing work[9–12] has been devoted to determine the long term mechanical performance of these composites under various deleterious environmental conditions. However, because of the high costs and long times involved in carrying out realistic testing experiments, various accelerated ageing protocols have evolved as the standard test procedures for any of the newer systems. As an example, the use of high temperature exposures are common and there have even been discussions on whether higher temperatures can be considered an equivalent to high humidity situations, i.e., hot/hot versus hot/wet testing. While for many types of epoxy composite these conditions should obviously not be considered equivalent (due to their high moisture absorption levels in high humidity environments) the results of testing at the other commonly-used extreme test conditions (such as water immersion) could be equally doubtful.

One suggested [13] method of avoiding the high cost of mechanical testing of commercial composites under the many different and accelerated conditions required would be to look at the chemical changes that occur to the matrix resins under more realistic conditions, and relate these to mechanical property differences. Chemical and physicochemical analysis methods are more sensitive and require very much less material than mechanical testing protocols and are not so heavily influenced by the problems of sample preparation and testing variables. A large amount of academic research has been carried out on the chemistry of environmental ageing of all types of epoxy resin materials (not composites), and standard ageing mechanisms for both thermal ageing and hot/wet ageing have been proposed. Unfortunately, most of the work has been carried out with neat resins of non commercial (simplified) formulations and largely under highly accelerated ageing conditions[4–7], except for Burton's[14] work on the diglycidyl ether of Bisphenol A, epoxy resins cured by mainly aliphatic amines.

We recently completed a detailed chemical ageing study with a number of different, commercial epoxy and bismaleimide composite systems, fabricated by the correct aerospace procedures. These have been aged under both highly accelerated and very standard environmental conditions ranging from straight thermal ageing to a variety of hot/wet conditions.[13] The full results of this study will be reported at a later date but one notable result from the thermal ageing of the epoxy composite materials at 70, 120, 170, and 200°C was that different types of chemical ageing occur near the surface of the composite almost exclusively, at each different temperature. In particular, it was noted that at the lower temperatures, the chemical changes (as determined by the Fourier transform infrared spectra (FTIR)) were very sharp and occurred mainly in one area of the spectrum. This indicated that only one
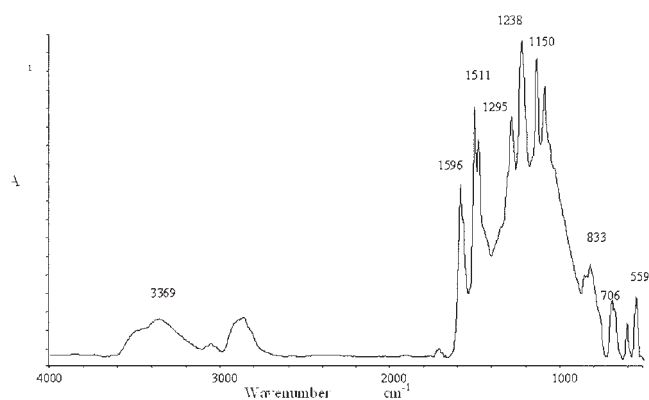
type of molecular unit in the matrix structure was affected by the low temperature ageing. This is in contrast to the broad general oxidation of the higher temperature (accelerated) ageing conditions. As the temperatures below 120°C are relatively close to the actual composite use temperatures, these results would indicate that only a small part of the matrix resin structure is responsible for most of the real ageing problems in these particular aerospace composites. Knowledge of their degradation chemistry could therefore be used to extend the life of these materials.

This report details our studies of thermal ageing chemistry of the various mixtures of resin and hardener believed to be used in one of the common commercial aerospace composites (8552/IM7) in an effort to determine the nature of the oxidation sensitive groups present in this commercial formulation.
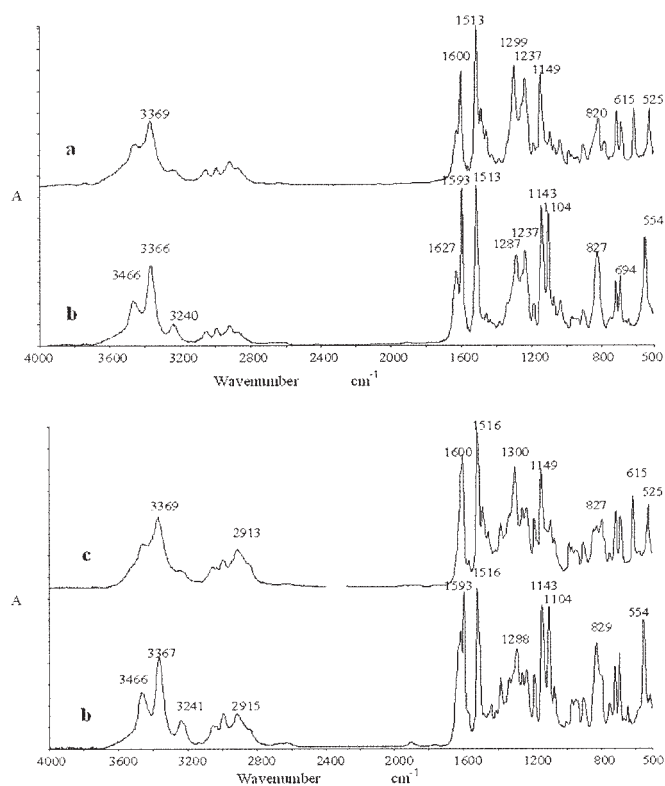
EXPERIMENTAL

The epoxy monomers, tetraglycidyldiaminodiphenylmethane (TGDDM) and triglycidylaminophenol (TGAP) and the diaminodiphenylsulphone (DDS, 3,3′ or 4,4′) mixture were heated under vacuum at 130°C on a rotary evaporator until the DDS was dissolved. The resin mixture was then coated onto a NaCl plate and cured at 170°C for 120 min. The prepared sample was then aged at 120 and 170°C and sampled for mid-FTIR analysis at regular intervals for up to 65 days.

The mid-FTIR analysis was conducted on a Bomen MB Series Spectrophotometer. The use of a stable reference peak within the mid-FTIR spectra was required for the FTIR analysis. Our wide temperature range studies[15] however show that no peak is completely stable, not even the sulfone peak at 1145 cm^{-1} remains unchanged (probably due to other underlying structures). The most commonly used reference peak, the aromatic peak at 1510 cm^{-1}, has been shown to be one of the first to show change, even at the lower ageing

Figure 2 (a) Mid-FTIR spectra of TGAP/DDS resin cured at 170°C for 120 min (**a**: 4,4′ DDS; **b**: 3,3′ DDS). (b) Mid-FTIR spectra of TGDDM/DDS cured resin at 170°C for 120 min (**c**: 4,4′ DDS; **d**: 3,3′DDS).
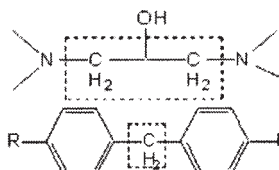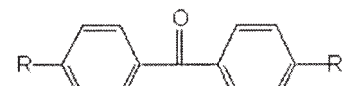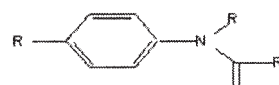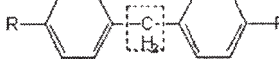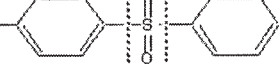
temperature of 70°C, due to defective aromatic structures and this is highlighted in our differential spectra. The most stable peak used in the 120°C studies appears to be the 1600 cm^{-1} aromatic peak, and this is the peak chosen for reference purposes in the following work. (For the sake of spectral image clarity, not all of the spectra obtained are included in each figure.)
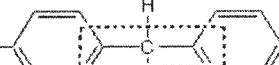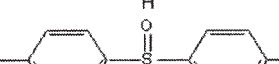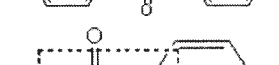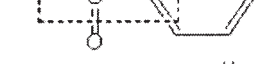
RESULTS

Over a number of years, we have been able to develop simple FTIR techniques for obtaining high quality spectra from fully-cured, commercial, advanced composites even when there are high volumes ($\cong$70%) of carbon fiber present. Using these spectra, as well as literature information[16,17] and model compound spectra, it has been possible to obtain an indication of the major resin and hardener molecules present in the 8552/IM7 composite matrix. This commercial material (Fig. 1, 8552/IM7 spectrum) appears to contain both TGDDM and TGAP epoxy monomers and 4,4′ and 3,3′ DDS hardeners. The spectra of cured, neat resin mixtures of the four different materials are shown in Figures 2(a) and 2(b).

To study the possible degradation mechanisms present (at 120 and 170°C) in the commercial compos-

Figure 1 Mid-FTIR surface spectra of cured 8552/IM7 Composite.

TABLE I
Spectral Peak Assignments Above 1000 cm^{-1}

Approximate peak position (cm^{-1})	Tentative assignment	Functional group
3600–3550	Water	H_2O
3400 region (broad)	ν(O—H); hydrogen bonded	R-O-H······
3380–3200	ν(N—H)	R—N—H
3028–3006	ν(Ar—H)	
2980–2780	ν(C—H) and ν(CH$_2$) TGDDM, DDS	
1725	ν(C=O) aldehyde or ketone	
1710	ν(C=O) aliphatic carboxylic acid	
1695	ν(C=O) aromatic carboxylic acid	
1685	ν(C=O) ketone	
1667	ν(C=O) amide	
1611	ring quadrant stretching I TGDDM	
1594	Ring quadrant stretching I, DDS	
1514	Ring semi-circle stretching I, TGDDM	
1453	δ(CH$_2$) TGDDM	
1359–1341	ν(Ar—N), TGDDM, DDS	
1289	ν_{4F}(SO$_2$)	
1232,1188	ν(Ar—C—Ar)	
1144	ν_s(SO$_2$)	
1105	ν(Ar—S)	
1075	ν(C—C—O), secondary alcohol	

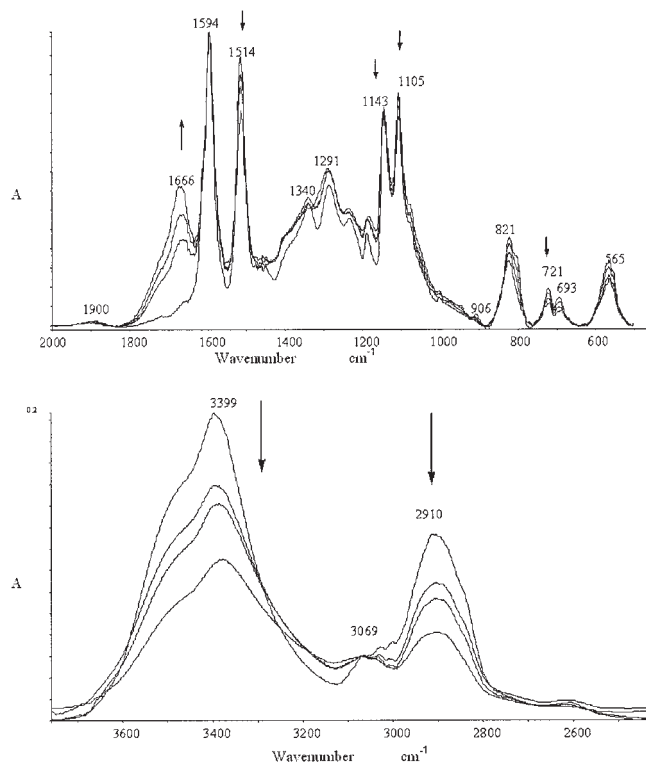ite, the four different neat resin formulations were aged as films on sodium chloride plates for up to 65 days. The FTIR spectral changes were followed in both the original aged spectra (Figs. 3, 6, 9, and 12) and by differential spectra, as compared to the starting (cured) formulation (Figs. 4, 7, 10, and 13). The spec-

tral assignments detailed in Table I rely on the work of many previous groups[4–8,16] as well as references to the original monomer spectra. Only peaks above 1050 cm^{-1} are detailed in this study, but the area below this also carries extensive information on chemical changes.
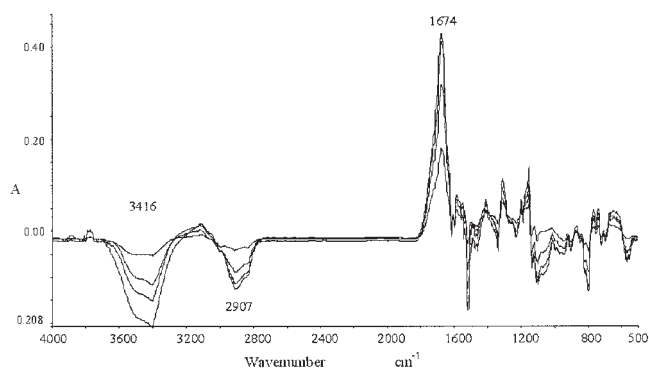
Thermo-oxidative degradation of the TGDDM/4,4' DDS System

Musto et al.[16] have carried out a very similar FTIR study of the degradation chemistry of some of the above systems, although at a significantly lower TG-DDM/DDS stoichiometric ratio (50%, compared to the current work, 80%) and, more critically, higher temperatures (200°C versus 120°C) and shorter times (30 h versus 1200 h). Although the stoichiometry of the commercial 8552/IM7 formulation was unknown, the higher figure is believed to be more realistic.

The initial FTIR spectra of fully cured material in both studies (Musto and the current work) are very similar with the major, noticeable differences being the higher and broader absorption values for the hy-
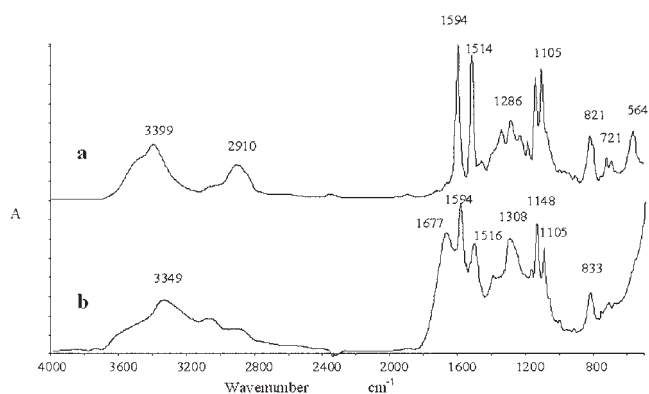
Figure 4 Differential spectra of TGDDM/4,4' DDS resin aged at 120°C over 50 days. (7days to 18, 29, 39, and 50 days).

droxyl groups (≈ 3500 cm^{-1}) in the literature spectra and a higher DDS aromatic peak (1594 cm^{-1}) absorption when compared with the 1514 cm^{-1} TGDDM in the current work (Fig. 3). Both changes would be expected from the higher DDS levels (and hence less epoxy/hydroxyl reactions) involved in the commercial type formulation versus the literature material.[16] Such difference could be critical to the mechanisms of degradation.

Figures 3(a) and 3(b) show the spectra collected in the 4000–500 cm^{-1} range at different time intervals (over 1250 h) during the 120°C isothermal degradation experiment. It is noticeable that the major changes occur in one small section of the spectrum (1740–1660 cm^{-1}) and while four other areas (3550–3200 cm^{-1} OH groups, 2950–2820 cm^{-1} CH groups, 1514 cm^{-1} aromatic CH, 670–610 cm^{-1}) have significant changes, the bulk of the material is relatively unaffected. This is also confirmed with the differential spectra in Figure 4. This result contrasts with our results of isothermal ageing at 170°C (for example Fig. 5, over 450 h) or the Musto et al.[16] work with ageing at 200°C where broad general degradation behavior starts almost immedi-

Figure 3 (a) Expanded (2000–500 cm^{-1}) mid-FTIR spectra of TGDDM/4,4' DDS resin aged at 120°C over 50 days. (The arrows indicate the increases ($\uparrow$) and decreases ($\downarrow$) observed in the peak intensity with increasing ageing time: from time 0 to 18, 29, and 50 days at 120°C). (b) Expanded (3750–2450 cm^{-1}) mid-FTIR spectra of TGDDM/4,4' DDS resin aged at 120°C over 50 days. (The arrows indicate the peak intensity changes observed with increasing ageing time: from time 0 to 18, 29, and 50 days at 120°C).
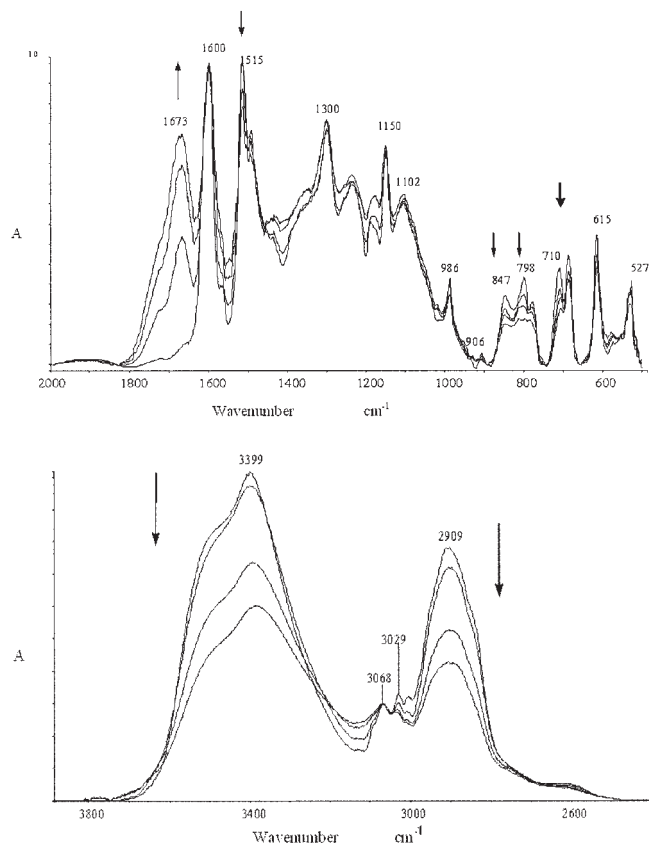
Figure 5 Mid-FTIR spectra of TGDDM/4,4' DDS resin aged at 170°C (**a**: 2 h; **b**: 20 days).

Figure 6 (a) Expanded (2000–486 cm^{-1}) mid-FTIR spectra of TGDDM/3,3' DDS resin aged at 120°C over 63 days (The arrows indicate the peak intensity changes observed with increasing ageing time: from time 0 to 18, 39, and 63 days at 120°C). (b) Expanded (4000–2400 cm^{-1}) mid-FTIR spectra of TGDDM/3,3' DDS resin aged at 120°C over 63 days. (The arrows indicate the peak intensity changes observed with ageing time: from time 0 to 18, 39, and 63 days at 120°C).

ately. The groups degraded during ageing at 120°C are of the same general structure as those highlighted in previous work[6,7] (OH and aliphatic CH$_2$ structures near the TGDDM unit) but these and the major product formed (the amide group at 1670 cm^{-1}) must be part of a much more specific structural unit.

Thermo-oxidative degradation of the TGDDM/3,3' DDS System

The isothermal FTIR measurements of this formulation were carried out under exactly the same temperature conditions as the previous 4,4' DDS system and are shown as the original traces in Figures 6(a) and 6(b), and as the differential traces in Figure 7. While the full spectra are very different between the systems containing the different hardeners, the major degradation areas are almost identical, except that the formation of amide was considerably greater in the 3,3' DDS system. These results confirm the finding of Musto et al.[16] and others that the TGDDM section of the mole-
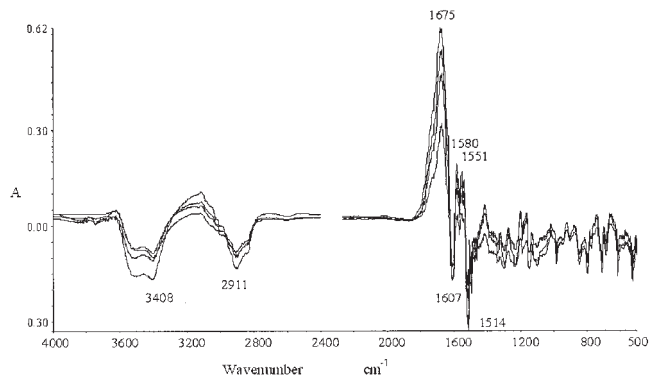

Figure 7 Differential spectra of TGDDM/3,3' DDS resin aged at 120°C over 63 days. (Time 0 to 18, 29, 39, and 63 days).

cule is more oxidation sensitive than the hardener units, but it also indicates that the hardener structure has some influence on this sensitivity. The sharpness of the peak changes also indicates that there is more specificity in the oxidation changes in this second system. Again, thermal ageing at 170°C produced large and broad general oxidation changes instead of the above sharp effects (Fig. 8).

### Thermo-oxidative degradation of the TGAP/3,3' and 4,4' DDS Systems

The isothermal FTIR measurements of the chemical degradation of these two systems were also carried out under the same time and temperature conditions as the TGDDM systems but the degradation changes, although similar, were very minor even in the 1720 and 1665 cm^{-1} regions. Figures 9(a), 9(b), and 10 show the mid- FTIR spectra and differential spectra of the TGAP/3,3' DDS collected at various times of thermal-oxidative ageing (to 1250 h) at 120°C. The TGAP/4,4' DDS spectra showed a similarly low level of change, Figures 11(a), 11(b), and 12. The Figure 10 shows the
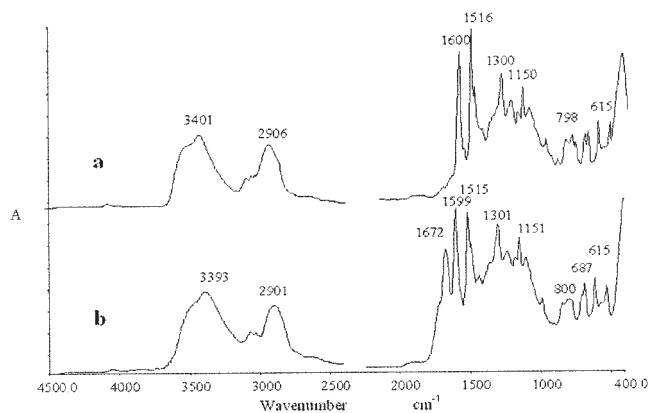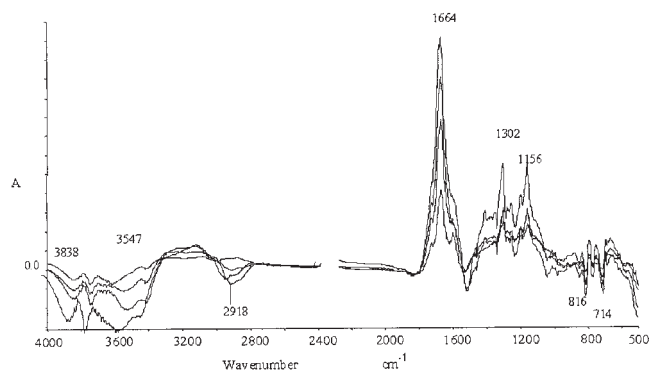

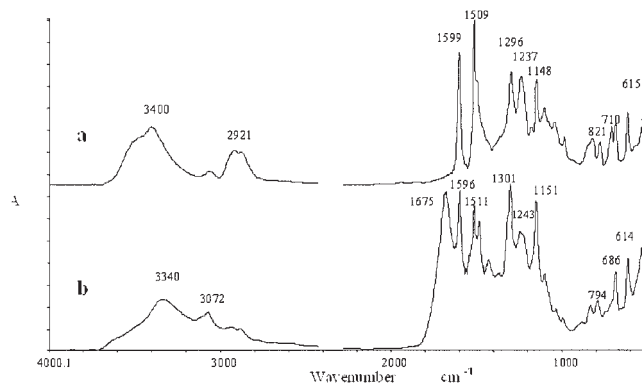**Figure 8** Mid-FTIR spectra of TGDDM/3,3' DDS resin aged at 170°C (**a**: 2 h; **b**: 18 days).
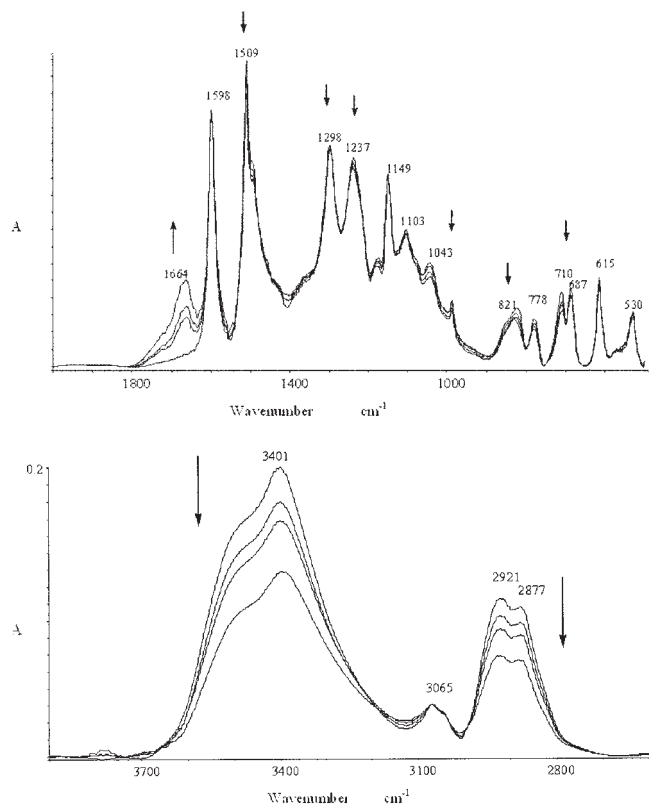
Figure 9 (a) Expanded (2000–500 cm^{-1}) mid-FTIR spectra of TGAP/3,3'DDS resin aged at 120°C over 50 days. (The arrows indicate the peak intensity changes observed with increasing ageing time: from time 0 to 18, 29, and 50 days at 120°C). (b) Expanded (3900–2600 cm^{-1}) mid-FTIR spectra of TGAP/3,3'DDS resin aged at 120°C over 50 days. (The arrows indicate the peak intensity changes observed with ageing time: from time 0 to 18, 29, and 50 days at 120°C).

difference spectra and emphases that the low level of change in the TGAP/3,3' DDS formulation shown is much more evenly distributed. Ageing at 170°C produced large and broad oxidative changes in both systems (Figs. 13 and 14).

**Figure 10** Differential spectra of TGAP/3,3'DDS resin aged at 120°C over 50 days. (Time 0 to 18, 29, 39, and 50 days).

Figure 11 Mid-FTIR spectra of TGAP/3,3' DDS resin aged at 170°C (**a**: 2 h; **b**: 18 days).

Comparative degradation changes in the four systems

To make a more quantitative comparison of the evolution of the increase in the amide oxidation peaks in the various systems, the amide peak heights (as related to the most stable group peak in the resin—the
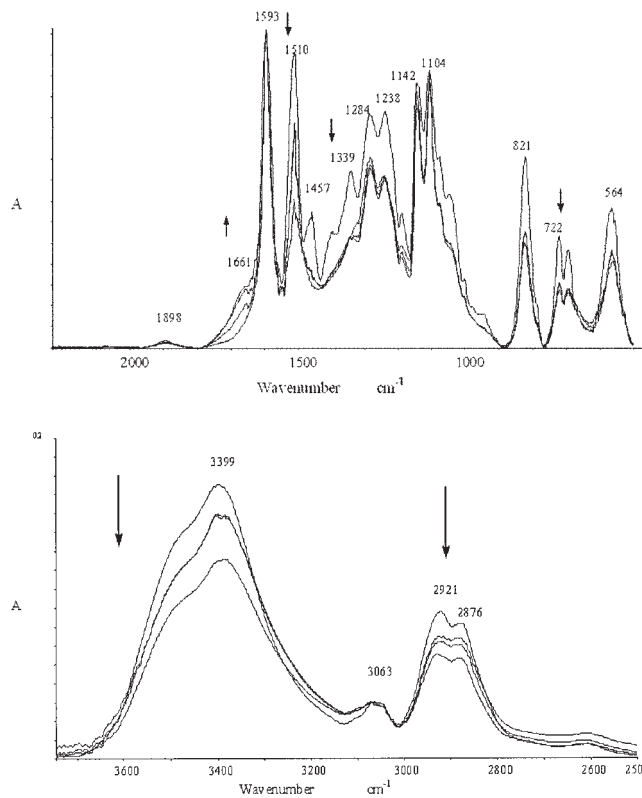
Figure 12 (a) Expanded (2200–500 cm^{-1}) mid-FTIR spectra of TGAP/4,4' DDS resin aged at 120°C over 63 days. (The arrows indicate the peak intensity changes observed with ageing time: from time 0 to 29, 39, and 63 days at 120°C). (b) Expanded (3750–2500 cm^{-1}) mid-FTIR spectra of TGAP/ 4,4' DDS resin aged at 120°C over 63 days. (The arrows indicate the peak intensity changes observed with ageing time: from time 0 to 29, 39, and 63 days at 120°C).

aromatic peak at 1600 cm^{-1}) were plotted against degradation time. Figure 15 details the results. The major point to note is the much faster rate of amide build up in the TGDDM containing systems, especially the TGDDM connected to 3,3' DDS. This indicates that in the commercial composite (8552/IM7), which contains all four molecules, the weakest link in the system should be in the TGDDM unit near attachment to a 3,3' DDS molecule. The second point to note from Figure 15 is that the decrease in amide formation rate after about 40 days indicates that the particular susceptible groups in both of the TGDDM systems have been completely oxidized, even at 120°C, but for the TGAP systems oxidation is minor but still continuing.

DISCUSSION

A considerable amount of previous research work has been carried out on the mechanisms of thermo-oxidative degradation of aerospace type epoxy resin systems containing TGDDM and 4,4' DDS.[4–8,14] Most agree that the initial groups that are formed are caused by oxidation at aliphatic units associated with the TGDDM part of the molecular and are present as ketone (or aldehyde) and amide groups. Our work with the more complex formulations of commercial composites such as 8552/IM7 indicates that similar groups are involved in their thermo-oxidative degradation. However, almost all of the previous workers have proposed reaction pathways that arise from "perfect" epoxy structures such as is shown in Figure 16 and in some cases have proposed complex and fairly high energy degradation pathways.[1–8]

While these may be reasonable for highly accelerated thermal ageing conditions, we feel that in more realistic ageing of commercial composites, degradation is much more likely to arise from changes in the more susceptible "defect" groups. These defect groups will arise in three major ways:
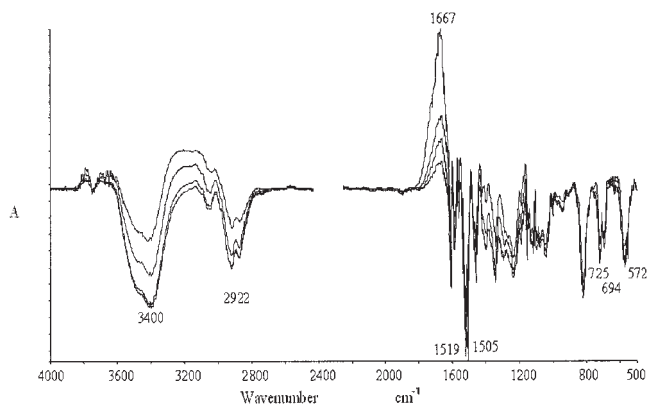

Figure 13 Differential spectra of TGAP/4,4' DDS resin aged at 120°C over 63 days (time 0 to 18, 29, 39, and 50 days).
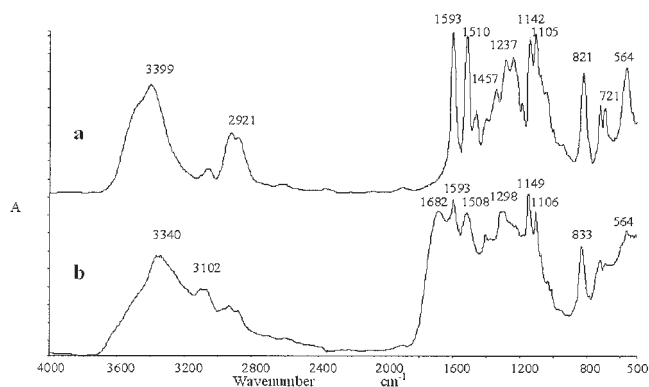
Figure 14 Mid-FTIR spectra of TGAP/4,4' DDS aged at 170°C (**a**: 2 h; **b**: 18 days).

a. Defects in the starting monomers.
b. Defects in the cure reactions due to the highly crosslinked network entanglements.
c. Surface defects (e.g., on fibers) and additives.

Commercial TGDDM monomer is particularly prone to defects with figures as low as 63% of pure tetra functional structures being suggested for the standard commercial material (MY 720) in the literature.[18] Structures such as I, II, III (Fig. 17) are common and chemically active impurities, which could easily be the oxidation sensitive units in the composite. Commercial TGAP and the aromatic amine hardeners tend to be much purer materials. As far as defects caused by the network structure formation, it would be expected that the reactions of these highly functional monomers, with their relatively stiff and small molecular units, would contain many partially reacted or even non reacted (widowed) functional groups even in a fully cured composite. The uneven stoichiometry in commercial composites, with their quite large (20%) excess of epoxy groups, could further enhance these types of defects and they would be somewhat greater in the tetra functional TGDDM unit when compared with the trifunctional TGAP units.

The third type of defect (surface defects) would be enhanced in a composite when compared with a neat resin system because of the very high level of carbon fiber surface areas in contact with the matrix. However, all four monomer units should be equally affected.

The results obtained in this study suggest that the most susceptible part of the 8552/IM7 structure concerns the TGDDM unit, especially when connected to a 3,3' DDS unit. The changes involved loss of OH, CH$_2$, and aromatic absorptions and a gain in aldehyde (or ketone) peaks as well as amides. One defect group that is undoubtedly present from the original monomer and could account for the amide and aromatic changes at the low temperatures would include a tri-
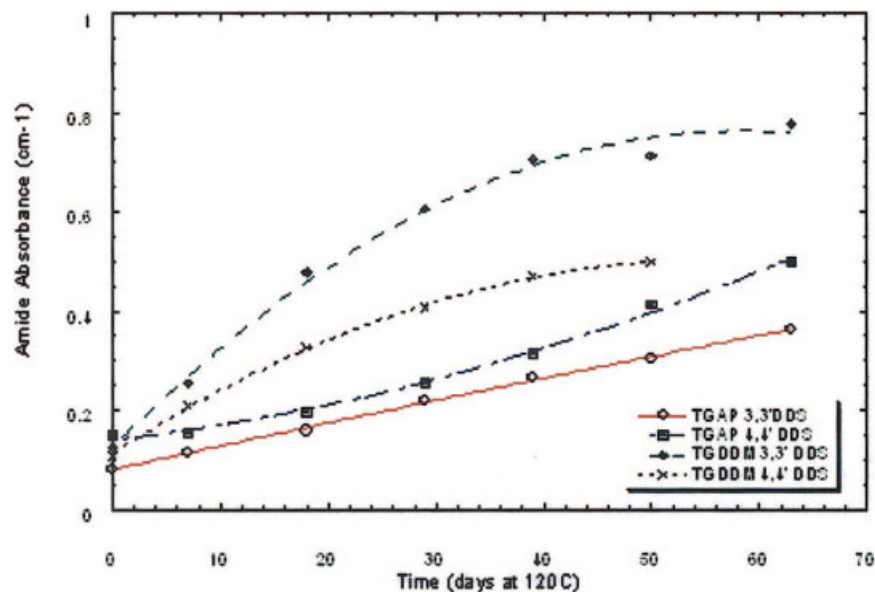
Figure 15 Absorbance increases of the oxidation product amide peak at (1660 cm^{-1}) in the various systems versus degradation time (days) for samples aged at 120°C using 1600 cm^{-1} as the reference peak. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

functionalised TGDDM structure such as shown in Figure 18.

This proposal contrasts with the suggestion by Musto et al.[16] and others[5,8] that stable aromatic ring structures are lost; a highly unlikely occurrence for a tertiary aromatic amino structure aged at only 120°C. The relatively small drop in FTIR absorption at 1510 cm^{-1} could instead be accounted for by amide conjugation and peak shift and broadening effects on the aromatic vibrations as amide groups are formed adjacent to the ring.

Structural changes that may account for the 3400 and 1725 cm^{-1} changes are the oxidation of glycol or chlorohydrin defects with the loss of OH absorption and the formation of ketone or aldehyde groups (Fig. 19).

Because of the complex and not fully known chemistry present in the 8552/IM7 commercial composite, it has not yet been possible to determine which particular defect or additive structure is responsible for the 1725 cm^{-1} carbonyl group formation during 120°C ageing, but our studies of 70°C thermo-oxidative ageing of this composite for almost 1 year indicated that this particular chemical change was the only signifi-

cant chemical change noticed (on the surface only), and so it must be a highly oxidation sensitive group. Studies of similar aerospace composite samples from "In Service" ageing for 10 years also highlighted this one type of change.[13] As the higher (accelerated) thermal ageing studies indicated that very different functional groups were oxidized, it is obvious that the mechanical changes in the composite could be very different under different conditions.

These results may help confirm suggestions by other studies[4,19] that because the chemical mechanisms of epoxy degradation vary greatly with ageing temperature (and humidity) and because the straight thermo-oxidative degradation changes occur from the surface of a composite, mechanical testing of thermally accelerated materials is unlikely to ever be a reliable predictor of "In Service" performance.

SUMMARY AND CONCLUSIONS

1. Model epoxy structures based on the known chemistry of the commercial aerospace composite 8552/IM7 were thermo-oxidatively aged at
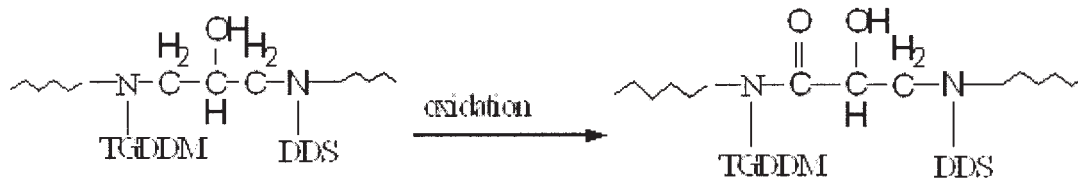
Figure 16 Proposed reaction pathways that arise from "perfect" epoxy structures.
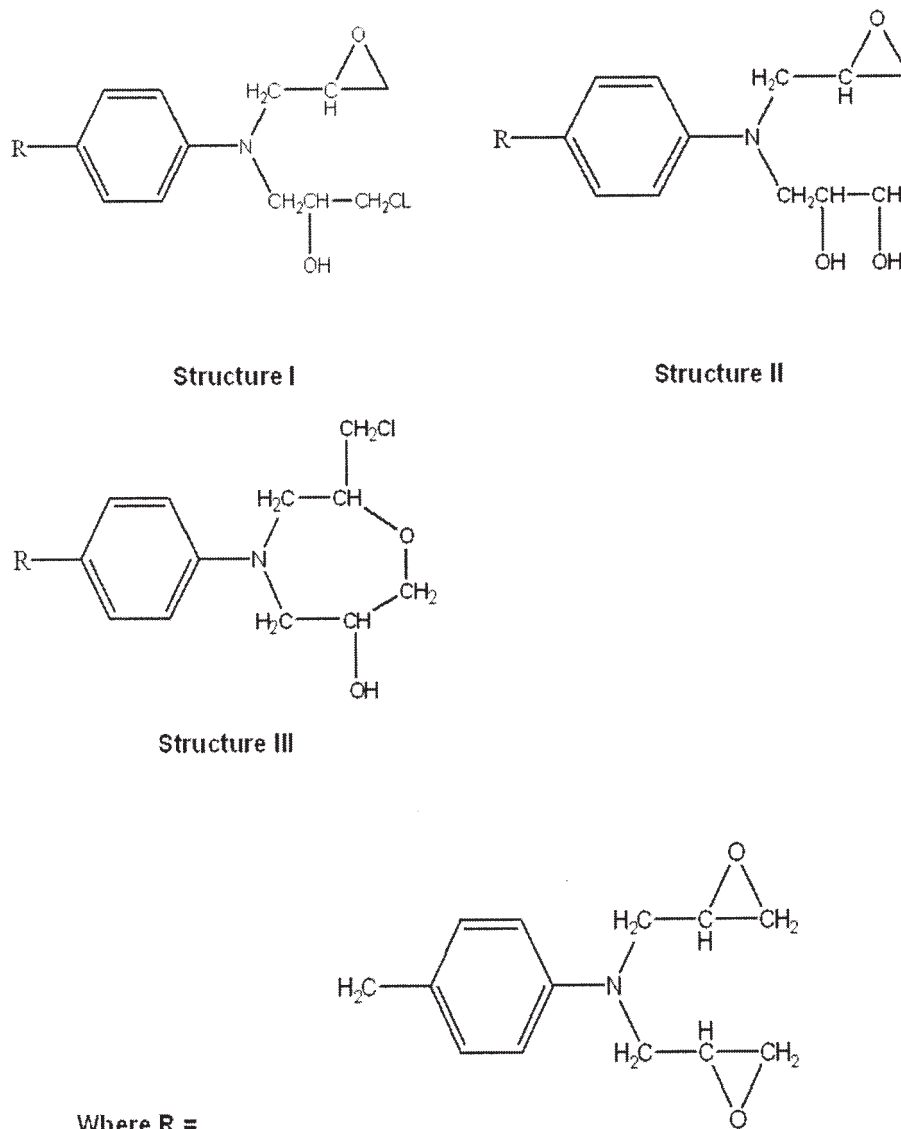
Figure 17 Structures I, II, and III; TGDDM Impurities.

120 and 170°C for over 60 days and analyzed by FTIR to highlight the chemical changes that take place during environmental ageing.

2. Using literature interpretations of peak positions, it was possible to determine the type of chemical changes that occurred and show that the 120°C ageing oxidized a very limited number of susceptible functional groups, whereas 170°C ageing gave broad, general oxidative changes in all areas of the matrix.

3. The oxidation susceptible groups were mainly in the aliphatic region of the TGDDM unit and the
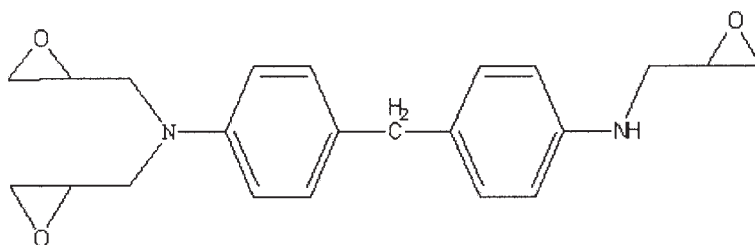

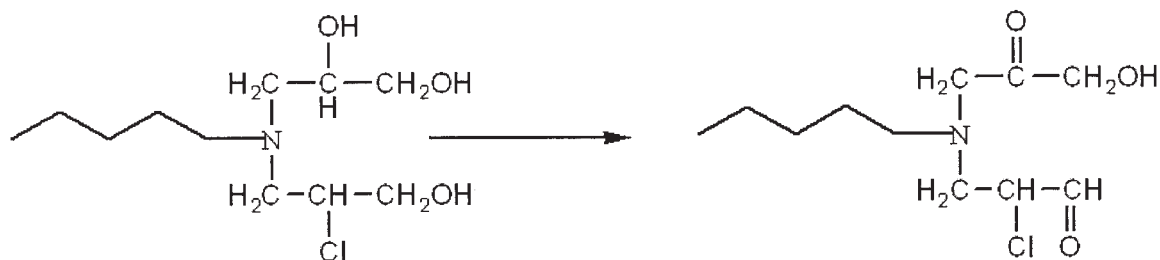**Figure 18** Trifunctionalised TGDDM structure.

Figure 19 Oxidation of glycol or chlorohydrin defects.

indication was that they were associated with "defect" structures.

The main conclusion from this study of the thermal degradation of model structures related to aerospace epoxy matrix resins is that at different temperatures the mechanism of oxidative degradation of the organic structures can be very different. At the temperature commonly used in many accelerated ageing studies (around 170°C), broad general oxidation, especially of surface chemical groups, is the main degradation mechanism. At temperatures of 120°C and below, which are more representative of real "in service" conditions of even military aircraft, the degradation (oxidation) reactions are more specific to a few susceptible functional groups in the molecule and it is only when they are heavily oxidized that the other groups are attacked. While such groups include the —CH$_2$— adjacent to the nitrogen in TGDDM, the most susceptible groups in a commercial matrix resin will be the "defect" groups. These will include impurities in the original (unreacted) resin components and un-reacted functional groups "widowed" during the formation of the network structure.

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