

Long-Term Aging in a Commercial Aerospace Composite Sample: Chemical and Physical Changes

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ABSTRACT: A section of a carbon-fiber-reinforced composite horizontal stabilizer skin from a 737-200 aircraft that had been in service for 20 years was analyzed with Fourier transform infrared spectroscopy and dynamic mechanical thermal analysis in an effort to determine the molecular changes that occurred in the epoxy matrix resin over the service life. Comparisons were made with a similar matrix resin system that had been aged under various accelerating conditions. As expected, the results showed that the molecular changes were slight and occurred only on the unpainted (internal) surface areas of

the composite. The changes in the commercial materials during the in-service aging were most similar to those in a composite that had been artificially aged at 120°C for 3000 h, but they included two chemical changes not seen previously. There was an increase in the number of aliphatic hydrocarbon molecules (a fuel chemical) as well as a decrease in the number of molecules containing $-\text{SO}_2-$ units. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2981–2985, 2010

Key words: composites; ageing; FTIR; curing of polymers

INTRODUCTION

For the prediction of long-term aging changes that may occur in the mechanical properties of new materials used in engineering structures, a great amount of reliance has been placed on the use of Arrhenius-type extrapolation methods. In these techniques, high aging temperatures and extreme moisture conditions for relatively short times are assumed to be equivalent to much longer times under realistic conditions. It is well understood that this type of extrapolation cannot be pushed too far, even for relatively simple materials such as metals and thermoplastic polymers,¹ but in the case of composites, the interactions of the multiple phases in the products can make such extrapolations even more unreliable. Thus, it is of great interest when important items with a composite structure become available for testing after a well-documented, long-term service experience. Such products have included one of the original Boeing CFRP 737-200 horizontal stabilizers after about 20 years of service. Detailed mechanical evaluations have been carried out on this item and previously reported,² but corresponding chemical and physical testing has not been provided.

In contrast to the ease of obtaining mechanical data from samples of aged composites, chemical and, to a lesser extent, physical information has generally been less easy to obtain. One complication in composites is that most of the chemistry of aging and the physicochemistry of moisture (or other product) absorption occurs slowly from the surface toward the center, whereas most mechanical testing results are averages (at best) over the whole composite thickness and a relatively large area. Some mechanical tests, such as double-cantilever beam tests, even test the least age-affected region at the center.

Fourier transform infrared (FTIR) spectroscopy has generally been considered the best technique for studying the chemical details of insoluble polymeric materials, but in the past, it has not been possible to obtain transmission spectra when carbon fibers are present,³ and surface spectral techniques have been unable to give high-quality quantitative evaluations, especially when the changes are small. Our recent experiments on the artificial aging of commercial carbon fiber composites has shown that it is possible to obtain highly reproducible and accurate transmission spectra of such composites by minor modifications of previously used FTIR methods.^{4–7} This previous research has also confirmed that, in the aging of a composite of a reasonable thickness, the central region of the composite remains chemically unchanged even under quite vigorous aging regimens. A further advantage of this FTIR analysis technique is that it also allows the removal of volatile

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substances (e.g., moisture) from a composite and hence can be used to determine real chemical changes in the material.

It was, therefore, interesting to use this new FTIR technique to obtain high-quality spectra from samples of in-service (aged) materials and compare the results with those obtained from similar commercial materials that were artificially aged^{4,7} and those obtained from chemical studies on model compounds.⁸ Comparisons of composite physical property changes were made with dynamic mechanical analysis (DMA) of the surfaces (as opposed to the internal sections) of the composite samples.

EXPERIMENTAL

Material

Samples of the composite skin (ca. 12 cm × 8 cm) were obtained from a decommissioned Boeing CFRP 737-200 horizontal stabilizer used for approximately 59,000 h on approximately 48,000 flights (entry into service: August 14, 1984). This kind of aircraft is used for short distances, so it has more flights with high mechanical stress than average. The composite parts had been in storage for a few years, so the moisture levels were not relevant to the usage conditions.

FTIR spectroscopy

FTIR spectra were obtained in accordance with a standard operating procedure written for this project. Approximately 1.5 mg of the composite was removed from the surface or center of the aged laminate. This was very finely ground with approximately 50 mg of dry KBr and left in a desiccator over P₂O₅ before being pressed into a disc. The disc was analyzed (256 scans) in a PerkinElmer 2000 FTIR spectrophotometer (Beaconfield, UK) in the transmission mode with KBr as the background reference. An analysis was undertaken by a direct comparison of the spectra and by the use of difference spectra.

DMA

DMA was conducted on a Rheometrics Scientific V machine (Piscataway, NJ). This instrument was completely computer-controlled, and the proprietary software used is known as Orchestrator. All samples were run on a large frame in a dual-cantilever mode. The sample was cut in a jig with a diamond-blade saw to produce a reproducible sample width of approximately 10 mm. A multifrequency analysis was undertaken at 1, 10, 50, and 100 Hz over a temperature range of 50–350°C at a heating rate of 5°C/min. Glass-transition temperatures (T_g 's) were

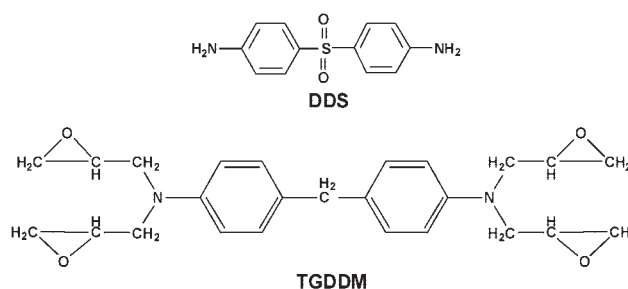


Figure 1 Chemical structures of TGDDM and DDS.

derived from the onset of the decline in the loss modulus and by the $\tan \delta$ peak position at 1 Hz.

RESULTS AND DISCUSSION

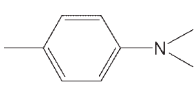
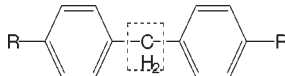
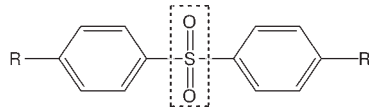
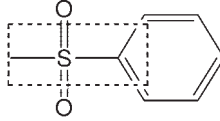
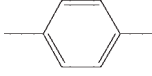
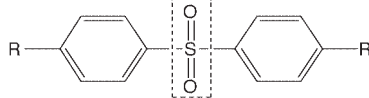
Two small sections of the composite (~ 8 cm × 12 cm) from the lower skin of the decommissioned Boeing 737-200 horizontal stabilizer were provided for testing. One surface was painted on each sample, but no visible defects were seen on any of the surfaces. The composite matrix resin was a BMS-8-212 type, which is believed to be mainly a tetraglycidyl-diaminodiphenylmethane (TGDDM) epoxy cured with diamino diphenyl sulfone (DDS; Fig. 1). The presence of other significant additives is not evident from the FTIR spectra.^{7,8}

Composite chemistry

Although it was not possible to obtain an exact unaged comparison sample for background FTIR studies, our previous accelerated aging work has shown that the center of a mildly aged composite is identical in chemistry (by FTIR) to that of the original composite, with the important proviso that both samples are dried. Almost all the peaks in aerospace epoxy resins of this type have been previously identified with specific chemical groups,^{4,8,9} so even minor chemical changes can be readily identified (Table I).

Figure 2 details a comparison of the spectra of different areas of the composite, and it shows that the FTIR spectra are very repeatable in most areas, so the bulk of the resin has not been greatly changed. A more detailed look at one of the major areas of change on the inner surface, the carbonyl region (Fig. 3), shows that there has been significant surface oxidation (consistent over different surface areas). Previous work on model compounds and so forth^{9,10} has identified areas of increased oxidation at approximately 1660 and 1735 cm^{-1} . Amide group formation and general oxidation of susceptible structures (e.g., hydroxyls) to carbonyl groups are responsible. The former appears to occur near the nitrogen on the aromatic ring of TGDDM and is

TABLE I
FTIR Spectral Peak Assignments

Approximate peak position (cm^{-1})	Tentative assignment	Functional group
3610	$\nu(\text{O-H})$, nonbonded	R-O-H
3460–3300	$\nu(\text{O-H})$, hydrogen-bonded	R-O-H
3300–3200	$\nu(\text{N-H})$ amide, amine	RNHC=O
2980–2800	$\nu(\text{C-H})$ and $\nu(\text{CH}_2)$	$-\text{CH}_2-$, $-\text{CH}_3$
1740–1730	$\nu(\text{C=O})$ aldehyde	$-\text{CH=O}$
1665–1650	$\nu(\text{C=O})$ amide	NHC=O
1593	Aromatic ring vibration	
1513	Aromatic ring vibration	
1231	Aromatic ring	
1220–1120	$\nu(-\text{C-O}-)$	Many different types of $-\text{COR}$
1142	$\nu_s(\text{SO}_2)$	
1104	$\nu(\text{Ar-S})$	
860–800	Aromatic para-substituted	
600–545	$\nu_s(\text{SO}_2)$	

accompanied by a decrease in the 1513-cm^{-1} peak, which is due to an aromatic ring vibration mode. The higher wavenumber peaks are believed to be due to the oxidation of anomalous or defect groups in the epoxy structure.

There are other significant areas of oxidation change that can be seen in both the carbonyl region ($>1735\text{ cm}^{-1}$) and the fingerprint region ($1500\text{--}1100\text{ cm}^{-1}$). More noticeable in the original spectra (Fig. 2) are two unusual and large changes at 2916

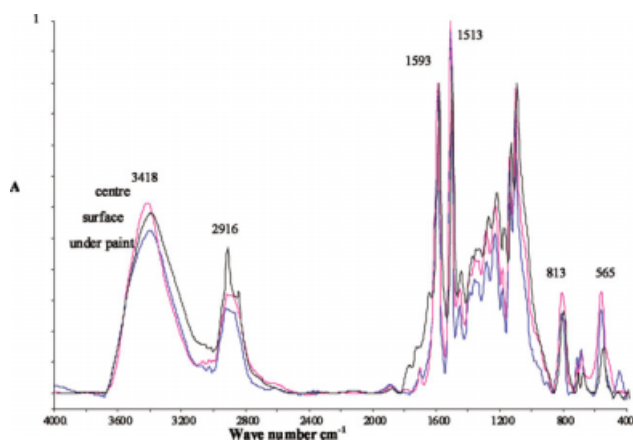


Figure 2 Three different areas of FTIR analysis of the 737-200 composite plaque. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

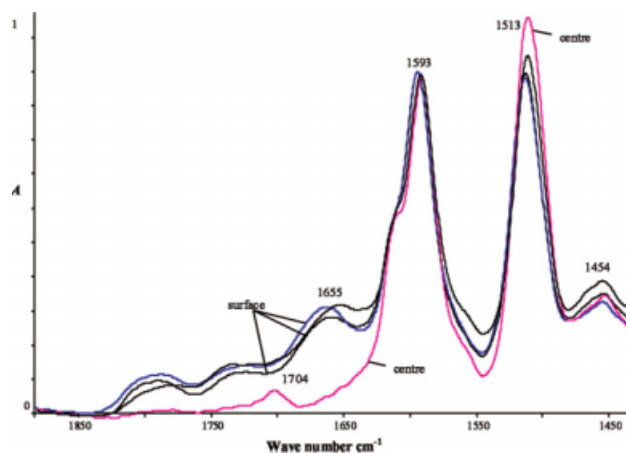


Figure 3 FTIR spectra showing aging changes between 1900 and 1500 cm^{-1} . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

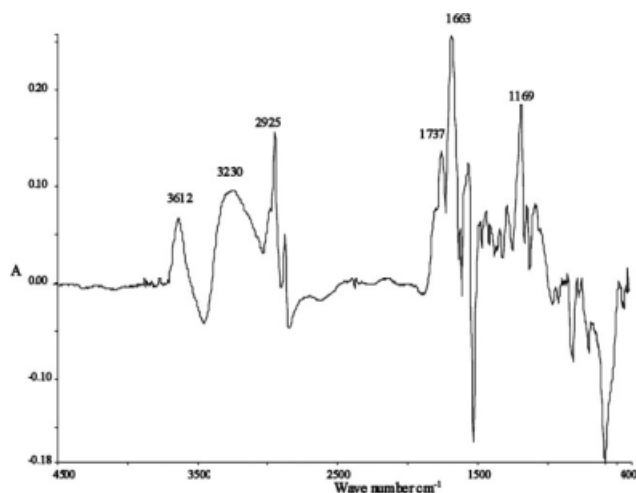


Figure 4 Differential spectrum between the surface and center of the composite plaque (see Fig. 2 for the original spectra). A. absorption.

(increase) and 565 cm^{-1} (loss). The former is due to an aliphatic $-\text{CH}_2-$ group vibration and was most likely caused by fuel absorption in the composite over time. The latter appears to be a loss of $-\text{SO}_2-$ group absorption (maybe DDS), and neither of these had been seen in our previous studies of accelerated aging in these types of materials.

Another way of enhancing the molecular changes seen in the FTIR spectra of composite samples is the use of difference spectra between the surface and the center, as shown in Figure 4. The carbonyl, $-\text{CH}_2-$, and aromatic peak changes mentioned previously show up very strongly, but the figure also highlights a number of lesser aging changes. These include a loss of hydrogen-bonded $-\text{OH}/-\text{NH}-$ peaks at 3460 cm^{-1} and an increase in nonbonded $-\text{OH}$ at 3612 cm^{-1} . This may be consistent with the extraction of low-molecular-weight polar oligomers by moisture and is similar to what we have observed in accelerated aging under hot/wet conditions.⁷ Other changes that can be observed include the broad $-\text{NH}-$ peak (amide) showing increased absorption at 3230 cm^{-1} and a sharp $-\text{C}-\text{O}-$ absorption peak at 1169 cm^{-1} consistent with further oxidation.

The important point to make from the composite aging perspective is that only the very surface of the unpainted composite has been changed chemically. The paint has protected the other side of the composite from any noticeable changes. Almost the exact chemical changes seen on the BMS-8-212 composite after 20 years in service were seen on the 8552/IM7 composite after accelerated aging at 120°C for approximately 3000 h.⁶ This chemistry was in considerable contrast to our studies of the same composite at higher temperatures and our 45, 65, and

85% relative humidity conditioning studies (at 70°C for up to 7500 h).⁷

Composite physical changes

Previous DMA of composite samples from the Boeing stabilizer skin showed a noticeable drop in the T_g value ($\sim 10^\circ\text{C}$) versus that of the control, although the value remained well above the service temperatures encountered.² This testing was done on a full-thickness sample, and so this was an average value. As we were interested in the long-term aging changes to the different sections of the composite, the samples were split into two-layer sections, one from the unpainted surface and another from the central areas of the composite. These were tested separately by the standard DMA method, as shown in Figure 5 for the 1-Hz test results. Previous work has shown that most aerospace composites show either a drop in the $\tan \delta$ peak with moisture absorption or sometimes multiple peaks; this depends on the test frequency.^{11,12}

At all frequencies, the DMA plots showed small but significant changes in the $\tan \delta$ peak position at the surfaces of the composite versus that of the center. This change in $\tan \delta$ may be due to oxidation stiffening of the surface layers; however, the change is small because such a thin layer has been affected. The 100-Hz plot showed a much broader and flatter peak at the surface, which may indicate a start of the double peak often shown in high-humidity-aged samples.^{11,12}

Another common result of accelerated aging testing of composites under high-humidity and spiking conditions that is also thought to occur in real environmental situations is surface microcracking.^{10,11,13} A microscopic examination of the unpainted surface

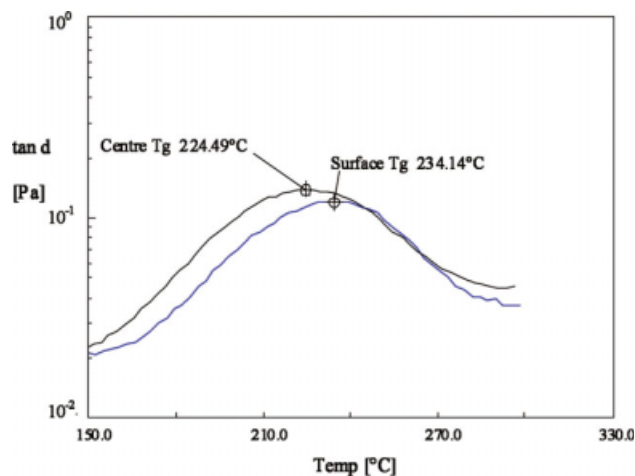


Figure 5 DMA of the surface and central areas of the composite at 1 Hz. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

did not reveal any cracking in the Boeing 737-200 samples.

CONCLUSIONS

The chemical and physical analysis of the Boeing 737-200 samples indicates that aging changes to the composite after more than 20 years in service are chemically detectable but are very minor and are confined to the immediate surface of the unpainted areas of the composite.

The chemical changes seen in these commercial samples are most similar to changes in related composite samples isothermally aged at 120°C for 1 year, but the analyses also point out striking differences. One of these is the absorption of aliphatic hydrocarbons onto the surface; the other is a loss of what appears to be a $-\text{SO}_2-$ -containing compound (most likely a DDS-derived residue). Another unexpected finding of this work is the detection of a significant increase in the composite T_g value at the surface of the material versus the center, where normally a drop in T_g due to moisture plasticization would be expected. However, molecular chain stiffening caused by surface oxidation is likely the reason.

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