

STUDIES ON THE DURABILITY OF POLYMERIC MATERIALS FOR HIGH PERFORMANCE COMPOSITES *

Michael A. Grayson
 Sr. Principal Technical Specialist
 McDonnell Douglas Aerospace Corporation
 St Louis MO 63166 USA

Introduction

Overview

The durability of a material and its aging behavior are complementary aspects of the same problem. This is apparent if we consider the following definitions of durability and aging:

Durability: The ability of a material to survive the use-environment unchanged

Aging: The changes in a material from exposure to the use-environment.

As organic resin matrix composites are used for more parts and more critical applications in aerospace vehicles, it is imperative that we develop a better understanding of how such materials age, how durability is affected by aging and how we can safely and accurately accelerate aging.

In this work, a variety of analytical tools were applied to study the effect of the use-environment on a cyanate ester thermoset resin at the macroscopic, microscopic and molecular levels. These tools provide useful insights into both the physical and chemical aspects of aging in polymeric materials.

Experimental Approach

Every material is exposed to a complex variety of environmental stress factors during its lifetime in the use-environment. The complexity of the problem of aging in high performance aerospace matrix resins precludes the application of any one analytical technique to provide all of the answers. It is also crucial that any study be performed in such a way that the effect of each individual environmental stress factor can be studied independently. Later, combinations of environmental stress factors can be used to determine combined effects and discover any synergies that may critically influence long-term

durability of the material in question. This is a slow and tedious process, but the only way that one can obtain reliable data on the effects of aging on a material system.

Analytical tools In this work, vaporization/gas chromatography (Vap/GC) was used to characterize the indigenous volatile compounds remaining in the cured laminate and provide information on the cure state of the resin matrix. Thermogravimetric analysis (TGA) in both inert and oxidative environments was used to obtain information about the thermal and thermo-oxidative degradation of the laminate material. In particular, this tool permits calculation of kinetic parameters to determine reaction rates and, when combined with the kinetic map ⁽¹⁾, estimate the lifetime of a material system in a specific use-environment. Evolved gas analysis mass spectrometry (EGAMS) was used as an independent means to determine indigenous volatile compounds and also to investigate thermal degradation mechanisms. Dynamic mechanical analysis (DMA) was used to measure the softening point and glass transition temperature.

Material system As an example of this approach to the study of durability in organic matrix resin materials, data will be reported on the Dow cyanate ester resin XU71787.09L on G40-800 carbon fiber. Sixteen-ply quasi-isotropic laminates were fabricated from prepreg according to the processing schedule recommended by the vendor. Specimens of appropriate shape were cut for baseline measurements and the remaining material aged up to 5000 hours in air at various temperatures. In the case of Vap/GC, TGA, and EGAMS, the sample was in the form of a fine powder milled from the laminate. In the case of DMA, samples were in the form of small 16-ply quasi-isotropic laminate specimens, typically 13 by 40 mm.

Experimental Results

Thermogravimetric Analysis Laminate powder samples on the order of 10 mg were

analyzed by TGA in nitrogen to determine the onset of thermal degradation and the char remaining. A typical result from this experiment is shown in Figure 1 where the weight loss (Wt%) and derivative weight loss (Wt%/min) are shown as a function of temperature for a linear heating rate of 10°C/min.

The onset of weight loss for this material system is around 250°C. This is a higher temperature than observed in most epoxy resins, but lower than observed in other high performance resins. The char remaining at the end of the run is on the order of 78 Wt%. Thus, approximately 55% of the resin degrades to volatile products in an inert environment. This is typical for most thermosetting resin systems.

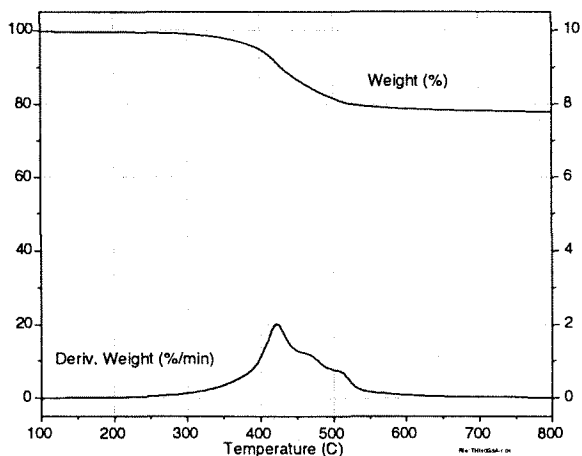


FIGURE 1 Weight loss from cyanate ester laminate powder during heating at 10°C/min in nitrogen

It is apparent from the shape of the derivative weight loss peak that the thermal degradation mechanism consists of a series of competing reactions as the sample is heated. Under these circumstances, it is impossible to use the data from the TGA experiment to compute kinetic parameters. Other, more sophisticated approaches, such as that proposed by Westall and Pidduck⁽²⁾ may be used to calculate kinetic data for individual degradation reactions if necessary.

A second set of TGA experiments was performed using air as the purge gas. As can be seen in Figure 2, the presence of oxygen during the TGA experiment has a dramatic effect on the weight loss behavior of this material system. In particular, note that at the end of the run, the sample mass has been reduced to zero; thus, both the resin and the fiber are oxidized away during the TGA experiment. Note in the derivative weight loss curve the appearance of several peaks. Each peak signals a maximum in the reaction rate during the TGA experiment. The data in Figure 2 indicates that there are at least three reactions associated

with the resin and two reactions associated with the fiber in the

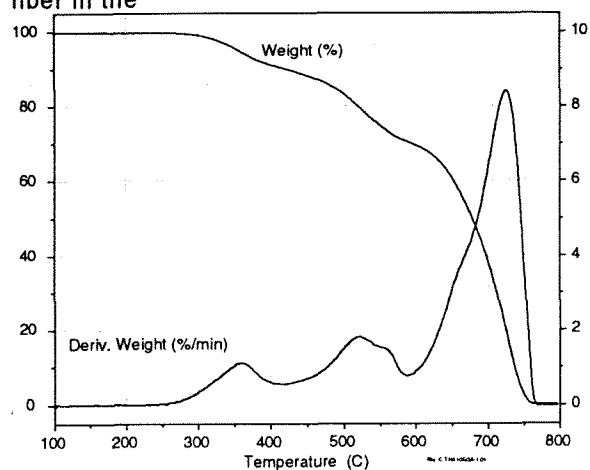


FIGURE 2 Weight loss in cyanate ester laminate during heating at 10°C/min in air.

thermo-oxidative degradation of this laminate.

The weight loss data can also provide us with an estimate of the resin content. It can be determined by measuring the weight loss at the minimum in the derivative weight loss curve prior to the onset of fiber degradation. Thus, for this system, the resin content is on the order of 36 Wt%. This is lower than other methods measure, suggesting that some of the resin degradation may actually be occurring on the low temperature side of the fiber degradation.

The shape of the lowest temperature derivative weight loss peak indicates that only one reaction is occurring during this thermo-oxidative degradation process. In most instances, the lowest temperature reaction in the TGA experiment is also the reaction that is most likely to affect the material in the use-environment. If we assume a first order reaction rate, the analysis proposed by Westall and Pidduck⁽²⁾ can be used to calculate kinetic parameters. This analysis requires that several different TGA experiments be performed over a range of heating rates. In our case, heating rates (M) of 1, 2, 3, 4, 6, 8, 10, and 12°C/min were used. The temperature (T_{max}) at which the first peak in the derivative weight loss curve occurs was determined for each heating rate and used to construct a plot of $\ln[M/T_{max}^2]$ vs $1/T_{max}$. The slope (m) of a line fit to these points is used to calculate the apparent activation energy for the reaction (E_a) according to Equation 1:

$$E_a = -mR \quad (1)$$

where R is the universal gas constant. The intercept (b) can be used to determine the

frequency factor or pre-exponential factor (K_0) according to Equation 2:

$$K_0 = -me^b \quad (2)$$

Thus, the kinetic parameters necessary to compute the reaction rate (r) at various temperatures can be used with the Arrhenius equation (Equation 3) to determine weight loss rates in the use-environment at various temperatures (T):

$$r = K_0 e^{(-E_a/RT)} \quad (3)$$

Generally speaking, reactions that have high apparent activation energies and low frequency factors are indicative of more stable polymeric materials. In order to portray this relationship and develop a means of extrapolating this result to the use-environment, we developed the concept of the kinetic map in 1991⁽¹⁾. Using this concept, the kinetic parameters for the primary reaction of the matrix resin (box) are compared with those for the aging limit-line defined by a specific reaction conversion (1%) at the upper limit of the use-environment (dashed lines). In Figure 3, the kinetic parameters determined for the cyanate ester resin are shown along with aging limit-lines for a use-environment of 10,000 hours at 150°C (250°F) and room temperature.

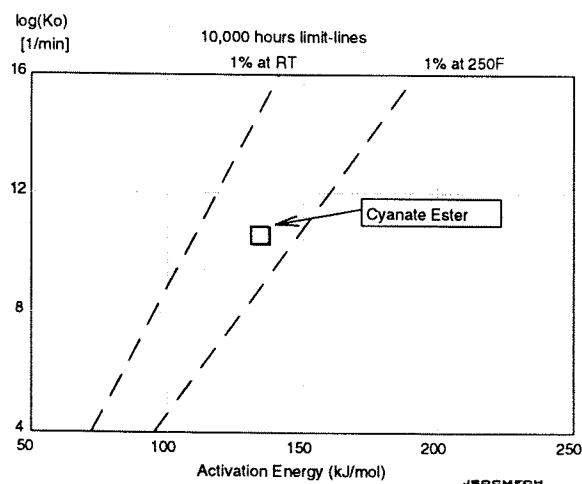


FIGURE 3. Kinetic parameters for the primary thermo-oxidative degradation reaction in XU71781.09L cyanate ester

The fact that the kinetic parameters measured in the TGA experiment fall to the left of the upper aging limit-line indicates that the resin will undergo more than 1% reaction conversion if the material were held at 150°C for 10,000 hours. If we accept this criterion as a limit for the amount of resin degradation that is acceptable, we must conclude that this material system cannot provide the necessary thermo-oxidative stability to withstand

the rigors of the anticipated use-environment. Thus, the kinetic map provides a convenient and useful means to rapidly determine whether or not a material might withstand the harshest use-environment. The fact that the kinetic parameters for the primary thermo-oxidative degradation reaction fall to the right of the room temperature limit-line indicates that the material is thermo-oxidatively stable at room temperature for very long times; much greater than 10,000 hours. Based on the results of the TGA experiment and kinetic map analysis, this material system, while better than epoxy thermoset resins thermo-oxidatively, is not sufficiently robust to withstand the anticipated use-environment.

Vaporization/gas chromatography In this technique the inlet of the chromatograph is modified to accept a sample desorption apparatus (Figure 4). Several milligrams of powder milled from the laminate are loaded into a clean quartz tube approximately 6mm in diameter. After the tube is inserted into the sampling apparatus, it is heated while a helium purge gas flows over the sample. Volatile compounds desorbed during the heating period are cryogenically trapped at liquid nitrogen temperatures

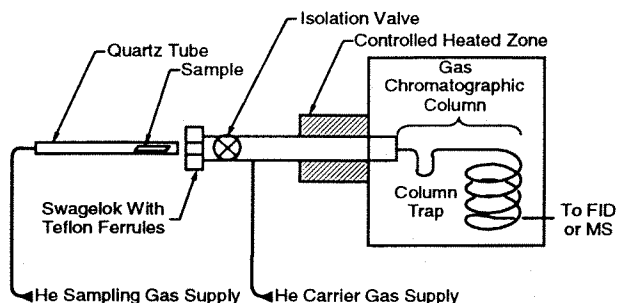


Figure 4. Block Diagram of Vaporization GC Sampling System

in a small bore diameter tube connected to the sampling apparatus. After a specific heating period, the sample tube is removed from the purge gas stream and cooled while the gas flow through the cryogenic trap and chromatographic column stabilizes. Subsequently, the chromatographic oven is temperature programmed according to standard practice for the column type and phase, permitting separation of the mixture of compounds that were desorbed during the heating period.

A typical result from this experiment is shown in Figure 4 where the compounds desorbed from the cyanate ester laminate powder are shown after heating for 20 minutes at 150°C (lower trace) and a subsequent heat for 20 minutes at 250°C (upper trace). The temperature selected for the first heat

of the sample is the absolute upper temperature in the use-environment and the temperature for the second heat is the processing temperature. Note that only a small amount of volatile material is evolved from the laminate powder at the use-temperature. However, when the sample is

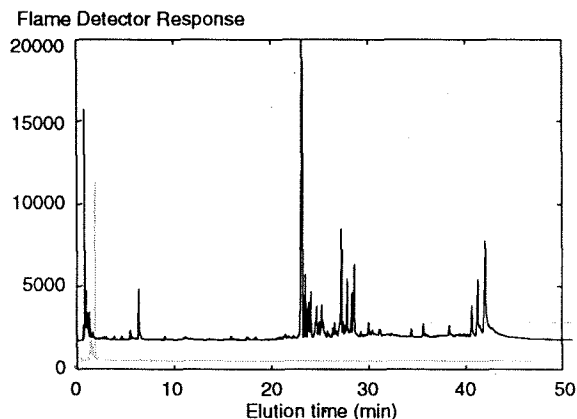


FIGURE 4. Volatile compounds desorbed from cyanate ester laminate powder at two different desorption temperatures

reheated to the processing temperature, a complex mixture of materials is evolved; indicating that the cure reaction did not go to completion during processing. This is a common observation with thermosetting resins and has been reported in our work in the past.^(3,4) Other results discussed below support this conclusion.

Evolved Gas Analysis Mass Spectrometry In this technique, sub-milligram quantities of laminate powder are heated from 200°C to 500°C at 20°C/min with the solids probe of the mass spectrometer. The compounds that are evolved from the sample are ionized and mass analyzed immediately. Mass spectra are recorded continuously during sample heating over the mass range of 10 to 1000 daltons at the rate of 20 seconds per mass decade.

Initially, Indigenous volatile compounds are desorbed from the sample prior to the onset of thermal degradation. At higher temperatures, the polymer chain begins to degrade and volatile products from that process are evolved. A typical result from EGAMS of the carbon fiber/cyanate ester laminate is shown in Figure 5.

Note that this experiment is carried out in a vacuum, but the evolution profile is similar to the derivative weight loss curve for this material heated in nitrogen as shown in Figure 1. Mass spectra were acquired at approximately 5°C intervals during heating of the sample, so information regarding the mixture of compounds

evolved can be obtained by examining mass spectra in the vicinity of 300°C. Spectra taken immediately following degradation onset show that a compound with a mass of 320 daltons dominates the degradation products. Separate EGAMS

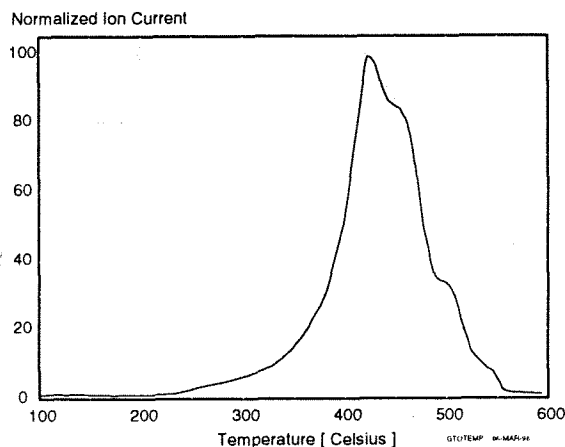
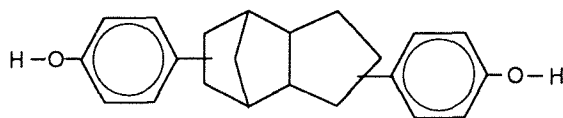


FIGURE 5. Total ion current profile showing evolution of compounds during EGAMS of laminate powder from carbon fiber/cyanate ester

experiments were performed at higher resolving power to determine the mass of this compound to be 320.178 daltons within ± 3 parts per million. From this information, only a limited number of compounds can have an elemental composition with this exact mass. The best elemental composition consistent with the data and knowledge of the chemical structure^[5] of the resin is $C_{22}H_{24}O_2$. The suggested structure for this degradation product is:



This compound is the portion of the polymer chain between tricyanurate rings in the cured cyanate ester resin. It is the most abundant compound in the thermal degradation of the resin through 500°C (See Figure 6). The formation of this compound suggests that the polymer molecule undergoes an unzipping reaction in which the bond between the ether linkage and tricyanurate ring is cleaved, and a hydrogen atom is abstracted from the nearest phenyl group. Such a mechanism would predict that the mechanical properties of the resin will decrease rapidly with aging/weight loss since the degradation mechanism attacks the main chain of the polymer.

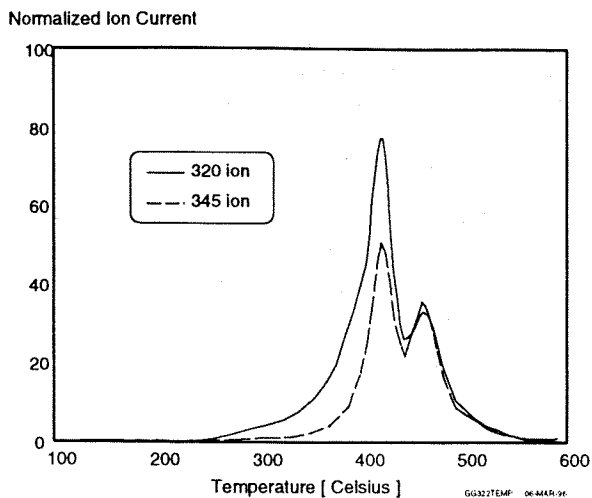
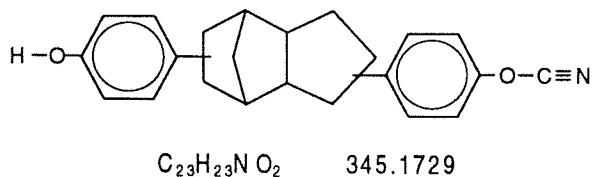


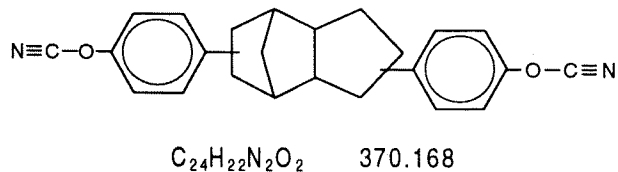
Figure 6. Reconstructed ion current profiles showing the evolution of two important ions in the thermal degradation of cyanate ester resin.

In addition to the 320 dalton ion, there is also an abundant ion with a mass of 345 daltons. A similar experiment was performed as for the 320 ion to obtain an accurate mass of 345.173. A plausible structure for this degradation product is the nitrogen containing compound:



This material is similar to the compound at mass 320 except that one of the hydroxy groups on the phenyl terminus has been replaced by a cyanate group. It would appear that this compound arises from portions of the polymer molecule in which one end of the monomer is sterically constrained so that it cannot react with another cyanate group. During heating, the phenyl-ether-tricyanurate bond cleaves and hydrogen abstraction occurs to form the compound shown above.

As a point of reference, the monomer for this cyanate ester system is shown below.



It is apparent that both of the major thermal degradation products that arise from the polymer chain are generated by the same basic mechanism. The product evolved at mass 320 probably has a greater effect on the macroscopic

properties of the resin since it represents loss of an intra-network link in the polymer. Consequently, small weight losses could lead to significant changes in the mechanical properties.

Dynamic Mechanical Analysis Small 24-ply laminate samples with dimensions of 10 by 40 mm were used for dynamic mechanical analysis (DMA). The measurements were performed with a TA Instruments Model 983 operating in the resonant frequency mode. Typical sample displacement was 0.3 mm. The results from a baseline unaged laminate are shown in Figure 7.

The flexural storage modulus decreases slowly with temperature until about 230°C at which point it begins to drop off rapidly, indicating softening of the matrix resin. At the highest temperature in the experiment, the flexural storage modulus is nearly zero.

Frequently, the peak in the flexural loss modulus is used as a measure of the glass transition temperature of a polymeric material. In the case of this cyanate ester, the loss modulus peak is actually several ill-resolved peaks (See dashed line in Figure 7.).

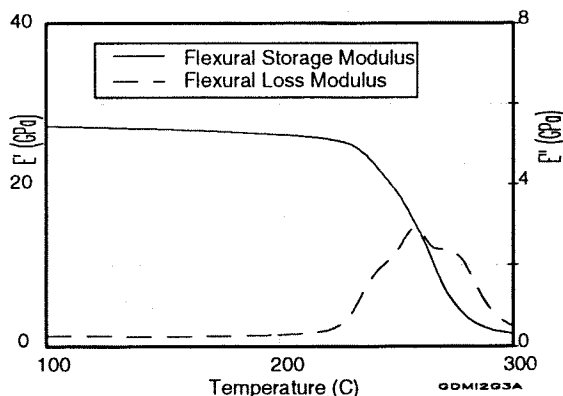


Figure 7. Flexural storage (solid line) and loss (dashed line) moduli from dynamic mechanical analysis of G40-800/XU71787 laminate unaged.

The small shoulder on the low temperature side of the loss modulus peak is interpreted to indicate that some of the resin did not fully react during the recommended cure procedure. The central peak represents the glass transition temperature of the baseline polymer. The small shoulder on the high temperature side of the loss modulus peak is interpreted as further reaction of the cyanate ester as the sample is heated past the glass transition temperature. The structure observed in the loss modulus peak of this thermosetting resin is not observed in typical thermoplastic resins. For such systems, a single clean peak is normally recorded for the loss modulus.

Thus, there are three pieces of data that independently indicate that the cyanate ester resin is not fully cured at the end of the recommended cure process: 1) the evolution of volatile compounds at the cure temperature in the Vap/GC experiment;

2) the presence of unreacted cyanate groups in the early thermal degradation products observed in the EGAMS experiment; and 3) the shape of the flexural loss modulus peak in the DMA experiment.

Results from Aged Laminates

Laminate panels of the cyanate ester material system were aged at 149°C and 177°C in an air circulating oven for times up to 5000 hours. In addition, some panels were exposed to accelerated aging conditions for 5000 hours at 204°C in air at ambient pressure. During all aging experiments, panel weight was monitored. In addition, at selected time intervals, some panels were removed and specimens cut from the aged panel for DMA and mechanical measurements.

Weight loss data from the aged panels is shown in Figure 8. Note that as the severity of aging

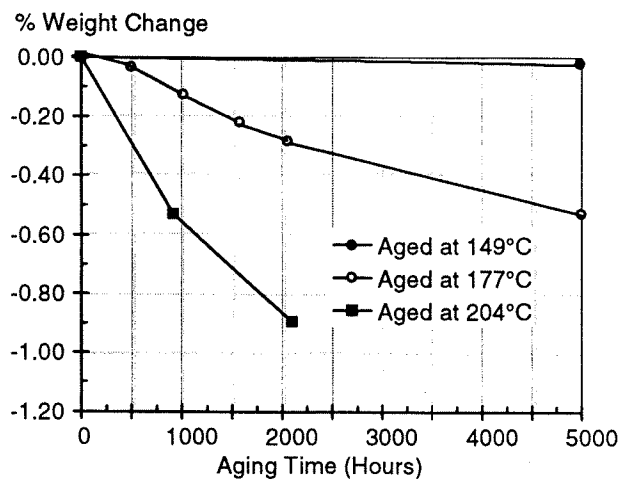


Figure 8. Weight loss in carbon fiber/cyanate ester laminate panels aged in an air oven at various temperatures

increases, the weight loss becomes more dramatic. Note also that, as predicted on the basis of the TGA experiment with an air purge and the kinetic map analysis, this material system loses weight at conditions below the most aggressive use-environment. Recall that the TGA experiments were performed on laminate powder that had been milled from the material with a tungsten carbide end mill; and the air aging weight loss determinations were performed on laminate panels.

Aged samples were tested with each of the analytical techniques discussed above. Only minor changes were observed in the TGA, EGAMS, and Vap/GC experiments. However, each of these experiments used samples in the form of laminate powder. When aged samples were milled, the end mill was drilled into the sample, thus the powder was a mixture of laminate from the surface and from the interior. If aging proceeds from the outer surface to the inner surface as suggested by Nam and Seferis⁽⁶⁾ then the sample preparation technique mixed surface aged laminate with interior unaged laminate. The fact that only small differences between samples were observed is a reflection of this sampling method.

However, dynamic mechanical analysis provided very clear evidence of property changes in the laminate with aging. This can be seen in Figure 9 where $\tan\delta$ is plotted as a function of temperature for laminates from three different aging treatments.

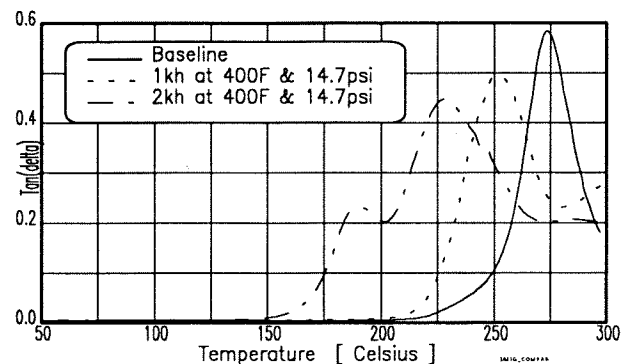


Figure 9. Comparison of $\tan\delta$ as a function of temperature for G40-800/XU71787.09L laminates after various aging treatments

These data indicate that aging of the laminate results in a decrease in the glass transition temperature. The more aggressive the aging, the greater the decrease. For the case shown here, accelerated aging at 204°C results in a drop in the glass transition temperature on the order of 25°C; a significant change for a relatively short aging period. At longer aging times at this temperature, the glass transition temperature continues to decrease and a secondary peak appears on the low temperature side of the major $\tan\delta$ peak. In neat resin materials, this would be interpreted to indicate the appearance of side-chain motion in the polymer network. However, for an anisotropic material, such as a laminate, it is not clear how to interpret this result. In any case, aging of the cyanate ester material system is readily detected with the DMA technique.

A drop-off in glass transition temperature with aging can sometimes signal free volume relaxation or physical aging. Normally, this would account for a small decrease in the glass transition temperature, and would be accompanied by a sharpening of the loss modulus peak. However, the large drop-off in T_g observed in this work and the development of structure in the loss modulus peak indicates that chemical aging is occurring during these aging experiments.

In such a case, the drop-off in glass transition temperature suggests that the aged matrix has either lost some network crosslinks, or that the polymer chain length has decreased. This observation is consistent with the mass spectral data from the EGAMS experiment in which we note that a significant portion of the polymer network is excised during thermal degradation to produce the volatile degradation products described above. In addition, if we assume that cooling the laminate from the initial DMA run would 'reset' physical aging, this would be reflected in a second DMA run by a return of the $\tan\delta$ peak to the shape and location of that observed for the baseline laminate. Such was not observed.

Conclusions

Chemical aging rather than physical aging dominates the changes in mechanical response of this material system. Furthermore, purely thermal degradation controls the aging of this material system. The degradation reaction is mitigated by the presence of oxygen, but there does not appear to be a synergistic effect of oxygen and temperature. This work shows that the use of several different analytical tools provides a means of correlating molecular level changes in the polymer resin with macroscopic changes in the laminate. Such information provides guidelines for the worst case use-environment that a material can withstand over its lifetime. In addition, it provides a basis of comparison with other cyanate ester chemistries⁽⁷⁾ as well as with other material systems.

Acknowledgements

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Paul McClellan obtained panel weight loss data shown in Figure 9.

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