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Viscoelastic Properties of Addition-Cured Polyimides Used in High Temperature Polymer Matrix Composites

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ABSTRACT

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Viscoelastic properties of the addition-cured polyimide, PMR-15, were investigated using dynamic mechanical and stress relaxation tests. For temperatures below the glass transition temperature, T_g , the dynamic mechanical properties measured using a temperature scan rate of 10 °C/min were strongly affected by the presence of absorbed moisture in the resin. Dynamic mechanical properties measured as a function of time during an isothermal hold provided an indication of chemical changes occurring in the resin. For temperatures above ($T_g+20^\circ\text{C}$), the storage modulus increased continuously as a function of time indicating that additional crosslinking is occurring in the resin. Because of these changes in chemical structure, the stress relaxation modulus could not be measured over any useful time interval for temperatures above T_g . For temperatures below T_g , dynamic mechanical properties appeared to be unaffected by chemical changes for times exceeding 1 hr. Since the duration of the stress relaxation tests was less than 1 hr, the stress relaxation modulus could be measured. As long as the moisture content of the resin was less than about 2 percent, stress relaxation curves measured at different temperatures could be superimposed using horizontal shifts along the $\log(\text{time})$ axis with only small shifts along the vertical axis.

KEYWORDS: Dynamic mechanical properties; Matrix, polyimide; Neat resin; Stress relaxation; Test method; Viscoelastic

1. INTRODUCTION

Addition-cured polyimides are used as matrix resins in high temperature polymer matrix composites (PMC's) because of their processability and thermo-oxidative stability. At room temperature, the neat resins have linear stress-strain curves and fail in a brittle manner at strains of about 2 percent. At higher temperatures, the modulus and strength decrease, but the resins retain their linear elastic properties as long as the temperature remains well below the glass transition temperature, T_g . For temperatures approaching T_g , the resins become viscoelastic, and properties become strongly dependent on time and temperature. Composite structures are usually not used at temperatures exceeding $(T_g - 30^\circ\text{C})$. However, even at temperatures below $(T_g - 30^\circ\text{C})$, the viscoelastic nature of the matrix resin results in significant rates of stress relaxation or creep. A major limitation on the performance of high temperature polymer matrix composites in engine applications is the reduction in strength caused by formation of microcracks in the matrix upon thermal cycling (1). Since this type of failure can be viewed as time/temperature dependent stress-rupture within the matrix, the performance of PMC's depends on the viscoelastic properties in addition to thermo-oxidative stability of the matrix resin.

Although the matrix resins are definitely viscoelastic in nature under typical service conditions for high temperature PMC's, little is known about the viscoelastic properties of addition-cured polyimide matrix resins or the effect of viscoelastic properties on the performance of composite structures. The purpose of the present work is to establish test procedures for measuring the viscoelastic properties of addition-cured polyimide resins and to measure the effect of various thermal histories on resin properties. Since extended exposure at high temperatures is required for aging and testing, the effects of both physical aging (i.e., annealing) and changes in chemical structure (e.g. cross-linking) must be considered. In this paper, measurements of the time dependent shear modulus of the addition-cured polyimide, PMR-15, are reported. Procedures are established for handling, storing, and thermal conditioning of the resin prior to testing. Using these procedures, it is possible to obtain reproducible data and to form mastercurves by time/temperature shifting of the data.

2. EXPERIMENTAL PROCEDURES

2.1 Materials PMR-15 molding powder from Dexter Composites was used to mold $(10 \times 10 \times 0.2 \text{ cm}^3)$ sheets. The molding powder was placed in a tight

fitting compression mold, heated at approximately 10 °C/min to 316 °C, and cured at 316 °C for 2 hr. The cured sheets were then postcured for 16 hr at 316 °C in an air circulating oven. Aging of postcured sheets was also done in air circulating ovens.

2.2 Dynamic Mechanical and Stress Relaxation Tests Rheological measurements were obtained using a Rheometrics RMS-800 rheological spectrometer with rectangular testpieces deformed in torsion. Testpieces were 60 mm in length, 5 mm in width, and approximately 2 mm in thickness. They were mounted into the grips leaving a gauge length of 45 mm. The lower grip was rotated to give a zero torque reading on the transducer just prior to testing. Storage and loss moduli were measured as a function of temperature using a frequency of 1 Hz, a strain amplitude of 0.2 percent, and a temperature ramp of 10 °C/min. During these variable temperature tests, the autotension feature of the RMS-800 was used to maintain a constant normal force by increasing the clamp separation to account for thermal expansion. For stress relaxation tests, the sample was heated rapidly to the test temperature then held at the test temperature for 30 min prior to testing. During the 30 min conditioning period, the grip separation was adjusted to maintain a zero normal force. However, during the stress relaxation test the grips were maintained at a constant separation. The testpiece was deformed to a strain of 0.2 percent over a time interval of less than 0.1 sec, and stress relaxation was measured over a time interval of 2×10^3 sec.

3. RESULTS AND DISCUSSION

3.1 Dynamic Mechanical Properties The dynamic mechanical properties of viscoelastic solids are usually expressed in the form of a storage modulus, G' , and a loss modulus, G'' . G' is the elastic component of the complex modulus, while G'' is the viscous component. The ratio, G''/G' , is equal to the tangent of the phase difference, δ , between the applied sinusoidal strain and the measured sinusoidal stress. The magnitude of $\tan(\delta)$ is sometimes used in place of G'' to represent the viscous component of the modulus. In Figure 1, G' and $\tan(\delta)$ curves are shown for PMR-15 resins containing different amounts of moisture. The sample used to obtain the solid curves was dried in an oven at 120 °C for 150 hr to reduce the moisture content to less than a few tenths of a percent. The sample used to obtain the dashed curves was saturated with about 3.0 percent moisture by suspending it above refluxing water for 80 hr. For comparison, samples left exposed to ambient conditions in the laboratory equilibrate at about 2.0 to 2.2 percent moisture. The glass transition temperature, T_g , is measured by drawing tangents to the G' curve, as shown

in Figure 1. In a separate study it was found that the magnitude of T_g measured in this way is equal to T_g measured by thermo-mechanical analysis (TMA) within ± 5 °C. In Figure 1, the effect of moisture is to decrease T_g from 362 to 349 °C. However, the effect may actually be greater because some of the moisture is lost during the ramp up to T_g . At temperatures above 430 °C, the G' curves converge, indicating that all of the moisture has probably desorbed. The relatively rapid decrease in G' at $T > 410$ °C, is accompanied by resin weight loss. Although the resin is degrading at $T > 410$ °C, G' begins to increase at $T > 430$ °C. Samples which are retested after exposure to temperatures greater than 430 °C show a large increase in T_g , and an increase in the temperature at which the minimum in the G' curve occurs. This type of behavior has been observed for other addition-cured polyimides tested in our labs. One explanation for these results is that radicals are generated when small fragments of the polymer are released. The radicals then induce further crosslinking, and T_g is increased. Another possible explanation is that the resin is not completely reacted even after postcure. As the test temperature increases beyond T_g , further crosslinking occurs as a result of an increase in molecular mobility. Further information is needed about chemical reactions which occur at high temperatures before changes in viscoelastic properties can be related to changes in chemical structure.

For polymers, stress relaxation or creep curves measured at different temperatures can often be superimposed to form mastercurves which represent the properties over a much larger time scale than the original test interval (2). For addition-cured polyimides, chemical changes which occur during high temperature testing place a limitation on the time and temperature intervals over which this time/temperature superposition can be applied. This limitation is shown in the data of Figure 2. In this figure, changes in G' are shown as the temperature is increased at 10 °C/min then held at a constant temperature above T_g ($T_g = 362$ °C). G' remains nearly constant during the isothermal hold at 371 °C. However, G' increases gradually during the isothermal hold at 384 °C. Since, properties are not constant over any reasonable time interval when $T > T_g + 20$ °C, time/temperature superposition can not be used in this temperature range.

The $\tan(\delta)$ curves in Figure 1 have maxima at about 100 °C. Although the molecular motions associated with this maximum are not known, it is clear that moisture has a large effect on the shape of the $\tan(\delta)$ curve for temperatures between the peak at 100 °C (β peak) and the peak associated

with the glass transition (α peak). Struik (2) has referred to this temperature interval as the "aging range." A resin quenched from above T_g into the aging range is in a nonequilibrium state with excess volume. When held at constant temperature, the volume slowly decreases toward its equilibrium value. This sub- T_g volume relaxation is called physical aging. From Figure 1 it is clear that the presence of moisture can have a large effect on the rate of physical aging and on properties such as creep and stress relaxation which depend on the extent of physical aging.

3.2 Stress Relaxation Test Results In order to obtain reproducible stress relaxation data, it was necessary to condition testpieces at the test temperature for 30 min prior to testing. During the 30 min hold, the grip separation was adjusted to keep the normal force close to zero. Changes in the normal force occurred as a result of thermal expansion of the sample, thermal expansion of the test fixtures, and volume changes associated with desorption of water. Different testpieces behaved differently. But it was found that further changes in the normal force were small after the 30 min isothermal hold, and data were reproducible. In some cases testpieces would warp slightly during the 30 min isothermal hold. When this occurred, the clamps were rotated to obtain a zero torque reading before the strain was applied. For lower temperature polymers, warping and internal stresses can be eliminated by a short thermal treatment at $T > T_g$. However, the data of Figure 2 indicate that this type of thermal treatment can not be used for high temperature resins without inducing undesired changes in chemical structure.

The effect of moisture on the stress relaxation modulus, $G(t)$, of PMR-15 resin measured at 288 °C is shown in Figure 3. As mentioned earlier, the sample stored at room temperature contains about 2 percent absorbed moisture. This level of moisture has only a small effect on $G(t)$. The sample saturated with moisture at 100 °C contains about 3 percent moisture. The additional 1 percent of moisture causes a significant decrease in $G(t)$. If the water were acting simply as a plasticizer, a much larger effect would be expected at 2 percent moisture. Nuclear magnetic resonance (NMR) measurements and dielectric measurements on a condensation polyimide similar to PMR-15 have shown that absorbed water molecules can occupy two different sites in thick polyimide films (3). Some molecules are weakly bound to the polymer and occupy sites between the polymer chains. Other molecules exist in clusters which are at most loosely bound to the polymer. The effect of moisture on rheological properties would depend on which sites are occupied by the water molecules. Another possible explanation for the effect of moisture on $G(t)$ is that small

amounts of moisture can desorb during the 30 min conditioning period while larger amounts can not. Data for moisture desorption in an air circulating oven at 288 °C (550 °F) are shown in Figure 4. The initial moisture content of 4 percent was obtained by allowing the samples to reach equilibrium at room temperature and 100 percent relative humidity. After about 30 to 40 min at 288 °C, nearly all of the water has desorbed. Although little moisture remains after 30 min at 288 °C, the stress relaxation curves measured at 288 °C indicate that moisture can still have a significant effect on $G(t)$. It is clear that further studies are needed on the kinetics of moisture absorption and desorption in addition-cured polyimides and the effect of moisture on viscoelastic properties. This work is currently in progress.

Before the importance of moisture was recognized, a series of stress relaxation curves were measured at various test temperatures on samples which had been stored under ambient laboratory conditions. Results are shown in Figure 5. Data are plotted in log-log form so that time/temperature superposition can be applied. A small vertical shift is required in addition to the horizontal shift along the $\log(t)$ axis in order to form the mastercurve. The mastercurve is shown in Figure 6 along with the log of the horizontal shift factor, $\log(a_h)$, and the vertical shift factor, $\log(a_v)$. The arrows in Figure 6 indicate the maximum deviation from the mastercurve, which occurred for the test conducted at 324 °C. The conditions under which time/temperature superposition apply have been discussed by Struik (2). One requirement is that the aging time must be much greater than the test interval. This assures that additional aging during the test is insignificant, and that the mastercurve represents the "momentary" stress relaxation curve for a given aging condition. The samples used to obtain the data of Figures 5 and 6 have been postcured for 16 hr at 316 °C. Since this temperature is below T_g ($T_g=360$ °C), the postcure time can be considered to be the aging time. The test interval is then much shorter than the aging time. Preliminary results have indicated that data from samples aged for longer times and from samples postcured at higher temperatures can be superimposed on the mastercurve of Figure 6. However, additional crosslinking is likely to occur under these conditions. For lower temperature polymers, crosslinking has been shown to retard relaxation times and cause a shift in creep compliance data on the $\log(t)$ axis which is similar to the shift which would occur upon physical aging (2). If a similar effect occurs for high temperature resins, it will be difficult to separate the effects of physical aging and chemical changes on viscoelastic properties.

The data of Figure 3 indicate that the 2 percent moisture content of samples used to obtain the mastercurve of Figure 6 should have only a small effect on the data. However, these results are being repeated on dry resin samples. The following procedures are being used to obtain testpieces with nearly zero moisture content. All cutting or machining of resin samples is done after curing but before postcuring. After postcuring, samples are placed directly into a dessicator to cool. The dry weights of the samples are then measured, and the samples are returned to the dessicator. Since the completely dry resin absorbs moisture quickly, the samples are allowed to be outside of the dessicator for only the minimum time required for weighing. Samples are weighed again prior to the stress relaxation measurements to verify that no moisture has been absorbed. Weight loss during each stress relaxation test is also recorded. In addition to these studies, the kinetics of moisture absorption and desorption is also being studied in more detail.

4. CONCLUSIONS

Addition-cured polyimides show significant rates of stress relaxation for test temperatures and times characteristic of service conditions for high temperature PMC's. For temperatures below T_g , time/temperature superposition can be used to represent the stress relaxation modulus over more than 10^6 sec on a reduced time scale. Time/temperature superposition can not be used for temperatures above T_g because the chemical structure of the resin changes over the time scale of a stress relaxation test. Absorbed moisture in excess of 2 percent causes a significant reduction in the stress relaxation modulus. Further studies are needed to determine the effect of viscoelastic properties on the performance of high temperature PMC's during long term aging and thermal cycling.

5. REFERENCES

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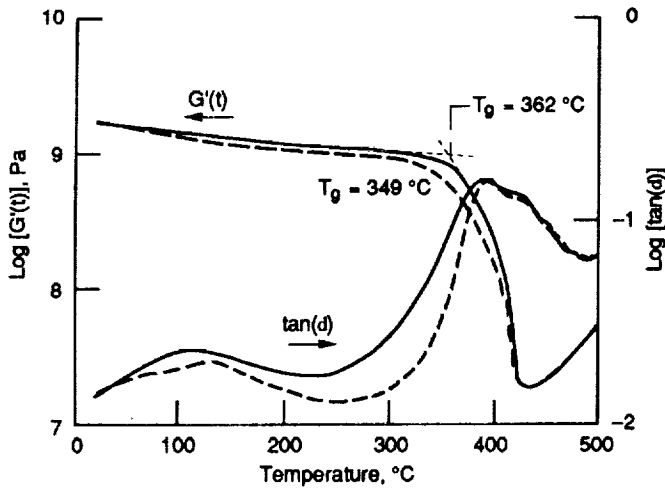


Figure 1.—Dynamic mechanical properties of PMR-15 neat resin. Solid line is for sample dried at 120 °C for 150 hours. Dashed line is for sample saturated with moisture at 100 °C and 100% relative humidity.

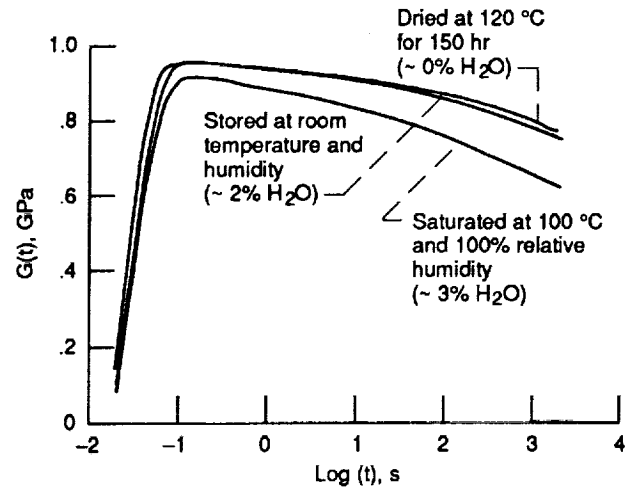


Figure 3.—Stress relaxation curves at 288 °C for PMR-15 neat resin samples conditioned in different ways to obtain various concentrations of H₂O.

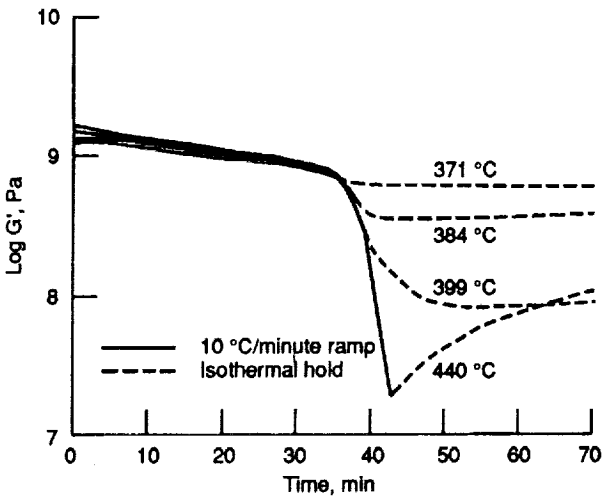


Figure 2.—Dynamic mechanical properties of PMR-15 neat resin using a constant temperature scan rate followed by an isothermal hold. Solid lines were measured at a scan rate of 10 °C/minute. Dashed lines were measured during isothermal holds at the temperatures indicated.

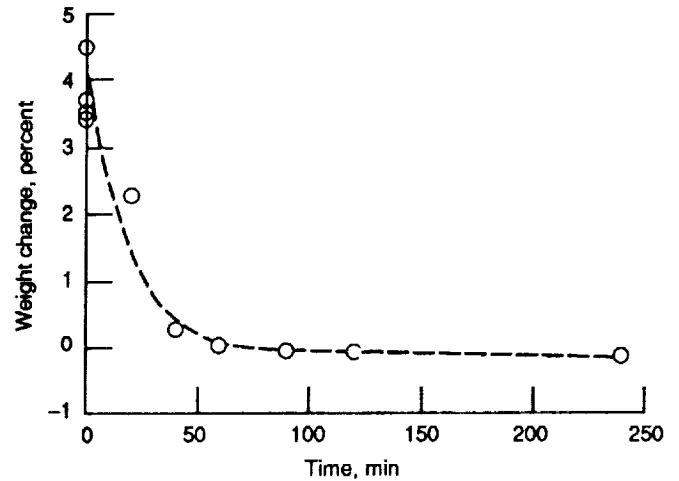


Figure 4.—Desorption of H₂O from PMR-15 neat resin samples at 288 °C.

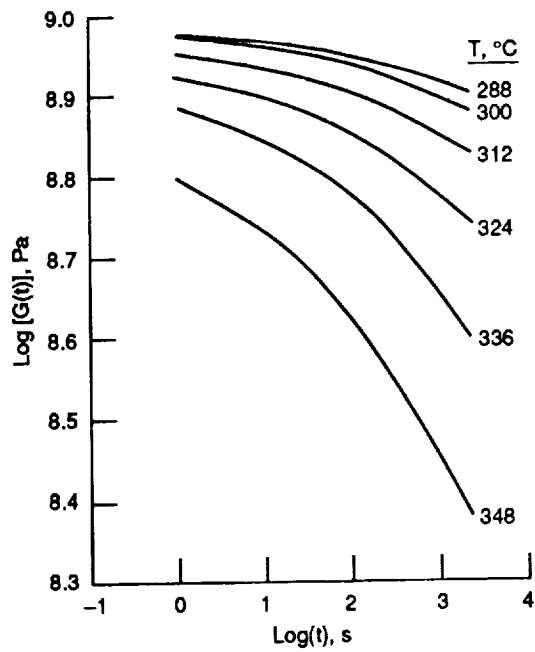


Figure 5.—Stress relaxation modulus of PMR-15 neat resin samples tested at various temperatures.

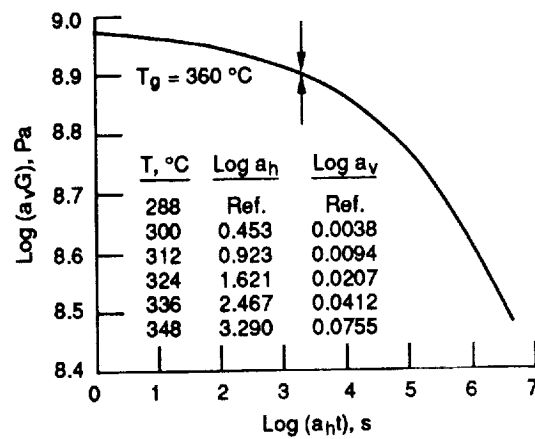


Figure 6.—Mastercurve obtained by horizontal and vertical shifting of curves in Figure 5. The reference temperature is 288 °C, and shift factors are indicated for data obtained at other test temperatures. Arrows indicate maximum deviation of data from the mastercurve.



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