Dynamic Mechanical Analysis of Curing in Polymer Composites

The application of the Rheovibron to the study of dynamic mechanical properties during cure of fiber-reinforced polymer composites is described. Composite rods containing a mechanically inert support wire permit flexural measurements to be made throughout the curing cycle. Measurement of the loss tangent and dynamic storage and loss moduli of a graphite–epoxy prepreg between −25° and 275°C reveals three rheological changes related to flow of the prepolymer, curing, and the glass-to-rubber transition of the cured composite. These results demonstrate that the Rheovibron technique can provide a sensitive measure of the physical state of a curing system and aid in quality control and processing of fibrous reinforced composite materials.

INTRODUCTION

The curing of thermosetting polymer composites involves a complex series of chemorheological changes as the low molecular weight prepolymer is transformed to a highly crosslinked network. Techniques for monitoring the curing process include those which are primarily sensitive to the chemical reactions taking place such as calorimetry and infrared spectroscopy or those related directly to the rheological changes occurring. These include torsional braid analysis,[1–5] dynamic spring analysis,[6] dielectrometry,[7,8] thermomechanical analysis,[9,10] and dynamic mechanical spectroscopy.[11] The objective of this study is to describe a modification of the Rheovibron technique to characterize the rheological properties during cure of fiber-reinforced prepreg materials.

EXPERIMENTAL

Hercules 3501/AS-5 graphite epoxy prepreg was obtained as a unidirectional tape containing 43% by weight resin. Dynamic mechanical measurements were conducted at 110 Hz in dry N_2 using the Rheovibron DDV-II-C (Toyo Baldwin Co. Ltd.). The Rheovibron applies a sinusoidal tensile strain at one end of the sample and the stress response is monitored at the other end. The value of the dynamic modulus $|E^*|$ can be calculated from the dynamic force, while the tangent of the phase angle ($\tan \delta$) between stress and strain is read directly from the instrument. The storage modulus E' and loss modulus E'' can then be calculated from $|E^*|$ and δ by the following relations:

$$E' = |E^*| \cos \delta \tag{1}$$

$$E'' = |E^*| \sin \delta \tag{2}$$

A modification in sample geometry was required to measure the mechanical properties of composite prepregs over the entire cure cycle. Measurements in tension cannot be made parallel to the fiber axis because of the high modulus of the graphite fiber reinforcement. On the other hand, measurements perpendicular to the fiber axis are not possible as a result of the low modulus of the polymer matrix during the flow stage of curing. These problems have been overcome by adopting a flexural sample geometry. The application of flexural geometry in Rheovibron measurements has been discussed by Massa and co-workers[12,13] and has been recently used in studying environmental effects on the mechanical properties of cured graphite–epoxy composites.[14] They show that modulus values obtained in flexure are in good agreement with tensile measurements also made on the Rheovibron. The present study extends these measurements to the entire curing cycle by introducing an inert elastic support core to the center of the flexural specimen.

A schematic of the flexural sample assembly is shown in Figure 1. A modification of the previously derived expression[12] for calculating the dynamic modulus E^* using flexural geometry with the Rheovibron is also given. Flexure specimens were prepared by tightly rolling prepreg tape onto a 0.0772-cm-diameter tungsten support rod with the graphite fibers parallel to the length of the support. Uniform diameter and close packing were accomplished by rolling the specimen between flat metal surfaces. It is possible to remain within the load limits of the DDV-II-C instrument throughout the curing cycle using the above diameter tungsten support rod and a total specimen diameter of less than 2 mm. Measurements were taken every few degrees between −30° and 275°C using a controlled temperature scan rate of 1.5°C/min.

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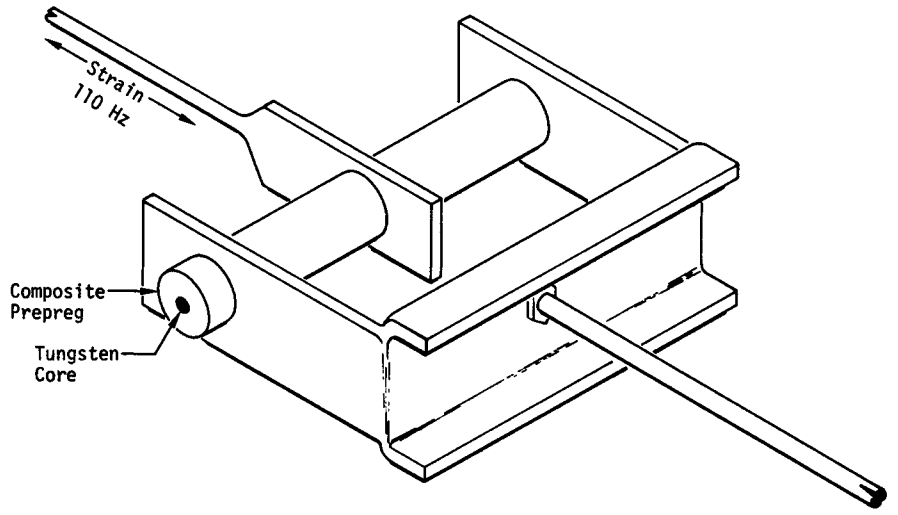

Fig. 1. Schematic representation of the Rheovibron flexural sample assembly where the equation derived to calculate the complex dynamic bending modulus is:

$$|E^*|_{\text{prepreg}} = \frac{4L^3}{3\pi[d_{\text{total}}^4 - d_{\text{core}}^4]} \frac{2 \times 10^9}{D_{\text{prepreg}} - D_0} \text{ dyn/cm}^2,$$

where L = sample length (= 3.25 cm), d_{total} = diameter of sample (= 0.190 cm), d_{core} = diameter of tungsten core (= 0.0772 cm), D = potentiometer reading inversely proportional to dynamic force (0–1000 units),

$$D_{\text{prepreg}} = \frac{D_{\text{total}} \times D_{\text{core}}}{D_{\text{core}} - D_{\text{total}}}$$

D_{core} = 236 independent of temperature, and D_0 = correction for mechanical compliance in instrument (= 32 units).

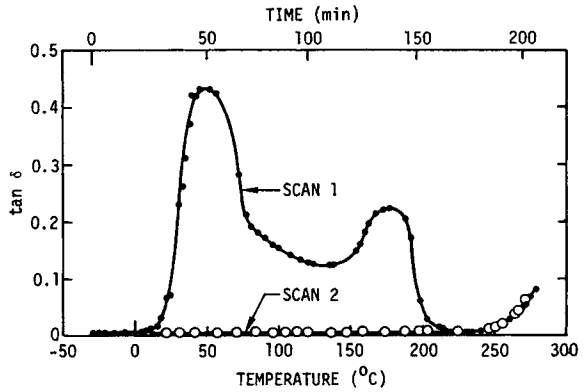

Fig. 2. Variation in loss tangent with temperature during the cure of 3501/AS-5 (scan 1) and after curing (scan 2).

RESULTS AND DISCUSSION

The variation of loss tangent (tan δ) with temperature is shown for two successive thermal scans of 3501/AS-5 composite in Figure 2. The temperature dependence of the corresponding dynamic storage E' and loss E'' moduli are presented in Figure 3. During the first thermal scan the curing system displays two mechanical damping peaks and the beginning of a third over the temperature range from −25° to 275°C.

The first damping peak at about 50°C on the first thermal scan can be attributed to flow of the

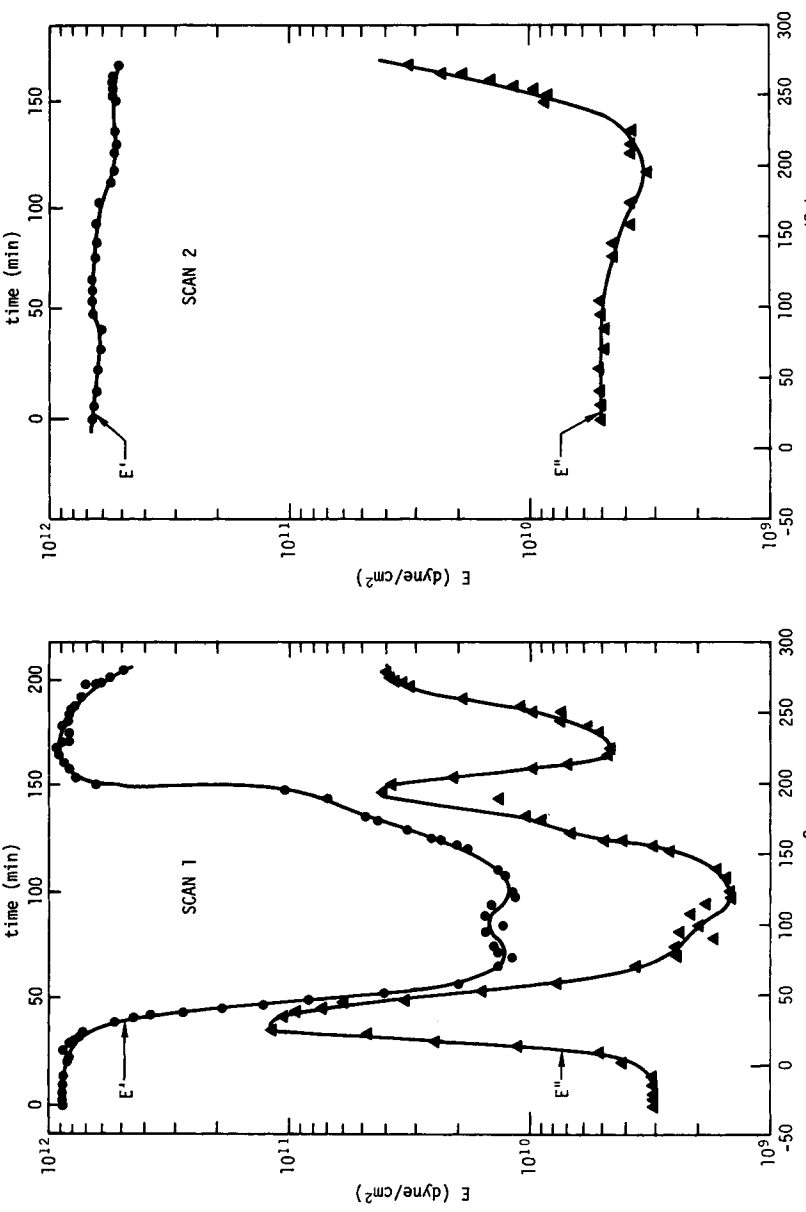

Fig. 3. Variation in the dynamic storage bending modulus E' and dynamic loss bending modulus E'' during the cure of 3501/AS-5 (scan 1, left view) and after curing (scan 2, right view).

uncured composite resin matrix. The concurrent decrease in the storage modulus E' and maximum in the loss modulus E'' resulting from this transition is shown in Figure 3. The measured dynamic force of the total system (D_{total}) between ~75° and 150°C in Figure 1 is nearly equal to that of the support core alone (D_{core}) and results in an uncertainty in the moduli values during this liquid stage of curing.

A second damping peak, shown in Figure 2 at about 180°C, results from a combination of gelation and vitrification of the epoxy matrix. Gillham and co-workers[4] have separated these two thermoset curing phenomena by isothermal torsional braid analysis. The slow thermal scan rate in the present experiments, however, allows the cure temperature to fall below T_g of the reacting system, resulting in vitrification that obscures the gelation stage of curing.

The composite specimen is shown in Figure 3 to attain a flexural modulus of 10^{12} dyn/cm upon completion of curing. This is in good agreement with the flexural modulus obtained by the same technique for sample rods machined from a cured panel of 3501/AS-5 composite.[14]

A third damping increase is noted in Figure 3 starting at about 250°C; it is caused by the onset of the glass to rubber transition of the composite matrix. Temperature limits of the oven system and degradation of the epoxy matrix prevented a full resolution of this peak being made.

Subsequent to the first thermal scan the specimen was allowed to cool to room temperature, and a second scan made. The only damping behavior indicated in Figure 2 (scan 2) is that due to the glass-to-rubber transition similar to that of scan 1.

These data demonstrate the potential of this technique in quality assurance of thermoset composite materials. The temperature at which the initial increase in damping is located (Fig. 2, scan 1) can be related to the extent of prepreg B-staging. The loss modulus peak associated with this damping is related to the temperature of maximum tack. This maximum is located at ~25°C for Hercules 3501/AS-5 composite to optimize for typical room temperature lay-up prior to curing. Finally, the curing curves as a whole can be used as a rheological "fingerprint" to monitor formulation changes in composite prepreg matrices.

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