

Torsional Braid Analyzer Measurements of Polymer Damping Factors

BRUCE HARTMANN and G. F. LEE, *Naval Surface Weapons Center, White Oak, Silver Spring, Maryland 20910*

Synopsis

Measurements were made in a torsional braid analyzer (TBA) and a torsional pendulum (TP) on a diglycidyl ether of bisphenol A cured with metaphenylenediamine over a broad temperature range that included the γ transition of this polymer. Based on a comparison of the results from the two instruments, we conclude that (1) the relative shear modulus measured in the TBA differs from the absolute modulus measured in the TP by a multiplicative constant that is independent of temperature in the glassy state; (2) the damping factor measured in the TBA is, at least approximately, equal to the damping factor measured in the TP, contrary to the usual assumption that only relative values are obtained from the TBA; and (3) as a result of (1) and (2), the TBA can be used to determine not only the temperature of a transition but also its activation energy.

INTRODUCTION

The primary purpose of this work is to demonstrate experimentally that the torsional braid analyzer (TBA) yields the absolute value of the damping factor of a polymer, at least for temperatures below the glass transition. This is contrary to the usual assumption that only relative values are obtained from the TBA. It will be shown here that in the glassy state, the TBA gives absolute values of damping factor and a relative modulus that differs from the absolute value by a multiplicative constant that is independent of temperature.

Absolute rather than relative values of damping factor are of interest because one can calculate the activation energy of a transition from the damping factor versus temperature curve provided absolute values of the damping factor are known.

In the following sections of this paper, we will discuss the relevant aspects of the TBA, the experimental measurements confirming that absolute values of damping factor are obtained in the TBA, and the calculation of activation energy from the TBA data.

TORSIONAL BRAID ANALYZER

The TBA has been shown to be a useful tool for studying polymers, particularly transitions in polymers.^{1,2} In brief, a multifilament glass braid is impregnated with a polymer, and this composite is excited into free torsional oscillations. The period P of these oscillations is related to the shear modulus G of the composite

specimen by the equation

$$G = \frac{8\pi LI}{R^4 P^2} \quad (1)$$

where L , R , and I are the length, radius, and moment of inertia of the specimen, respectively. The peak amplitudes of the oscillations are related to the damping factor (logarithmic decrement) by the equation

$$\Delta = \frac{1}{n} \ln \frac{A(r)}{A(r+n)} \quad (2)$$

where $A(r)$ is a reference peak amplitude and $A(r+n)$ is the peak amplitude n cycles later.

The modulus and damping factor determined using eqs. (1) and (2) are those of the composite specimen (polymer plus braid). Lewis and Gillham³ have shown that the polymer modulus can be obtained from the composite modulus, but only with some difficulty. For this reason, the TBA is generally used to give relative values. Measurements are made as a function of temperature, and any changes are assumed to result from changes in the polymer, since the glass braid is relatively insensitive to temperature. Since only changes are significant, the TBA is particularly useful for studying transitions. The relative modulus is then defined as $1/P^2$, since the other factors in eq. (1) are assumed to be independent of temperature.

Note, however, that Lewis and Gillham³ considered only the modulus and did not discuss damping factor. Furthermore, this point does not appear to have been studied elsewhere in the literature. It is usually tacitly assumed that only relative values of damping factors are obtained. Often, fixed values of $A(r)$ and $A(r+n)$ are used and $1/n$ is plotted rather than Δ . It is the primary goal of this work to determine experimentally the relation between polymer damping and composite damping in the TBA. This is most conveniently done by comparing TBA measurements with data obtained on the same polymer using a torsional pendulum (TP).

EXPERIMENTAL

The torsional braid analyzer used in this work was a commercial device manufactured by Chemical Instrument Corporation, while the torsional pendulum used was built following the design of Nielsen.⁴ In both cases, the data were recorded on a strip chart recorder and reduced manually.

An epoxy polymer was chosen for comparison in the two instruments. The epoxy was a commercial diglycidyl ether of bisphenol A (DGEBA, Shell Chemical Co. Epon 828, MW 340, mp 43–45 °C) cured with metaphenylenediamine (MPDA, Aldrich Chemical Co., MW 108, mp 63–64 °C). The MPDA was recrystallized from isopropyl alcohol under nitrogen to yield off-white crystals. To check the purity of the DGEBA, the epoxide equivalent weight (EEW) was determined by the pyridinium chloride–pyridine method. The EEW was 172, compared with the theoretical value of 170, indicating a relatively pure monomer.

The resin was prepared by using an equivalent weight of each monomer (27 g MPDA and 172 g DGEBA). Both monomers were heated to their crystalline

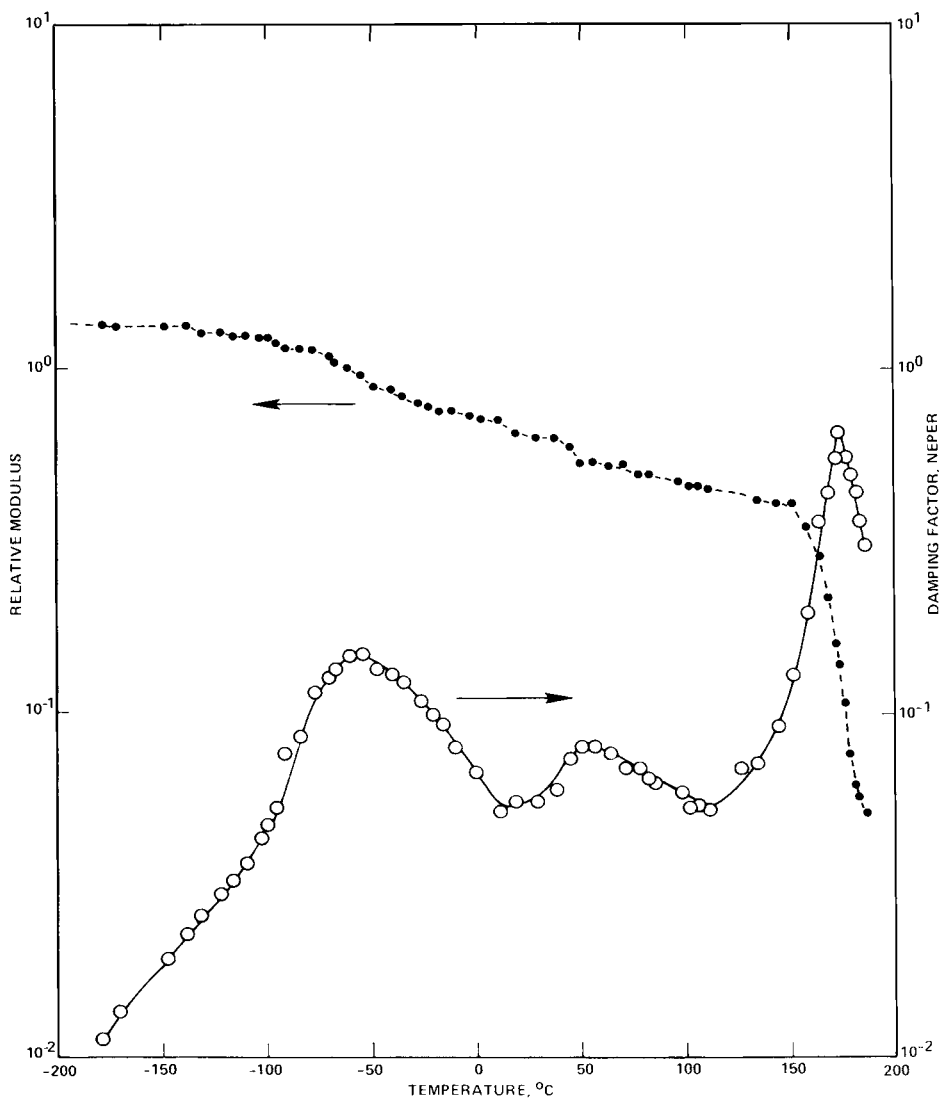


Fig. 1. TBA properties for an epoxy vs. temperature.

melting point in separate flasks and then mixed together for 5 min. The resin was then degassed under vacuum for 10 min. Finally, the resin was poured into an aluminum metal mold ($12.7 \times 7.6 \times 2.5$ cm) lined with aluminum foil for easy sample removal in order to make the torsional pendulum specimens. For the TBA specimens, the glass braid was dipped into the resin.

The resin, both in the mold and on the braid, was kept overnight in a desiccator containing Ascarite (for CO_2 absorption) and Drierite (for H_2O absorption) at room temperature. Then, the resin was placed in a forced-air oven for 4 hr at 50°C , 1 hr at 125°C , 2 hr at 175°C , and 1 hr at 200°C . The specimens were allowed to cool to room temperature and removed from the oven. The torsional pendulum samples were machined from the cured resin to dimensions of ap-

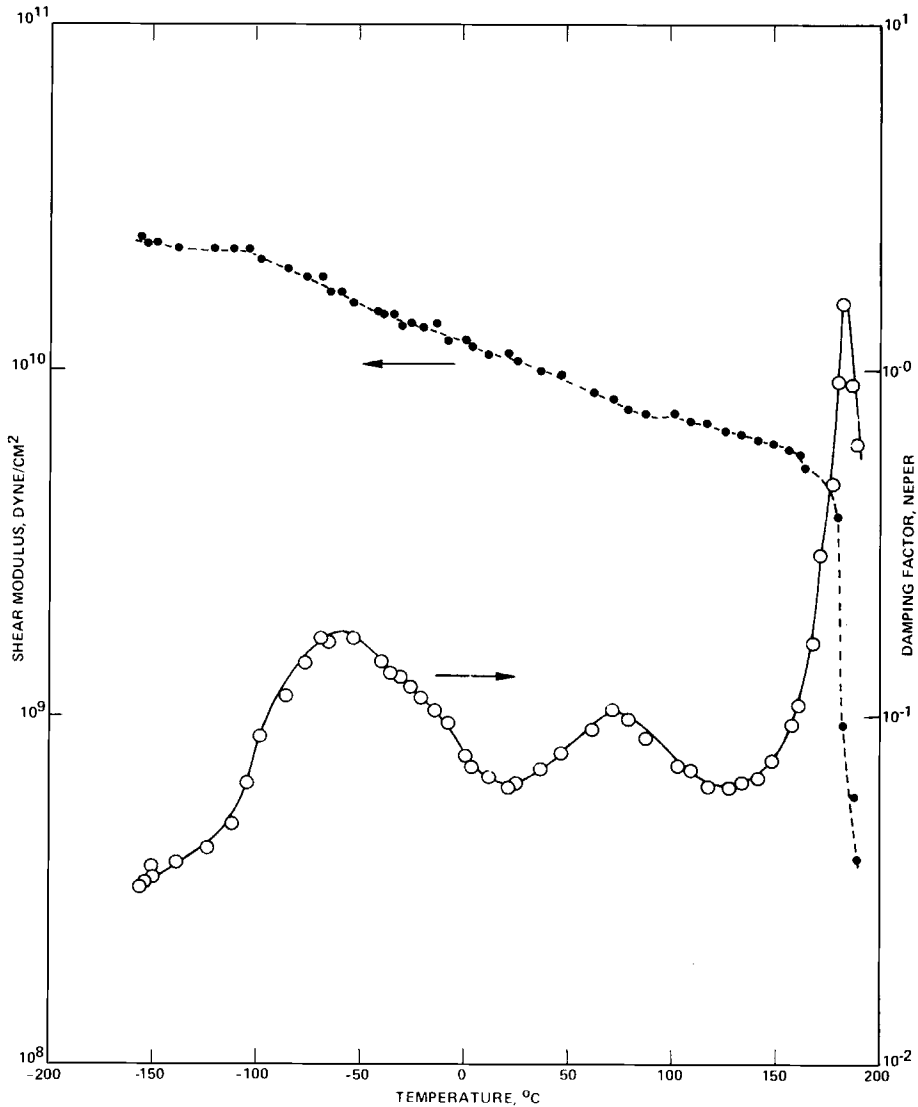


Fig. 2. TP properties for an epoxy vs. temperature.

proximately $10.2 \times 0.1 \times 0.03$ cm. The density of the cured resin was 1.203 g/cm³.

RESULTS

Typical results for the epoxy polymer are shown in Figure 1. The damping factor* indicates three transitions in the temperature range covered. The highest temperature transition, α transition, is observed at 175 °C and is the glass transition of the polymer. There are two subglass transitions. The β transition

* Note that Δ , eq. (2), is plotted in Figure 1 and not just $1/n$, as is commonly done with TBA data.

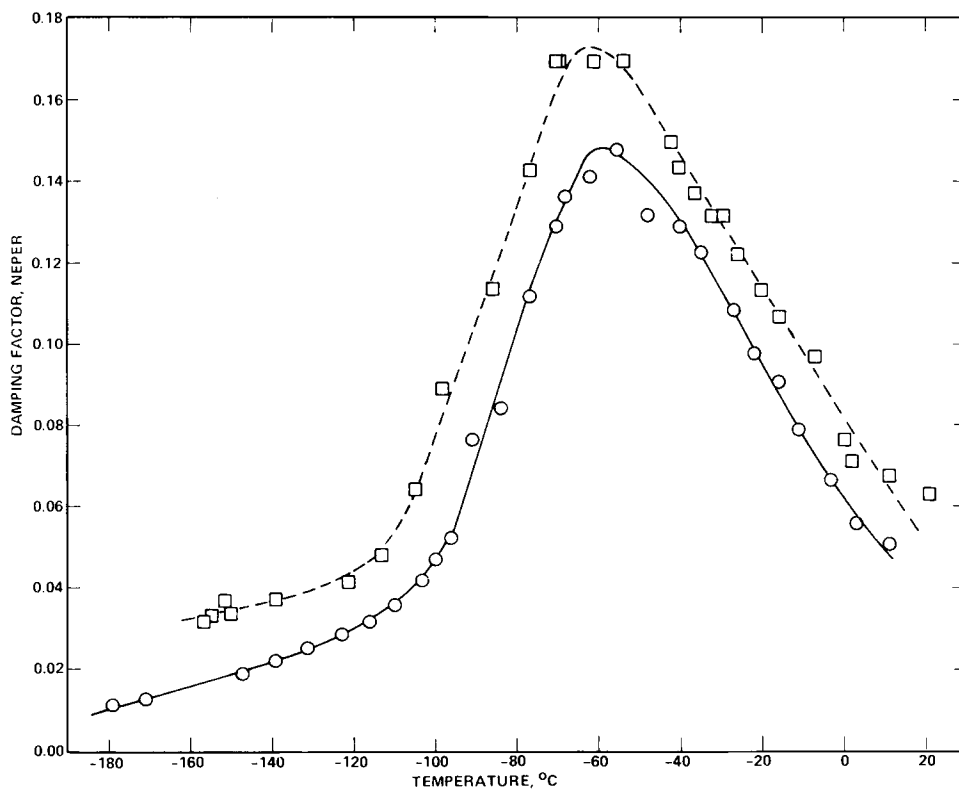


Fig. 3. Comparison of TBA and TP damping factors: (○) TBA; (□) TP.

at 55 °C has been shown⁵ to be associated with the main glass transition of the undercured resin network. Finally, the γ transition at -60 °C has been shown⁶ to be due to a crankshaft rotation of the segment $-\text{CH}_2\text{CHOHCH}_2\text{O}-$. It is this last transition that was selected for study in this paper.

Typical TP results for the epoxy are shown in Figure 2. The α transition is observed at 180 °C; the β transition, at 70 °C; and the γ transition, at -60 °C.

The damping factor curves from the two instruments, which are plotted using semilog coordinates in Figures 1 and 2, are plotted together, using a linear scale, in Figure 3, over the temperature range in the vicinity of the γ transition. Considering the sensitivity of damping factor curves to even relatively minor specimen-to-specimen variations, the agreement between the two curves is considered good. While it is difficult at this point to assess quantitatively the significance of the fact that the TBA damping is less than the TP damping, we can say that, at least to a first approximation, the TBA gives absolute values of damping factor.

Relative modulus, using a linear scale, is shown over the same temperature range as the damping factor in Figure 4. A typical relaxation curve is observed. We have indicated the unrelaxed modulus G_U and the relaxed modulus G_R . Here, relaxed and unrelaxed means above and below the transition, respectively. A similar plot for the TP is shown in Figure 5. A similar shape is observed. It is assumed here that the relative modulus, Figure 4, differs from the absolute

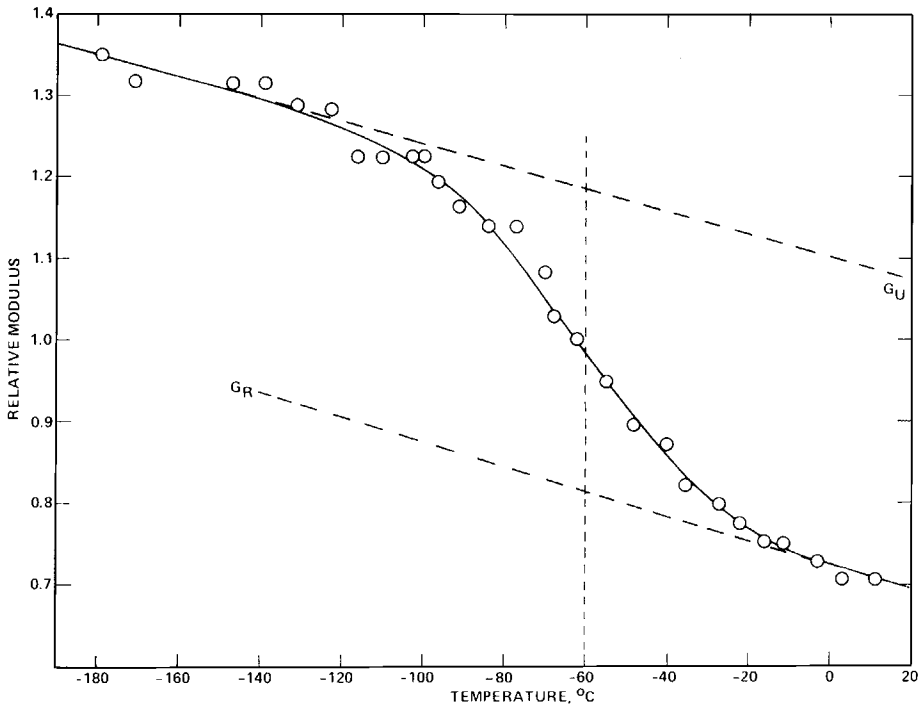


Fig. 4. TBA relative modulus vs. temperature.

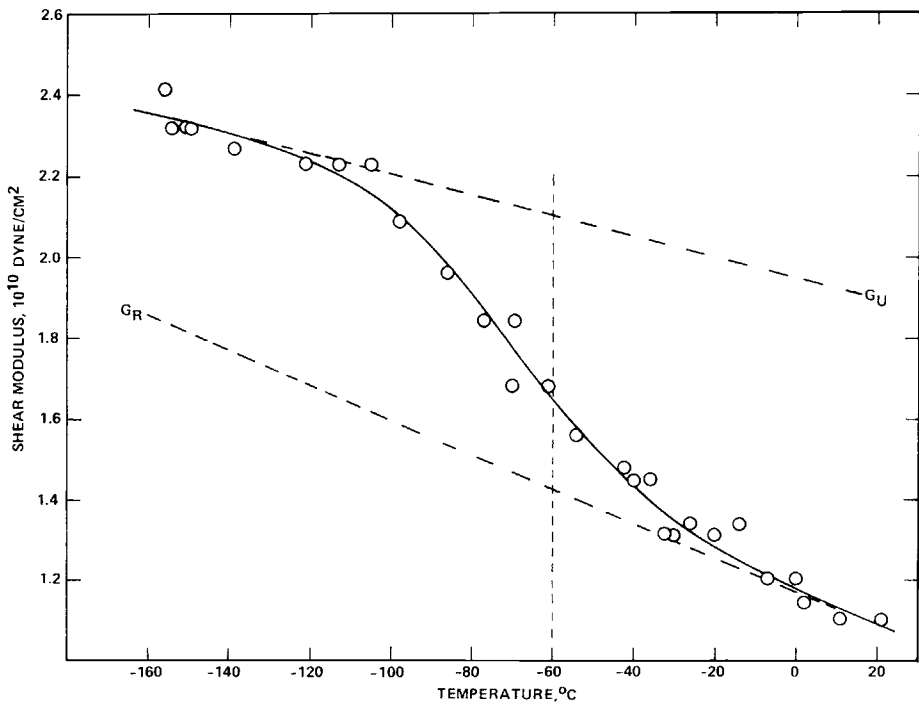


Fig. 5. TP absolute modulus vs. temperature.

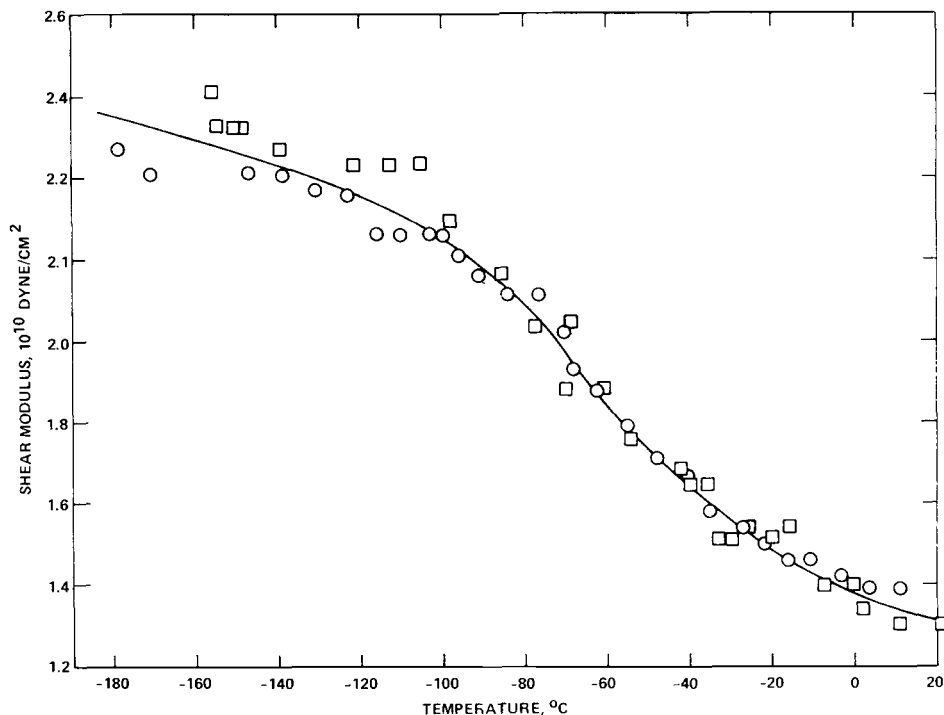


Fig. 6. Comparison of TBA and TP moduli: (O) TBA; (□) TP.

modulus, Figure 5, by a multiplicative constant that is independent of temperature in the glassy state, i.e.,

$$G = CG_r \quad (3)$$

where G is the absolute modulus (from the TP), G_r is the relative modulus (from the TBA), and C is a constant. Evaluating the constant at -60°C , we find $C = 1.68 \times 10^{10}$ dynes/cm². Multiplying each of the relative modulus values in Figure 4 by this same constant, we can plot the modulus values for both the TBA and TP together, as shown in Figure 6. One curve has been drawn through both sets of data since the results are in very close agreement. Figure 6 shows that one constant can be used to convert relative TBA moduli to absolute values over a wide temperature range in the glassy state.

ACTIVATION ENERGY

One advantage in having absolute values of damping factor is that it enables one to calculate the activation energy of a transition. Read and Williams⁷ have shown that the area under a TP damping factor versus temperature curve in the vicinity of a transition is directly related to the activation energy ΔH for that transition. Their result can be expressed in the form

$$\Delta H = (G_U - G_R) R \pi^2 \left[2 \int_0^\infty G \Delta d(1/T) \right]^{-1} \quad (4)$$

where R is the gas constant and T is absolute temperature.

By eq. (3), we can substitute a constant times the relative (or TBA) modulus for the moduli in eq. (4). But, since the constant is independent of temperature, it can be taken out from under the integral and the constant will cancel. Therefore, the value of the constant is not needed, only the fact that it is independent of temperature.

We have already shown that, at least approximately, the TBA gives absolute damping factors. Thus, using the TBA data from Figures 3 and 4 in eq. (4), we can calculate the activation energy for the γ transition. The difference between the relaxed and unrelaxed modulus is evaluated at -60°C from Figure 4. Values of G and Δ are then obtained from Figures 3 and 4, multiplied together and plotted vs reciprocal temperature. Before integrating, one must establish a baseline. This baseline represents a temperature-independent contribution to the damping factor. One can view the damping factor in a polymer as the sum of two terms:⁸ a background hysteresis independent of temperature (or frequency) and various relaxations that depend on temperature (or frequency). We are only interested in the relaxation (transition), so we subtract the constant baseline.

Following the above procedure, an activation energy of 24 kcal/mole was calculated for the γ transition in this epoxy. In a similar manner, we can calculate the activation energy for the same transition using the TP data. As shown in Figure 6, the moduli values are essentially identical to within a multiplicative constant. In Figure 3, however, the area under the TP damping factor curve is greater than the area under the TBA curve which implies, by eq. (4), that the activation energy calculated for the TP will be less than that calculated for the TBA, and this gives a quantitative measure of the difference between the two curves. The activation energy calculated from the TP data is 19 kcal/mole. We, therefore, conclude that the TBA can be used to estimate the activation energy of a transition to an accuracy of $\pm 25\%$.

The activation energies calculated here are in reasonable agreement with the values obtained by Arridge and Speake⁹ who found values that varied from 16 to 25 kcal/mole depending on the cure temperature and the amount of curing agent. Note that these authors calculated ΔH using eq. (4) and data from a TP and found that the result was in very close agreement with the value obtained by making measurements at several frequencies and using the Arrhenius equation, a much more tedious experimental procedure than calculating the area under one curve.

CONCLUSIONS

Measurements were made in a TBA and a TP of the γ transition in a diglycidyl ether of bisphenol A cured with metaphenylenediamine. Based on a comparison of the results from the two instruments, we conclude:

1. The relative shear modulus measured in the TBA differs from the absolute modulus measured in the TP by a multiplicative constant that is independent of temperature in the glassy state.
2. The damping factor measured in the TBA is, at least approximately, equal to the damping factor measured in the TP.
3. As a result of 1 and 2, the TBA can be used to determine not only the temperature of a transition but also its activation energy.

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