

A New Method for Torsional Pendulum Analysis of Polymers Through the Glass Transition Region

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Synopsis

A freely oscillating torsional pendulum has been used to measure the dynamic-mechanical loss of polymers through the softening temperature by encapsulating the polymer in a rigid matrix of cured phenolic resin. The method is illustrated with loss curves through the glass transition region of poly(vinyl chloride), polystyrene, a styrene-maleic anhydride copolymer, poly(phenylene oxide), and two binary alloys involving these polymers. The advantages and simplicity of the technique are emphasized.

INTRODUCTION

A freely oscillating torsional pendulum has found widespread use in the determination of the dynamic-mechanical properties of polymers. A specimen bar, which can have either circular or rectangular cross section, is clamped at one end while the free end with added inertial mass is twisted and released, producing a damped free torsional oscillation. The damping, measured as a logarithmic decrement Δ , is used to calculate the dynamic-mechanical loss tangent, $\tan \delta$, of the material through the formula

$$\begin{aligned}\Delta &\equiv \ln(A_n/A_{n+1}) \\ &= \pi \tan \delta\end{aligned}$$

where A_n and A_{n+1} are the amplitudes of successive swings of the pendulum. The procedure is fully described, for instance, by McCrum et al.¹ The mechanical loss is a result of internal friction created by molecular relaxation processes.

One of the major restrictions of measuring dynamic-mechanical loss with such a simple apparatus is that the frequency of vibration depends directly on the shear modulus of the specimen under test, and, at temperatures where the specimen softens, no oscillation can be induced at all. Loss measurements are particularly important in the glass transition region since a major peak in the loss-versus-temperature curve occurs here. The loss curve cannot generally be followed beyond the peak using the torsional pendulum method unless the sample is in some way supported or is crosslinked to prevent viscous flow. Two ways of solving this problem are described in the literature. The first is the torsional braid technique^{2,3} in which the specimen is an inert support of braided

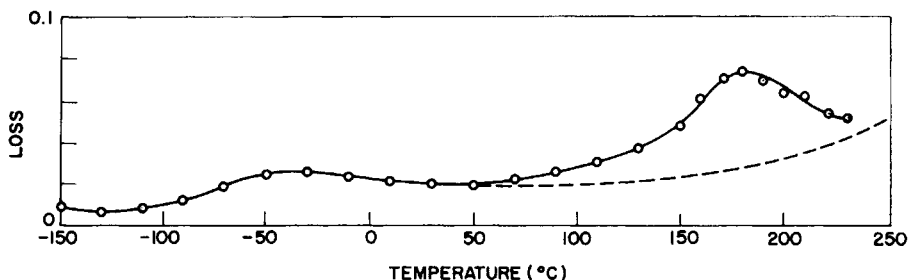


Fig. 1. Dynamic-mechanical loss of phenolic specimen cured at 150°C (solid line) and 200°C (dotted line).

glass yarn soaked in the polymeric sample to be examined. The method gives qualitative information on modulus and loss changes in the polymer. Originally designed to follow cure in initially liquid thermosetting resins, it has subsequently been used to make dynamic-mechanical measurements on solid thermoplastic polymers. A solid polymer must first be dissolved in a solvent before it can impregnate the yarn. In a second more absolute method, described by Szilágyi et al.,^{4,5} the sample is bonded to a metal strip or rod and dynamic-mechanical properties measured on the composite. The authors presented a theory wherein the dynamic-mechanical modulus and loss of the composite were expressed in terms of those of the components.

We wish to present here a new qualitative technique which, we feel, is simpler and presents fewer experimental problems than those described above. Briefly, a powdered sample is supported in a matrix of a cured phenolic resin. Such resins are stable at temperatures up to at least 250°C, and the composite specimen may be used in a conventional torsional pendulum.

EXPERIMENTAL

The polymeric sample to be examined is intimately mixed, in finely divided form, with a phenolic resin molding powder in the ratio of 1:3. We have found Durez 13527 wood flour-filled, general-purpose molding powder from Hooker Chemical Corporation to be suitable. The dry blend is cured under pressure in a preheated mold and the specimen is machined from the molding. Our torsional pendulum utilizes a specimen measuring $2\frac{1}{4}$ in. long with a rectangular cross section of $\frac{1}{8} \times \frac{1}{4}$ in. Only 2 or 3 grams of powdered sample are required in such a specimen. The free end of the specimen carries an inertial disk, and torsional vibrations are sensed by a rotating differential transducer and are plotted on an oscillographic recorder. With a rigid plastic as the specimen, the frequency of free torsional vibrations is in the range of 10–20 Hz.

The effectiveness of phenolic resin as a matrix material relies on incompatibility between the resin and the sample while providing a key which transmits mechanical strain across the interface. It will be shown that the dynamic-mechanical loss of a cured phenolic resin is sufficiently low and temperature independent to provide a flat baseline.

To illustrate the method, some results of dynamic-mechanical loss through the softening temperature are given on the following polymers: polystyrene

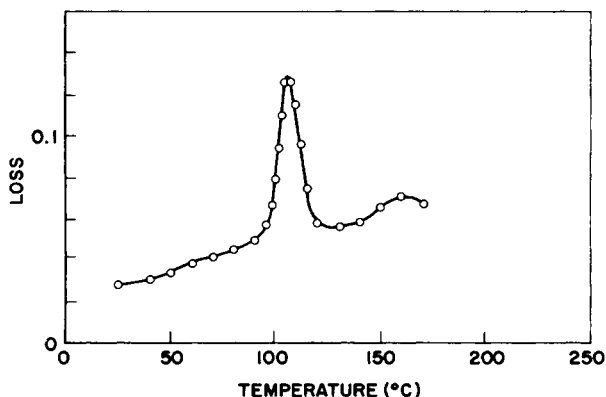


Fig. 2. Dynamic-mechanical loss of polystyrene beads encapsulated in cured phenolic resin.

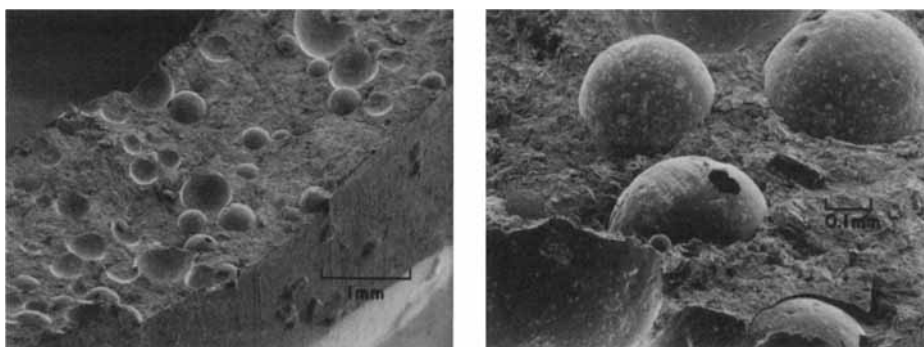


Fig. 3. The dispersion of polystyrene beads in the phenolic matrix. Scanning electron micrographs of fracture surface at two magnifications.

(Dylene 8 type from ARCO/Polymers, Inc.); poly(phenylene oxide) [PPO poly-(2,6-dimethyl-1,4-phenylene ether) from General Electric Company]; poly(vinyl chloride) (Geon 85297 type from B. F. Goodrich Co.); styrene-maleic anhydride copolymer (Dylark 232 type from ARCO/Polymers, Inc.). The polystyrene was in bead form, while the other samples were pelletized and had to be ground through a 20-mesh screen before mixing with phenolic resin powder.

Additionally, melt blends of these polymers were tested. Dynamic-mechanical loss is commonly used in a test for compatibility between pairs of amorphous polymers. A double peak in the loss-versus-temperature curve of the alloy, indicative of the glass transition temperatures of the components, demonstrates incompatibility.

RESULTS AND DISCUSSION

Figure 1 shows the dynamic-mechanical loss between -150°C and 230°C for a specimen of phenolic resin cured at 150°C . Apart from a broad, shallow hump around -50°C , the loss is uniformly low until the temperature of cure is approached. The curve then rises toward a peak. This is believed to be caused

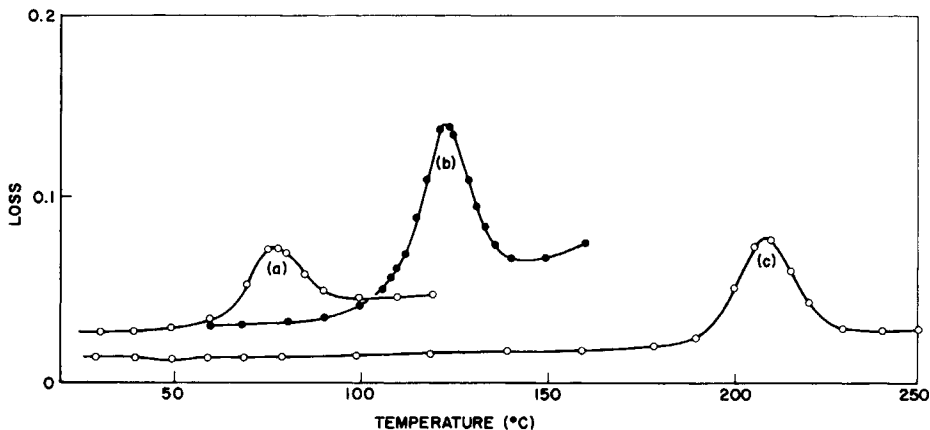


Fig. 4. Dynamic-mechanical loss of encapsulated samples of (a) poly(vinyl chloride), (b) styrene-maleic anhydride copolymer, and (c) poly(phenylene oxide).

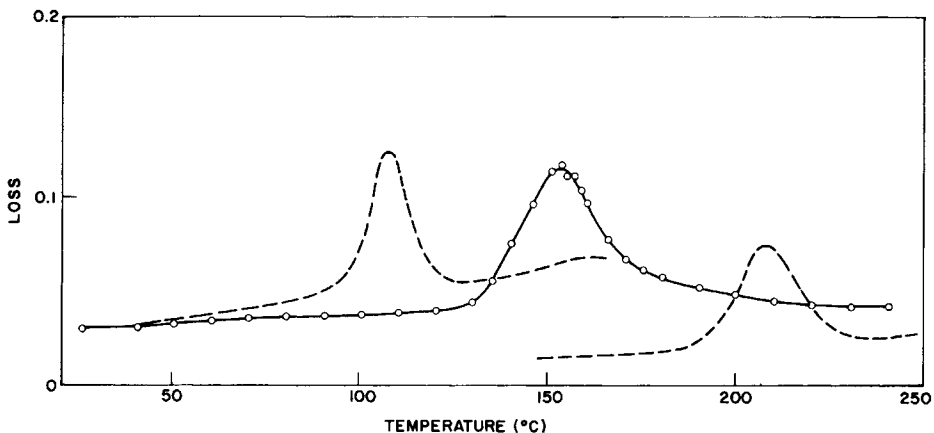


Fig. 5. Dynamic-mechanical loss of 50:50 blend of polystyrene and poly(phenylene oxide). The loss curves of the component polymers are shown dotted.

by softening and residual cure in the phenolic. Thermosetting resins are known to cure until they become glassy hard, i.e., until the glass transition temperature has reached the curing temperature. Then, no further reaction can take place.^{6,7} When a specimen of phenolic resin was cured at 200°C, the change in loss characteristic indicated by the dotted line in Figure 1 was obtained. A flat baseline may, therefore, be extended to as high a temperature as is necessary.

The dynamic-mechanical loss of polystyrene through the softening temperature, using the technique described, is shown in Figure 2. The polystyrene beads were mixed with the phenolic resin and the composite cured at 150°C. The dispersion of beads in the phenolic matrix is indicated in Figure 3, a scanning electron micrograph of a fracture surface. Note that, although taken to 150°C, the spherical shape of the beads is not distorted nor is there any evidence of interdiffusion at the polystyrene/phenolic interface.

The dynamic-mechanical loss curves for poly(vinyl chloride), styrene-maleic anhydride copolymer, and poly(phenylene oxide) in the phenolic resin matrix

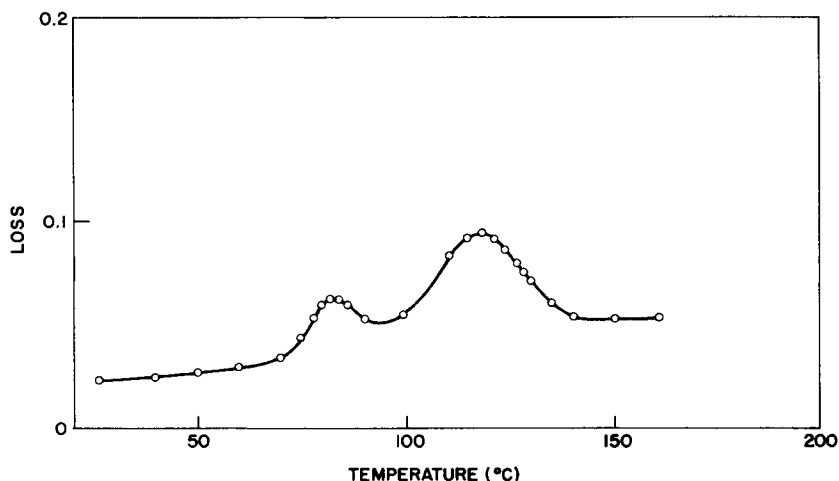


Fig. 6. Dynamic-mechanical loss of 50:50 blend of poly(vinyl chloride) and styrene-maleic anhydride copolymer.

are shown in Figure 4. In the case of poly(phenylene oxide), it was necessary to cure the phenolic at 240°C to get the appropriate baseline.

The loss characteristics of two polymeric alloys are also presented here. The first is a blend of polystyrene and poly(phenylene oxide), a well-studied system^{8,9} which is believed to be compatible. The dynamic-mechanical loss of a 50:50 melt-blended alloy is shown in Figure 5, together with the loss curves of the component polymers for comparison. The single intermediate loss peak of the alloy suggests compatibility at a molecular level. In contrast, an alloy of poly(vinyl chloride) and styrene-maleic anhydride copolymer is opaque and brittle, bearing all the marks of incompatibility. The dynamic-mechanical loss of this alloy is shown in Figure 6. The separate peaks denote the existence of separate phases in the mixture and prove incompatibility.

The foregoing examples illustrate the resolution and precision attainable with an encapsulation technique and also show its effectiveness over a wide range of temperatures. At subambient temperatures, it is possible, of course, to encapsulate samples with many materials other than phenolic resins. Polystyrene, for instance, may be used to support butadiene or isoprene rubbers which soften below 0°C. In fact, the torsional pendulum is used extensively to analyze the dispersed rubber phase in high-impact polystyrene.^{10,11} The only requisites for an effective matrix material are the provision of a low-loss baseline in the temperature range of interest, incompatibility with the sample tested, and ease of processing into a torsional pendulum specimen containing a dispersion of the sample. A filled phenolic resin appears to satisfy all these requisites and is particularly useful at temperatures above 200°C, where no thermoplastic matrix material would survive.

References

1. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967, p. 192.
2. A. F. Lewis and J. K. Gillham, *J. Appl. Polym. Sci.*, **7**, 685 (1963).
3. J. K. Gillham, *Crit. Rev. Macromol. Sci.*, **1**, 83 (1972).

4. L. Szilágyi, G. Locati, and M. Pegoraro, *Kolloid-Z. Z. Polym.*, **223**, 97 (1968).
5. L. Szilágyi and G. Locati, *Rheol. Acta*, **9**, 535 (1970).
6. R. A. Fava, *Polymer*, **9**, 137 (1968).
7. R. G. C. Arridge and J. H. Speake, *Polymer*, **13**, 443 (1972).
8. J. Stoelting, F. E. Karasz, and W. J. MacKnight, *Polym. Eng. Sci.*, **10**, 133 (1970).
9. W. M. Prest, Jr., and R. S. Porter, *J. Polym. Sci. A-2*, **10**, 1639 (1972).
10. H. Keskkula, *Appl. Polym. Symp.*, **No. 15**, 51 (1970).
11. G. Cigna, *J. Appl. Polym. Sci.*, **14**, 1781 (1970).

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