Characterization of Polymer-Coated Optical Fibers Using a Torsion Pendulum

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Synopsis

A freely oscillating torsion pendulum has been used to characterize the dynamic mechanical behavior of single polymer-coated optical fibers. The dynamical mechanical spectra of the polymer coatings exhibit a glass transition temperature (T_g), a cryogenic glassy-state relaxation (T_{sec}), and another cryogenic relaxation that is attributed to water present in the coating (T_{H_2O}). The shear modulus (G') of the coating was computed from the shear moduli of the composite specimen and the core, assuming that the coating and core deform through the same angle on oscillation. The glassy-state modulus was the same for both thin and thick coatings, although the intensity of the damping peaks, as measured by the logarithmic decrement, increased with coating thickness. Comparison of the dynamic mechanical behavior of a coated optical fiber and of a free film cast from the same reactive components shows that the polymer itself can absorb water at ambient conditions and display a mechanical relaxation at cryogenic temperatures. The T_{H_2O} and T_{sec} relaxations are coupled with respect to their intensities. Latent chemical reactivity was found in one coating above its maximum temperature of cure. In this, the temperature of cure determines the glass transition temperature.

INTRODUCTION

Polymeric coatings on optical telecommunication fibers provide long-term protection from abrasion and environment which preserves the pristine strength of the fibers.[1] Mechanical properties of the coating are also important because they influence optical attenuation through microbending loss.[2] To protect the fiber from immediate environmental damage and to prevent beading of the fluid resin, the coating is formed immediately after the silica has been drawn from a preform rod. The coating is applied by pulling the fiber through a reservoir of reactive prepolymer fitted with a flexible rubber die.[3] Hydrodynamic forces at the tip of the die center the fiber. The formulations used to produce the coatings studied in this report are UV-curable epoxy diacrylates.

Single optical fibers were employed as the specimens in conventional torsion pendulum experiments in which freely decaying waves were intermittently initiated. The sensitivity of a freely decaying torsion pendulum equipped with a nondrag optical transducer permits examination of the dynamic mechanical properties of coated and bare single filaments. The simple concentric geometry of the fiber and coating in a commercial optical fiber allows calculation of the actual in-phase shear modulus of the polymer coating from the composite properties, assuming that the coating is well bonded to the core and that the angular deformations of fiber and coating are the same.[4,5] In situ character-

ization of optical fiber coatings is attractive because it is difficult to reproduce the exact radiation doses, curing conditions, and properties when preparing unsupported film specimens.

This report concerns the dynamic mechanical behavior of optical fiber coatings and the evaluation of the effects of elevated temperature and water vapor on them using a torsion pendulum. A preliminary report has been published.[5]

EXPERIMENTAL

Specimens (5–6 cm) of coated fiber were cut from continuous lengths. They were examined closely to ensure that fiber and coating were concentric. Coatings were removed from some segments by soaking in tetrahydrofuran at room temperature for 12 h, and these were then used to obtain the shear modulus of the bare fiber. The diameters of the coated and bare fibers were measured to within ±0.0001 cm with an optical microscope.

Dynamic mechanical spectra (ca. 1 Hz) were obtained using an automated torsion pendulum,[6] a schematic diagram of which is shown in Figure 1. The specimen is mounted in clamps between the supporting and lower extender rods and lowered into the temperature-controlled chamber. The assembly is then
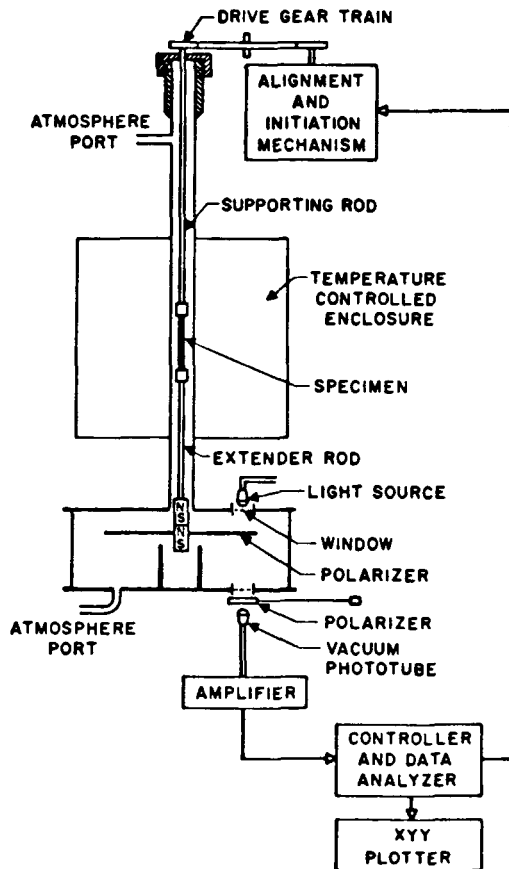

Fig. 1. Automated torsion pendulum.

coupled magnetically to the inertial disk; the latter remains permanently in the lower section of the instrument (see Fig. 2). The weight supported by the specimen is about 15 g. The polaroid disk serves as one part of the optical transducer. A beam of light passes through the oscillating disk and then through a second stationary polaroid sheet. The attenuated light is converted to an electrical analog signal by a linearly responding photodetector. The signal is monitored by an analog computer (6) which computes the period of the oscillation and the damping coefficient for each wave. Recent publications[7,8] report the use of digital computers for control and data processing of freely decaying torsion pendulum experiments. An automated instrument is commercially available from Plastics Analysis Instruments, Inc., P.O. Box 408, Princeton, NJ 08540.

The specimen is enclosed in a temperature- and humidity-controlled-and-measured environment of helium. Spectra were obtained between −190 and 115°C.
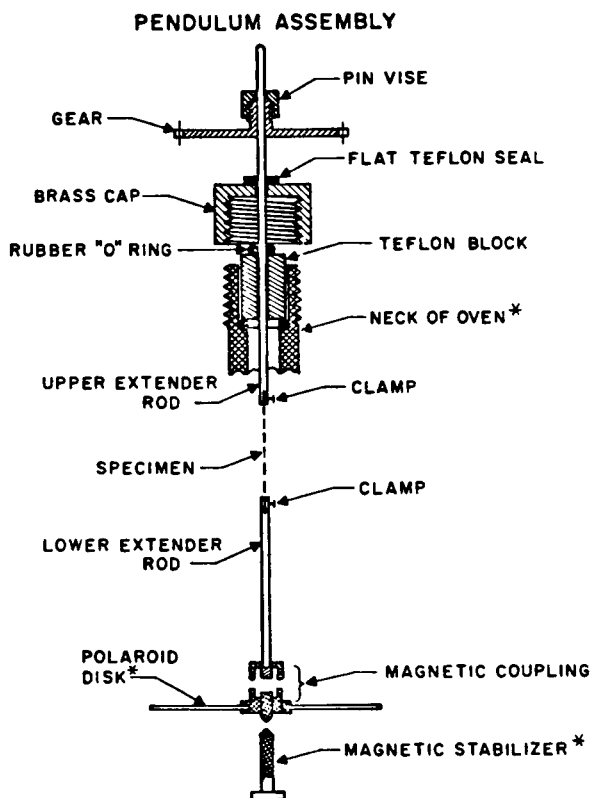

Fig. 2. Mounted specimen assembly ready for lowering into the vertical cavity of the temperature controlled enclosure.
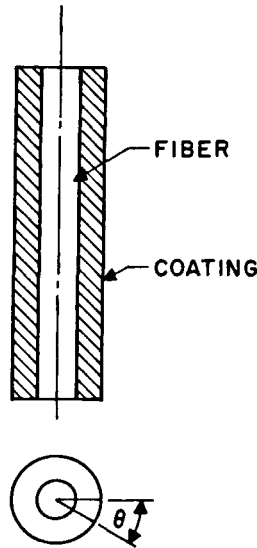
Fig. 3. Assumed geometry and deformation in a coated fiber under torsional loading.

Theory

The shear modulus of a cylindrical specimen can be defined as (see Notation section):

$$G' = \frac{\sigma}{\gamma} = \frac{\sigma}{r(d\theta/dl)} \tag{1}$$

For a long cylindrical shaft where $d\theta/dl$ is small and constant along the shaft, the shear stress is

$$\sigma = G'r\frac{d\theta}{dl} = \frac{G'r\theta}{L} \tag{2}$$

The torque per unit length is the summation of the moments of the shear forces:

$$T = \int_0^R \sigma r(2\pi r\, dr) = \frac{G'\theta}{L} \int_0^R 2\pi r^3\, dr = \frac{G'\theta\pi R^4}{2L} \tag{3}$$

For a composite shaft with no slip at the interface, the torque can be expressed[9] as (see Fig. 3)

$$T = T_1 + T_2 \qquad (\text{fiber} = 1, \text{coating} = 2)$$

$$= \frac{G_1'\theta_1}{L} \int_0^{R_1} 2\pi r^3\, dr + \frac{G_2'\theta_2}{L} \int_{R_1}^{R_2} 2\pi r^3\, dr \tag{4}$$

Assuming equiangular displacement in fiber and coating ($\theta_1 = \theta_2 = \theta$),

$$T = \frac{\theta\pi}{2L} [G_1'R_1^4 + G_2'(R_2^4 - R_1^4)] \tag{5}$$

This overall torque is related to an overall modulus of the composite (G') through eq. (3):

$$T = \frac{G'\theta\pi R}{2L} = \frac{\theta\pi}{2L} [G_1'R_1^4 + G_2'(R_2^4 - R_1^4)] \tag{6}$$

where G' of the composite is related to the period (P) of oscillation of the composite through[10]

$$G' = \frac{8\pi LI}{R^4 P^2} \tag{7}$$

The modulus of the coating can be determined from the period of oscillation of the composite and the shear modulus of the fiber through eqs. (6) and (7):

$$G'_2 = \frac{G'R_2^4 - G_1 R_1^4}{R_2^4 - R_1^4} = \frac{(8\pi LI/P^2) - G'_1 R_1^4}{R_2^4 - R_1^4} \tag{8}$$

The loss modulus (G'') of a specimen is related to the logarithmic decrement (Δ) and the shear modulus (G') of the specimen by

$$G'' \simeq \frac{G'\Delta}{\pi} \tag{9}$$

where

$$\Delta = \frac{1}{n} \ln\left(\frac{A_i}{A_{i+n}}\right)$$

in which n is the number of oscillations between the ith and $(i + n)$th peaks of a decaying wave, and A_i and A_{i+n} are the peak amplitudes of the ith and $(i + n)$th oscillations, respectively.

Calibration

Calibration required the determination of the moment of inertia of the inertial mass of the torsion pendulum using a calibrated wire. An aluminum rod of measured geometry and mass was used as the inertial mass for calibrating a chromium–nickel alloy wire. The period of the oscillation was obtained by averaging over a number of oscillations using a stop-watch; the procedure was repeated many times to decrease the statistical uncertainty. The shear modulus of the calibration wire was determined to be 8.612×10^{11} dyn/cm^2 using eq. (7) and the geometry and mass of the rod and the period of oscillation. The calibrated wire was then used as the specimen in the torsion pendulum, and the moment of inertia of the system was determined to be 31.56 g-cm^2. The bare fiber was then used as the specimen, and its shear modulus (G'_1) was determined: $G'_1 = 1.936 \times 10^{11}$ dyn/cm^2. G'_1 was taken to be independent of temperature over the temperature range in question (-190 to $115°$C).

RESULTS AND DISCUSSION

Results were obtained for two specimens having coatings prepared in the same manner but having different thicknesses. The coating thickness ($R_2 - R_1$) was 0.0050 cm for the thin coating and 0.0115 cm for the thick coating. The specimens were conditioned in the apparatus in dry helium at 22°C for 16 h prior to obtaining thermomechanical data. Plots of the shear modulus of the coating (G'_2) calculated from eq. (8) versus temperature for the thin and thick coatings are presented in Figure 4. Shear modulus data for the two specimens appear to be similar and within experimental error. Small differences are caused by
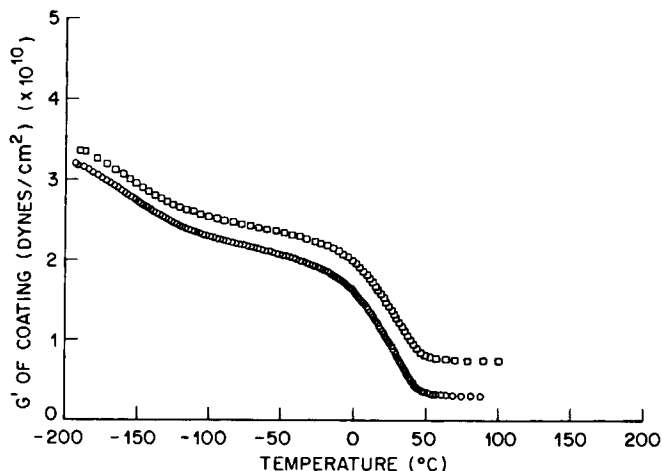
Fig. 4. Calculated in-phase shear modulus (G') of coating vs. temperature (°C) for two specimens with different thicknesses of coatings: (□) thin coating, R_1 = 0.0055 cm, R_2 = 0.0105 cm, L = 5.80 cm; (○) thick coatings, R_1 = 0.0055 cm, R_2 = 0.0170 cm, L = 5.70 cm. Conditioning: 22°C/16 h/dry helium. Experiment: 22 → −190 → 100°C. $\Delta T/\Delta t$ = 1°C/min. Plot shown: −190 → 100°C.

the experimental error in measuring the radii due to the fourth-order dependence of G_2' on the radius.

The values for G_2' appear to be valid in the glassy region of the spectrum when the contribution of the polymer coating to overall specimen rigidity is equivalent to that of the hard core. The modulus of the silica fiber is almost an order of magnitude higher than that of the glassy coating, but the fourth-power dependence of the modulus on the radius [see eq. (7)] enhances the contribution of the coating to the overall rigidity.

The coating becomes rubbery above its glass transition temperature (T_g) where its real modulus is expected to drop by at least an order of magnitude. The contribution of the coating to the composite rigidity above T_g is therefore greatly reduced in comparison with the contribution of the core fiber. The sensitivity of the technique is therefore poor above the T_g of the coating. In principle, the problem can be avoided by forming the polymer on a core support of low modulus. The values of the glassy shear modulus shown in Figure 4 appear to be in good agreement with an earlier report of mechanical properties of a free film of UV-cured epoxy acrylate obtained with a mechanical spectrometer. At −100°C and 1 rad/sec, where G' is relatively independent of frequency, the report[11] shows G' = 2.55 × 10^{10} dyn/cm². This compares well with the value of 2.45 × 10^{10} dyn/cm² obtained by averaging the values obtained herein using the thin (2.60 × 10^{10} dyn/cm²) and thick (2.31 × 10^{10} dyn/cm²) specimens.

Figure 5 is a plot of the logarithmic decrement of the composite for both the thin and thick coatings. Two thermomechanical transitions were found in the spectra. A glass transition was found slightly above room temperature in each: 25°C for the thin coating and 34°C for the thick coating. A secondary relaxation (T_{sec}) associated with epoxy acrylate materials was found at −144°C in both coatings.

The intensity of the damping peaks increases with the amount of coating in the composite. The intensity of the damping peak at the glass transition temperature of the coating is plotted against the volume fraction and also against
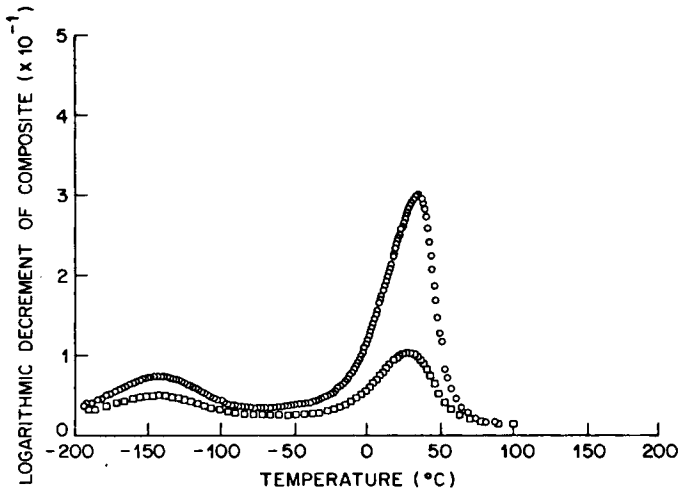
Fig. 5. Logarithmic decrement ($\triangle$) of composite vs. temperature (°C) for two specimens with different coating thicknesses (same specimens as for Fig. 4): ($\square$) thin coating, $T_g = 25$°C (0.27 Hz), $T_{sec} = -144$°C (0.33 Hz); (O) thick coating $T_g = 34$°C (0.39 Hz), $T_{sec} = -144$°C (0.72 Hz).

the volume of coating in Figure 6. The data plotted versus the volume of polymer coating provide a straight line that extrapolates to the low damping value of the glass fiber. It is accepted that the logarithmic decrement is proportional to the volume fraction of dissipative material,[12] provided that the geometry is unchanged.

A free film of coating material was formed and used as a conventional torsion pendulum specimen after ASTM D-2236.[13] The film was a rectangular solid with dimensions 0.063 cm × 0.254 cm × 5.40 cm. Figure 7 is a plot of the relative
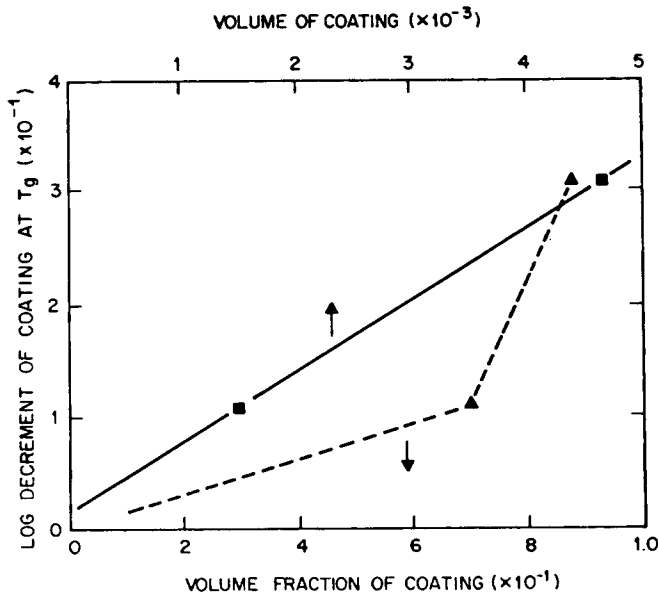

Fig. 6. Logarithmic decrement ($\triangle$) of composite at T_g of polymer coating vs. volume fraction ($\blacktriangle$) and volume ($\blacksquare$) of coating in the composite.
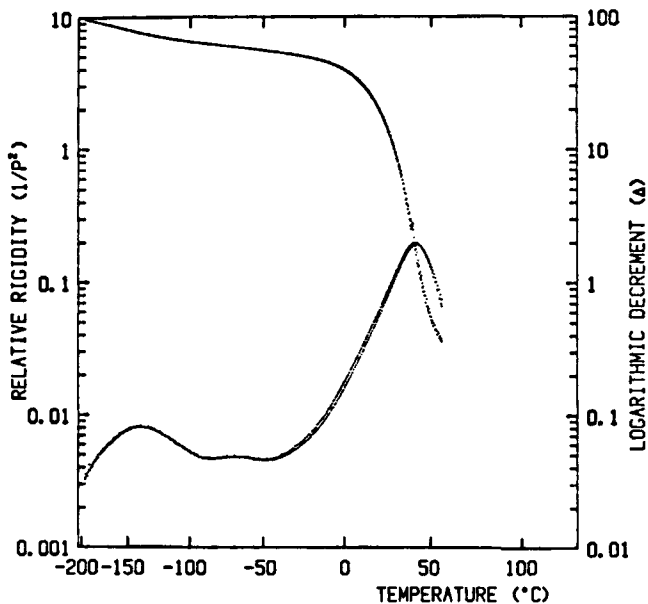
Fig. 7. Free film: relative rigidity ($1/P^2$) and logarithmic decrement (Δ) vs. T (°C). Conditioning: 60°C/1 h/dry helium. Plot: $60 \rightarrow -190 \rightarrow 60$°C; $\Delta T/\Delta t = 1$°C/min. $T_g = 40$°C (0.52 Hz) (decreasing temperature), 41.5°C (0.43 Hz) (increasing temperature). $T_{H_2O} = -71$°C (2.53 Hz), $T_{sec} = -138$°C (2.85 Hz).

rigidity ($1/P^2$), which is directly proportional to the shear modulus,[6,8] and logarithmic decrement versus temperature. The specimen had been conditioned 1 h in dry helium (ca. 50 parts per million H_2O) at 60°C, and its spectrum displayed a small but distinct damping peak between the more pronounced secondary (T_{sec}) and glass transition (T_g) damping peaks. The specimen was then further conditioned for 10 h at 60°C in dry helium, and the spectrum was again obtained (Fig. 8). The small damping peak was not present, indicating that it is associated with small amounts of water present in the polymer that are absorbed at ambient conditions. This relaxation, denoted T_{H_2O},[14] was found to be completely reversible and controllable through the humidity of the conditioning atmosphere. This result on the free film indicates that water relaxations will generally be present under use conditions of optical fiber coatings of the epoxy acrylate type when used in the absence of a dry atmosphere.

A final example consists of the dynamic mechanical analysis of a fiber coated with a different epoxy acrylate formulation from that discussed earlier. The initial temperature scan ($22 \rightarrow -190 \rightarrow 100$°C) obtained after conditioning in dry helium at 22°C for 16 h is presented in Figure 9. The spectrum shows a secondary relaxation (T_{sec}), a water relaxation (T_{H_2O}), and a complex glass transition region. The subsequent scan from 100°C ($100 \rightarrow -190 \rightarrow 115 \rightarrow 30$°C) showed no water relaxation, an increased intensity for the secondary relaxation (it has been reported[14] that the T_{sec} and T_{H_2O} relaxations are coupled), and a slightly elevated and somewhat narrower glass transition. This latter result indicates that this coating has latent reactivity at temperatures above its temperature of formation (which was essentially room temperature).
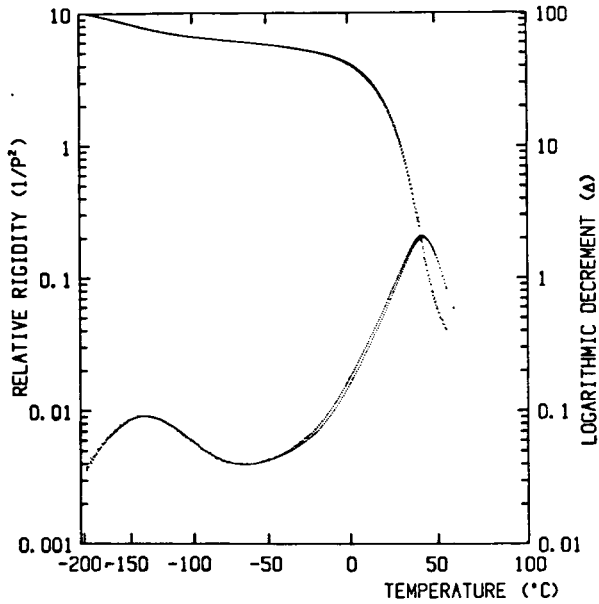
Fig. 8. Free film: relative rigidity $(1/P^2)$ and logarithmic decrement ($\triangle$) vs. T (°C) (same specimen as in Fig. 7). Conditioning: 60°C/11 h/dry helium (see also Fig. 7). Plot: $60 \rightarrow -190 \rightarrow 60$°C; $\triangle T/\triangle t = 1$°C/min. $T_g = 41$°C (0.41 Hz), $T_{sec} -134$°C (2.80 Hz) (decreasing temperature).
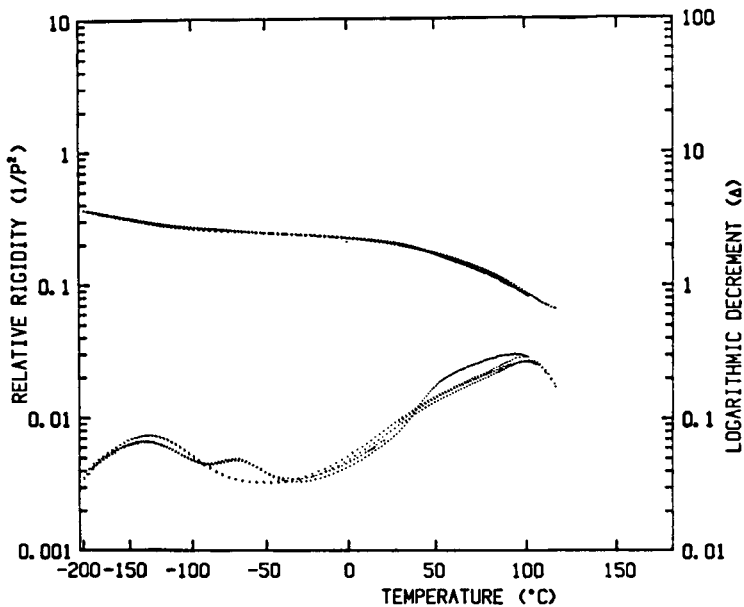
Fig. 9. Composite: relative rigidity $(1/P^2)$ and logarithmic decrement ($\triangle$) vs. T (°C). Conditioning: 22°C/16 h/dry helium. Plot: $22 \rightarrow -190 \rightarrow 100 \rightarrow -190 \rightarrow 115 \rightarrow 30$°C; $\triangle T/\triangle t = 1$°C/min. $R_1 = 0.0055$ cm, $R_2 = 0.0155$ cm, $L = 5.95$ cm; $T_g = 95$°C to 103°C, $T_{H_2O} = -67$°C (0.052 Hz), $T_{sec} = -136$°C (0.56 Hz) to -130°C (0.55 Hz).

CONCLUSIONS

Dynamic mechanical properties of the polymeric coatings of optical fibers have been measured in situ using an automated torsion pendulum. The shear modulus of the coating was calculated from the moduli of the composite and core. The glassy modulus of one coating at $-100°C$ was 2.45×10^{10} dyn/cm^2, which is in good agreement with a report on an unsupported film specimen.

Dynamic mechanical spectra of the coatings and free films were sensitive to water absorbed in the polymer which could be removed by extended periods of drying. A low-temperature water relaxation was coupled with a low-temperature relaxation of the dry polymer.

In one polymeric system, with the curing temperature ($\sim$RT) well below the maximum glass transition temperature, the material was incompletely cured. Heating above the temperature of formation increased T_g.

NOTATION

1, 2	subscripts denoting fiber and coating, respectively
A_i	peak angular deformation corresponding to cycle number i
G'	in-phase shear modulus (dyn/cm^2)
G''	out-of-phase shear modulus (dyn/cm^2)
I	moment of inertia (g-cm^2)
L	specimen length (cm)
l	spatial variable in axial direction
P	period (s)
R	radius (cm)
r	variable in radical direction
T	torque (dyn-cm)
γ	shear strain
Δ	logarithmic decrement
σ	shear stress (dyn/cm^2)
θ	angular deformation

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