

# A Tensile Rheometer for Solid Polymers Containing Volatile Diluents

M. D. MONAHAN\* and C. J. DURNING†

Department of Chemical Engineering and Applied Chemistry, Columbia University, New York, New York 10027

## SYNOPSIS

A tensile rheometer capable of confining diluent is described. This rheometer makes it possible to characterize solid samples with imbibed diluent. Tensile stress-relaxation data were obtained as a function of temperature for dry glassy semicrystalline poly(ethylene terephthalate) (PET) and as a function of composition for semicrystalline PET imbibed with dimethylformamide (DMF). Data on PET/DMF captures the glass-rubber transition as DMF content is increased. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

This article reports on the design and operating characteristics of a tensile rheometer for characterizing the linear viscoelastic properties of solid polymers imbibed with volatile diluents. We also report a preliminary set of measurements with the rheometer on a poly(ethylene terephthalate) (PET)-diluent system. There are a number of motivations for pursuing accurate rheological data on solid, polymer-diluent mixtures. First, a good understanding of the effect of diluents on the mechanical properties of thermosets and thermoplastics is critical for their effective application as load-bearing structural parts in a variety of technologies (e.g., automotive systems). Second, it is a goal of this laboratory to achieve an a priori quantitative description of non-Fickian diffusion of diluents in solid polymers. The modern theory of non-Fickian diffusion requires rheological data on a polymer-diluent system over a wide range of compositions for such predictions.<sup>1-3</sup> The measurement of the rheological behavior of polymers containing volatile diluents requires that the diluent concentration in the sample be maintained constant for the duration of the measurements. This is the important feature of the instrument described in this work. The paper is organized

as follows: First, we summarize the operating principle and physical configuration of the rheometer. Then, the rheometer's application to dry PET and to PET-diluent mixtures is discussed; this includes a detailed account of the measurement procedure and comparisons with literature data. Finally, the significant results are summarized.

## RHEOMETER DESIGN AND OPERATION

### Operating Principle of the Rheometer

A simple rheometer has been described in the literature by McLoughlin<sup>4</sup> for measuring the tensile-relaxation modulus of solidlike polymers, i.e., of polymer materials whose tactile properties are those of a solid. A linear-variable-differential transformer (LVDT) together with a calibrated, stiff spring is used to measure the force required to maintain a sample at a nearly constant tensile strain. An LVDT consists of a coil and a core and can detect a very small relative displacement of the two from the change in voltage at the coil's output. Together with a calibrated spring, an LVDT can serve as a force transducer. In the McLoughlin-Stein apparatus, the LVDT core is connected in series with a stiff calibrated spring and the sample. One applies a step strain to stretch both the sample and spring in series; this displaces the LVDT core, enabling measurement of the force. The spring is stiff enough to deflect less than 1% of the sample deflection at forces required to stretch the sample within the limit of

\* Current Address: Exxon Chemical Company, 1900 E. Linden Ave., P.O. Box 45, Linden, NJ 07036.

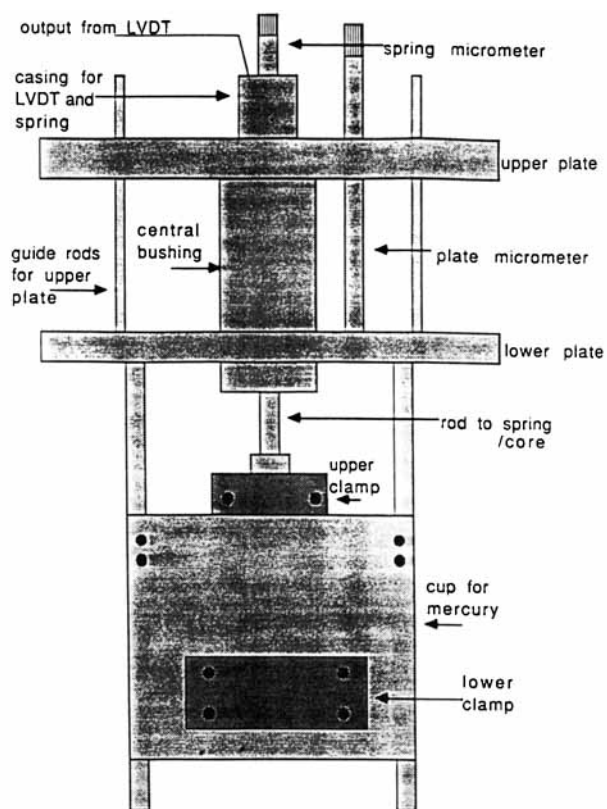
† To whom correspondence should be addressed.

linear response. So, to a good approximation, constant elongation is maintained after applying the step strain without the need of an elaborate servomotor mechanism to hold the sample length constant. The most serious source of error in the McLoughlin–Stein rheometer is the precision of the temperature control. Control to within  $\pm 0.01^\circ\text{C}$  is necessary to avoid artifacts due to thermal expansion of the structural parts in the device.

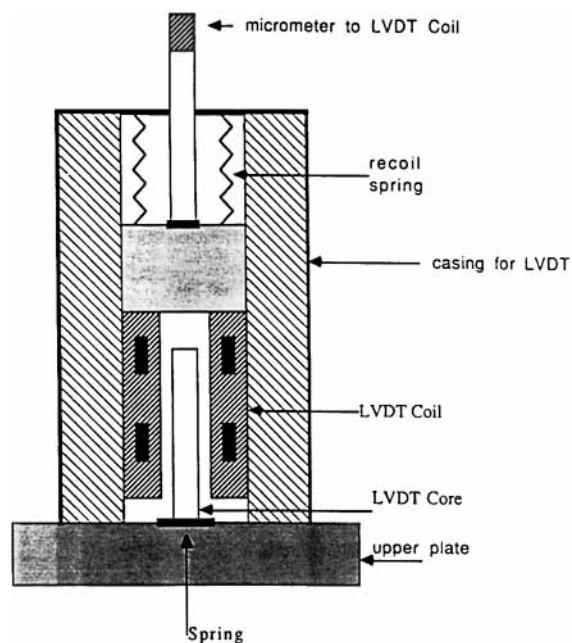
We designed and constructed a rheometer based on the McLoughlin–Stein device, with adequate temperature control and with the ability to maintain constant the concentration of a volatile diluent imbibed in the sample.

### Design of the Rheometer

As mentioned above, our device uses an LVDT as a force transducer. The LVDT that we used, a Schaevitz Model 005 MHR miniature, can accurately detect displacements on the order of  $10\ \mu$ . For a solid polymer sample 5 cm long and strained 1–2%, which is about the upper limit for linear viscoelastic response in typical cases, the sample is elongated about



**Figure 1** Schematic of clamping and stretching the sample.



**Figure 2** Schematic of mounting of the LVDT coil.

0.05–0.1 cm. The total force required to stretch a sample to this extent must displace the LVDT core by no more than 1–2% of the sample elongation, i.e., by less than about  $10^{-3}$  cm, if a nearly constant sample length is to be maintained during the relaxation experiment. To achieve this, the total force needed to deform typical polymer samples was calculated and linear springs were designed to give the required deflections. A flat circular diaphragm was chosen for the spring design. The LVDT core is screwed directly onto the flat diaphragm spring. The core therefore moves in unison with the diaphragm, which is firmly attached to a massive upper stainless-steel plate by two 2-56 Allen capscrews (see Figs. 1 and 2).

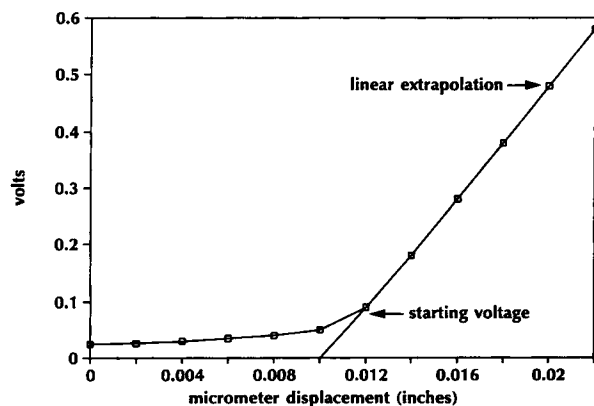
Figure 1 shows the method of clamping and stretching the sample. The lower clamp is equipped with a special cup that is filled with mercury to surround the sample and confine the diluent during operation. The polymer sample is clamped below the upper plate in series with the spring/LVDT core arrangement. The upper sample clamp is attached to a rod descending from the spring/core arrangement. The lower clamp is immobile and is rigidly attached to a separate, lower steel plate by massive steel rods. The upper plate translates vertically with respect to the lower plate. The movement is made precise by a central, annular bushing and three guide rods. Deflection of the sample is achieved by a measured vertical displacement of the upper plate relative to the lower plate after clamping the sample

as shown. The spring-core-upper clamp assembly moves with the upper plate while the lower clamp remains stationary with the lower plate. So, when the distance between the plates is increased, the polymer sample is stretched uniaxially. The vertical displacement is applied through a micrometer mounted on the upper plate and pressing against the lower plate. A nominal sample elongation is obtained from the micrometer. The clamped sample is not visible because of the cup, so the following protocol was developed to find a reproducible zero position from which the straining of the sample begins.

After clamping a sample, a series of micrometer displacements (each 0.002 in.) is executed and voltage readings are recorded. A plot of the voltage output vs. the displacement shows the onset of a linear increase of voltage with displacement. Figure 3 shows typical data for a PET film strip sample (dimensions  $0.015 \times 1.27 \times 10.16$  cm). A least-squares extrapolation is done of the linear portion of the data to intersect zero voltage. This extrapolated line makes clear where a linear response begins; the "starting" voltage corresponding to zero strain is taken as the point where the data first deviate significantly (by more than 5%) from the linear least-squares fit (see Fig. 3).

### The LVDT Force Transducer

When the sample is strained by displacing the upper plate, the upper clamp transmits a vertical force to the diaphragm-spring/core arrangement, causing a slight downward displacement of the core. (As mentioned, this displacement is a small fraction of the polymer sample elongation.) One can detect the displacement of the core as a change in the LVDT out-



**Figure 3** Representative data illustrating the protocol for determining zero strain.

put voltage and this supplies a continuous record of the force after suitable calibration (see below). The LVDT coil requires an ac excitation voltage for proper operation. The excitation is provided by a power supply built into a signal conditioning unit (Schaevitz Model CAS-025). The coil returns an ac output voltage proportional to the core displacement. This is rectified to dc and amplified by the signal conditioner to give a typical dc output of several volts for a 0.0025 cm core displacement.

For convenient set up and proper operation, the LVDT coil must have a stable mounting and be precisely movable. The coil of the LVDT is mounted on the upper plate inside a steel cylinder (see Figs. 1 and 2). The mount ensures that the coil and core are concentric and allows precise vertical displacements of the coil to enable set up. The vertical displacement is provided by a micrometer mounted in the cylinder and pressing on the coil. Springs attached to the coil ensure contact between the micrometer and coil, as illustrated in Figure 2.

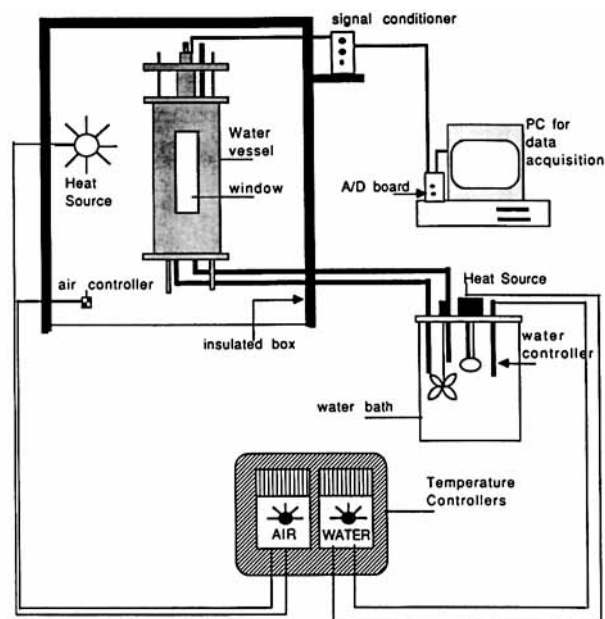
### Auxiliary Equipment

Dual temperature control was installed to ensure that temperature fluctuations do not exceed  $\pm 0.01^\circ\text{C}$  in the sample's environment. The upper/lower clamp assembly fits into a jacketed steel vessel through which temperature-controlled water is circulated. The temperature of the circulating water is controlled to within  $\pm 0.01^\circ\text{C}$  using an on-off temperature controller (Yellow Springs Instrument, Model 63RC). The clamp assembly and jacketed vessel are enclosed in an insulated box. The air temperature in the box is controlled to within  $\pm 0.1^\circ\text{C}$  using a second temperature controller. Figure 4 gives a schematic of the apparatus showing the temperature-control systems.

A data acquisition system consisting of an IBM-AT computer equipped with a data acquisition board (MetraByte Dascon-1 A-D) was the primary means of recording the LVDT output during a relaxation experiment.

### Calibration Technique

A calibration must be done so that the signal recorded by the computer can be interpreted as a force on the sample. A long calibration rod replaces the upper clamp and the lower clamp is removed entirely (see Fig. 1). Weights are then added to a pan on the end of the calibration rod. After aligning and zeroing the LVDT, a calibration is prepared for the computer output, proportional to the rectified LVDT



**Figure 4** Schematic representation of the stress relaxometer system.

coil output voltage, vs. the total weight deflecting the spring (pan weights and calibration rod weight). To test the procedure, calibrations were performed both before and after each of two series of relaxation experiments, one at 35°C and another at 55°C. There were no detectable differences between the calibrations done before and after each series of experiments. Also, the slopes of the calibrations performed at the two different temperatures were within a few percent of one another. The correlation coefficients of least-squares fits for the weight vs. computer output were typically 0.998–0.999. As a standard protocol, a new calibration was performed prior to each series of relaxation measurements.

## STRESS-RELAXATION EXPERIMENTS

### Material

Poly (ethylene terephthalate) (PET) was obtained from the DuPont Company. The material was received as quenched amorphous, unoriented sheets of nominal thickness 0.0127 cm. The actual thickness was  $0.015 \pm 3 \times 10^{-4}$  cm as determined from repeated measurements with a gauge micrometer. The dry film sheets were cut into strips suitable for stress-relaxation experiments. Each sample strip was roughly  $1.27 \times 10.16$  cm. The strips were annealed by the following procedure:

- (i) heating under vacuum at 80°C for 24 h,
- (ii) heating under vacuum at 120°C for 48 h, and
- (iii) slow cooling in oven to room temperature.

The above annealing procedure produces a stable, unoriented semicrystalline morphology. In our case, the crystalline volume fraction,  $\alpha_C$ , was determined by density to be about 0.27.<sup>5</sup> The semicrystalline morphology resulting from this procedure has been studied in great detail by others.<sup>6–8</sup> The crystallization takes place only slightly above the glass transition where the chain segments have limited mobility. Wide-angle X-ray<sup>7</sup> and FTIR<sup>6</sup> measurements indicate that imperfect lamellar crystallites develop (i.e., a small long-spacing results), and the remaining disordered phase contains stretched, taut tie molecules between crystallites. The latter feature is indicated by the relatively large fraction of *trans* conformers of the glycol linkage in the disordered regions.

The glass transition temperature of the annealed samples, determined from DSC experiments at 10°C/min, was found to be 80°C. This value is elevated over that for the amorphous polymer ( $\approx 75^\circ\text{C}$ ), presumably because of the restrictions on chain segment mobility imposed by the crystallites.<sup>9</sup> The linear viscoelastic properties of PET prepared in nearly the same way have been studied by Ward.<sup>10</sup>

The diluent used in this work was reagent-grade anhydrous dimethylformamide (DMF) obtained from Fisher Scientific and was used as received. Care was taken to avoid exposure of the DMF to ambient moisture.

### Preparation of Diluent-imbibed Samples

To obtain homogeneous samples imbibed with diluent, strips of the dry, semicrystalline film were placed in the liquid diluent at about 60°C until they were fully swollen. The diluent was then desorbed until the desired overall diluent weight fraction was obtained. These partially swollen samples were then confined under mercury for several weeks to eliminate concentration gradients. The homogeneous samples were finally reweighed after storage in mercury just prior to experimental measurements. All weighings were done on a Mettler electronic balance (sensitivity  $\pm 0.0001$  g).

The diluent absorbed does not significantly penetrate the crystals in the polymer, but resides mainly in the amorphous regions.<sup>11</sup> Knowing the crystalline

volume fraction for the dry polymer,  $\alpha_c$ , enables calculation of the diluent weight fraction in the amorphous phase,  $\omega_1^*$ :

$$\omega_1^* = \omega \frac{\rho_T}{\rho_a(1 - \alpha_c)} \quad (1)$$

where  $\rho_a$  is the density of the pure, amorphous polymer; and  $\rho_T$ , the overall, dry semicrystalline polymer density. Equation (1) assumes zero excess volume and no change in  $\alpha_c$  upon absorption of the diluent; both assumptions are reasonable.<sup>5</sup> The value of  $\rho_a$  was taken as 1.335 g/cm<sup>3</sup>; the value of  $\rho_T = 1.382$  g/cm<sup>3</sup> was measured by Billovits and Durning,<sup>5</sup> using the density gradient method.

In subsequent sections, we report the nominal diluent weight fraction,  $\omega_1^*$ , based on the final reweighing described above. A typical uncertainty in  $\omega_1^*$  is  $\pm 0.0005$  as determined by repeated measurements. One should note that to load a sample into the rheometer typically requires about 10 min. During this time, some desorption of diluent occurs; the significance of this depends on the initial weight fraction of the diluent. Control experiments showed that the amount of DMF desorption during a typical loading procedure was insignificant ( $< 1\%$ ) for initial overall weight fractions below about 10%; above this level, up to several weight percent of DMF could be lost during the loading process.

### Mercury as a Penetrant Barrier

The rheometer was designed to enable experiments on diluent-imbibed polymer films. A stainless-steel cup connected to the lower clamp structure and filled with mercury was intended to confine the diluent within the sample during operation. This section describes several simple experiments demonstrating that the mercury adequately confines a volatile diluent during typical stress-relaxation measurements.

In the simplest test, samples imbibed with DMF were immersed in mercury in ordinary test tubes and left for several weeks at room temperature. Weighing before and after showed that confinement under mercury kept the diluent concentration constant to within a fraction of a percent.

In a second series of experiments on DMF-imbibed samples, the DMF concentration was measured before and after typical stress-relaxation measurements. For samples with less than about 10 overall wt % DMF, the composition remained the same before and after the experiment to within a fraction of a percent. Samples with more than about 10 wt % showed a significantly lower DMF content

after a typical experimental run. We were able to show by the following two experiments that the loss of diluent for highly swollen samples was mainly from the clamped portion of the sample and not from where the stretching occurs, i.e., not from the part of the sample surrounded by mercury.

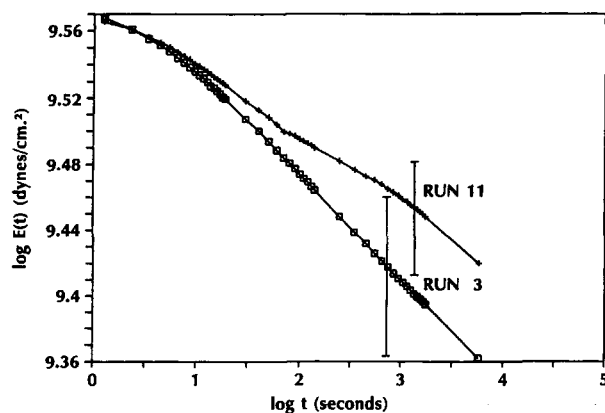
First, the DMF concentration in the stretched section of the sample (i.e., the portion not clamped) was determined before loading and after a typical run. To accomplish the calculation, a sample was subject to a stress-relaxation run. Afterward, the end portions that had been under the clamps were cut off and desorbed of diluent by air drying at room temperature for 8 h followed by leaching in boiling methanol for 24 h and then by drying under vacuum at 80°C for an additional 24 h. The weight of the dry ends was subtracted from the initial dry weight of the polymer sample to arrive at the initial dry weight of the stretched part. This allowed calculation of the final weight fraction of diluent in the stretched portion from the weight of the imbibed, stretched portion measured immediately after cutting off the clamped ends. The calculations showed weight losses of diluent from the stretched portion at the same level as found during the time for loading of the sample into the rheometer.

This finding was reinforced in a second experiment. A sample with diluent was introduced into the rheometer and a series of stress-relaxation runs was done. The initial set of runs was done at 35°C and gave reproducible stress-relaxation data after the first run. The same sample was kept in the rheometer and used to obtain data at 45 and at 55°C. Reproducibility was also achieved at these higher temperatures. The temperature was then returned to 35°C and the resulting relaxation data was found to be within an acceptable experimental uncertainty ( $\pm 10\%$ ) of the data measured nearly 2 weeks earlier. Figure 5 displays the data, which were obtained on a sample with  $\omega_1^* = 0.149$ .

The results of these tests strongly suggest that the diluent concentration remains essentially constant in the stretched portion of the sample confined under mercury during typical stress-relaxation runs.

### Procedure for Stress-relaxation Measurements

We performed stress-relaxation experiments on dry PET at various temperatures in the range 35–55°C and on DMF-imbibed samples at 35°C using the following procedure: After preparing a sample and introducing it into the rheometer, it was held without applied stress for about 1 day at the lowest temperature to be studied to ensure thermal equilibrium.



**Figure 5** Tensile-relaxation moduli on a PET-DMF sample ( $\omega_1^* = 0.149$ ) at 35°C. The two runs were performed nearly 2 weeks apart. Error bars show experimental uncertainty.

To begin a series of experiments, a step strain is applied from the starting voltage determined from the protocol described earlier. A sequence of runs was then performed to achieve acceptable reproducibility ( $\pm 10\%$ ) in the tensile-relaxation modulus,  $E(t)$ , in two consecutive runs; this usually occurred after the first or second run. After achieving reproducibility, the temperature in the rheometer was then increased and a new series of runs was performed.

Each relaxation experiment was carried out for at least 16 h. However, the details of the initial stretch affected the short-time scale data and instrument drift adversely affected the long-time scale data. Consequently, in what follows, we report the  $E(t)$  curves for the time scale  $10 < t < 35$  ks. Results over this time scale showed acceptable reproducibility.

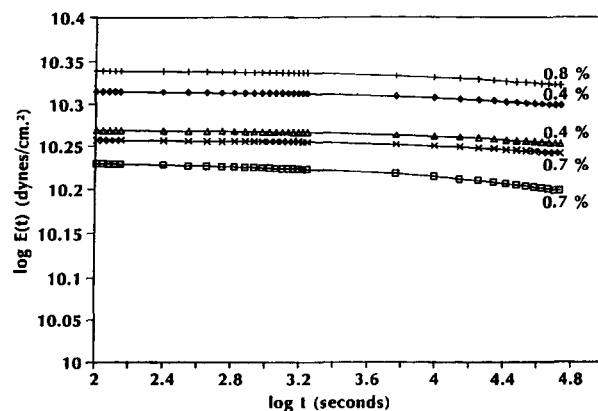
### Experiments on Dry PET

Table I shows the experiments performed on dry PET samples. In the linear viscoelastic limit, the measured relaxation modulus should not depend on the imposed strain. We therefore performed a series of experiments (runs 1–6 in Table I) to determine the limit of linear viscoelasticity for dry PET at 35°C, i.e., the imposed strain below which the relaxation modulus is only a function of time and temperature. Runs 1–6 are first-run data on separate virgin PET samples. Runs 6–10 were performed on the same sample to investigate if the first-run data differed significantly from subsequent data obtained from restraining a single sample.

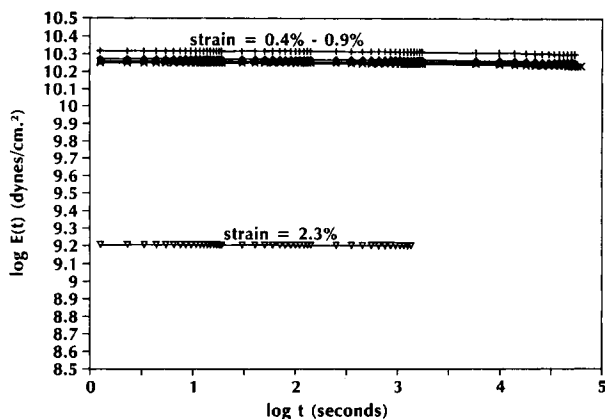
**Table I** Experiments Performed

Run #	Sample	$T$ (°C)	Strain (%)
1	A	35	0.4
2	B	35	0.4
3	C	35	0.7
4	D	35	0.8
5	E	35	2.3
6	F	35	0.7
7	F	35	0.9
8	F	35	0.7
9	F	55	0.7
10	F	55	0.9

Figure 6 shows the effect of strain for runs 1–4 and 6. As can be seen, there is no systematic variation with strain in this range. Figure 7 shows data including run 5 for a much larger strain of 2.3%; the  $E(t)$  curve is clearly depressed by about an order of magnitude relative to the data in Figure 6. The instantaneous modulus decreases from about  $1.9 \times 10^{10}$  dynes/cm<sup>2</sup> for the small strains in Figure 6 to about  $1.6 \times 10^9$  dynes/cm<sup>2</sup> for an initial nominal strain of 2.3%. Evidently, a nonlinear response appears for initial strains,  $\epsilon_0$ , greater than about 1%. This value is consistent with the limit of linear response reported by others for semicrystalline glassy polymers. For example, for a variety of semicrystalline linear aromatic polyesters, Ng and Williams<sup>12</sup> found that strains of less than 0.7% were necessary to remain within the linear viscoelastic limit. Also, the trend of a depressed relaxation modulus upon entering the nonlinear regime for semicrystalline polymers has been reported previously. Passaglia



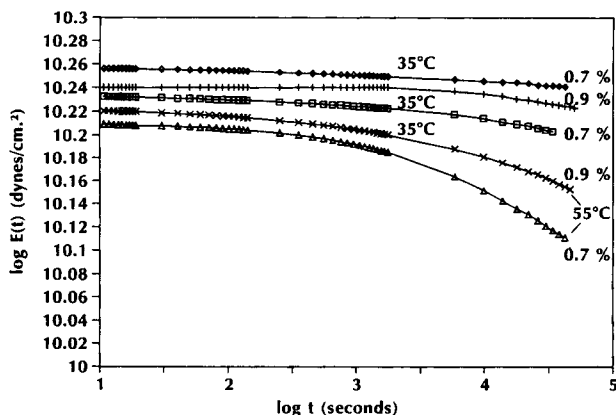
**Figure 6** Stress-relaxation data at 35°C for dry semicrystalline PET showing reproducibility for strains under 1%.



**Figure 7** Stress-relaxation data at 35°C for dry semi-crystalline PET showing nonlinear response at larger strains.

and Koppehele<sup>13</sup> studied unoriented cellulose monofilaments and found that the stress-relaxation modulus systematically decreased with  $\epsilon_0$  for  $0.56\% < \epsilon_0 < 4.5\%$ . Figure 6 shows that within the linear regime the rheometer can determine  $E(t)$  data reproducibly to within about  $\pm 10\%$ .

Figure 8 shows stress-relaxation curves for repeat runs on the same sample at 35 and 55°C. The sequential experiments gave  $E(t)$  curves to within  $\pm 10\%$  at each temperature for all runs. No significant difference was detected between the first run on the sample and subsequent runs. The instantaneous moduli,  $E_0$ , have an average value of  $1.8 \times 10^{10}$  dynes/cm<sup>2</sup> at 35°C and  $1.6 \times 10^{10}$  at 55°C and so are the same to within the experimental uncertainty. In fact, the  $E(t)$  curves at 35 and 55°C are within experimental error over the whole time scale of observation.



**Figure 8** Stress-relaxation data at 35°C for dry semi-crystalline PET.

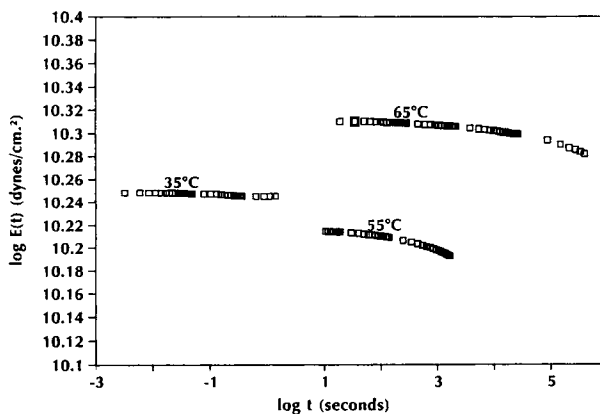
Ward<sup>10</sup> studied the linear viscoelasticity of unoriented, semicrystalline PET fibers by tensile creep experiments. The samples were unoriented, heavy monofilaments crystallized by annealing at 180°C for 1 h. The crystallinity reported, from X-ray diffraction, was 33%. Creep measurements were made at temperatures between 65 and 115°C to supply the creep compliance,  $J(t)$ . Ward's results can be converted into a relaxation modulus by the approximate relation  $E(t; T) \simeq 1/J(t; T)$ .<sup>14</sup> With this conversion, a direct comparison can be made between Ward's data and ours after appropriate corrections for temperature differences.

Ward reported that above the glass transition,  $T_g$ , the creep compliance data obeyed time-temperature superposition with  $a_T$  according to the WLF equation with universal constants. However, for conditions well below  $T_g$ , it is often found that  $a_T$  obeys an Arrhenius relation. For example, McCrum and Morris<sup>15</sup> found this for poly(methyl methacrylate) well in the glassy region. The Arrhenius form for  $a_T$  is

$$\log a_T = \frac{\Delta H}{2.303R} \left[ \frac{1}{T} - \frac{1}{T_0} \right] \quad (2)$$

where  $\Delta H$  is an activation energy, and  $R$ , the universal gas constant. McCrum and Morris found  $\Delta H = 26$  kcal/mol in glassy poly(methyl methacrylate). We used this value of  $\Delta H$  as a provisional calculation of  $a_T$  well in the glassy region for PET.

Figure 9 shows Ward's 65°C data, corrected in this provisional way, plotted together with ours. All the data were reduced to 35°C without vertical shifting. The vertical displacement of Ward's data from ours is within experimental error of  $\pm 10\%$ .



**Figure 9** Stress-relaxation data (our data at 35°C and 55°C; Ward's data at 65°C) for dry PET, all corrected to a reference temperature of 35°C using an Arrhenius relation.

Both our and Ward's data decay in a similar way over an equivalent time period. By this rough calculation, it appears that our data compare reasonably well with Ward's, indicating that the rheometer can reproduce literature data to within 10% under rather demanding circumstances (glassy, semicrystalline polymer).

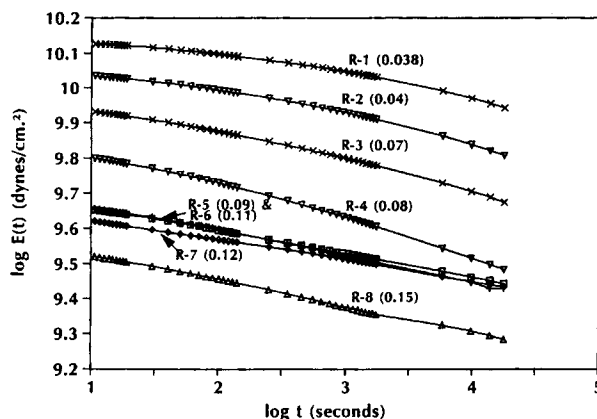
### Experiments on PET-DMF Mixtures

We now describe the results of stress-relaxation measurements on DMF-imbibed PET samples at 35°C. Table II gives nominal compositions ( $\omega_1$  and  $\omega_1^*$ ) and designators for the samples tested.

At each composition, an averaged relaxation modulus curve was prepared as follows: The sample was loaded into the rheometer and the first run was obtained. Experiments were then repeated until successive runs were within  $\pm 10\%$ . This always occurred within four runs beyond the first. Once two reproducible runs are obtained, they were averaged to obtain a relaxation modulus curve.

Figure 10 shows averaged relaxation data at 35°C. The relaxation modulus decreases strongly with increasing diluent concentration; there is almost an order of magnitude drop in  $E(t)$  between the least and most highly swollen samples.

The qualitative appearance of the plots strongly suggests that the experimental conditions span the transition zone as the composition increases. In particular, the data show a progression with increasing composition, resembling that expected for  $E(t)$  curves in a dry, glassy specimen as one increases temperature through  $T_g$ . For example, note that the curves at higher concentrations converge together beyond a certain critical value of  $\omega_1^*$ , rem-



**Figure 10** Stress-relaxation data at 35°C for different concentrations of DMF ( $\omega_1^*$  indicated in brackets) in PET prepared by LTA.

iniscent of encountering the plateau zone in a progression with increasing temperature through  $T_g$ .

The direct calorimetric measurements of  $T_g$  verify that the conditions summarized in Table I indeed span the transition zone.<sup>16</sup> The samples with low DMF weight fractions are glassy, but for higher DMF fractions, the samples are clearly rubberlike. The transition to rubberlike behavior occurs at  $\omega_1^* = 0.09$  for  $T = 35^\circ\text{C}$ . A complete account of the time-temperature-concentration shifting for this system can be found in Ref. 16.

### SUMMARY AND CONCLUSIONS

A tensile rheometer capable of characterizing solid samples with imbibed volatile diluents was designed and constructed. Tensile stress-relaxation data were obtained as a function of temperature for dry glassy semicrystalline PET and as a function of composition for semicrystalline PET imbibed with DMF.

The data on dry PET demonstrated the limit of linear viscoelastic response to be 1% strain. Agreement between our results for dry PET and those published by Ward<sup>10</sup> developed confidence in the rheometer.

We demonstrated that the ability of the rheometer to confine diluent is acceptable. Data on PET/DMF shows the glass-rubber transition as the DMF content is increased.

This device should prove useful in selecting thermosets and thermoplastics for applications as structure parts where aggressive liquid or vapor environments are expected. This instrument will provide the data needed for the critical test of the theory for non-Fickian diffusion of fluids in solid polymers.

**Table II** Samples\* for Stress-relaxation Runs

Designator	$\omega_1^b$	$\omega_1^{*c}$
R-1	0.027 $\pm$ 0.0004	0.038 $\pm$ 0.0005
R-2	0.028 $\pm$ 0.0004	0.040 $\pm$ 0.0005
R-3	0.050 $\pm$ 0.0005	0.070 $\pm$ 0.0007
R-4	0.055 $\pm$ 0.0005	0.080 $\pm$ 0.0007
R-5	0.066 $\pm$ 0.0005	0.090 $\pm$ 0.0007
R-6	0.078 $\pm$ 0.0003	0.110 $\pm$ 0.0004
R-7	0.08 $\pm$ 0.0008	0.12 $\pm$ 0.001
R-8	0.105 $\pm$ 0.0003	0.15 $\pm$ 0.0004

\* PET prepared by LTA procedure and imbibed with DMF.

<sup>b</sup>  $\omega_1$  = grams DMF/grams semicrystalline PET.

<sup>c</sup>  $\omega_1^*$  = grams DMF/grams amorphous PET.



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