

# Stress Relaxation Behavior of Biaxially Oriented Poly(ethylene Terephthalate)

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## Synopsis

The stress relaxation behavior of biaxially oriented semicrystalline poly(ethylene terephthalate) was studied by thermomechanical analysis. Experimental techniques were developed for thin films. Relaxation moduli were measured as a function of stress, time, and temperature. The relaxation modulus was shown to be independent of stress over the range tested. Rate of loss of the relaxation modulus was found to be a nonlinear function of time and temperature up to about 100°C, encompassing the  $T_g$  for the polymer. Over the temperature range of 100–120°C it was primarily temperature-dependent. An empirical time-temperature superposition showed that significant losses in modulus can occur at very short times. At temperatures above the  $T_g$  these losses can result in significantly reduced film physical properties.

## INTRODUCTION

Biaxially oriented, semicrystalline poly(ethylene terephthalate) (PET) film is extensively used as a base film for flexible magnetic recording media. It provides a unique combination of physical and chemical properties that meet the demanding technical and physical requirements of the industry. Coating processes for the application of magnetic oxides expose the thin PET films to elevated temperatures and tensions in the presence of organic solvents. Some of these solvents, e.g., cyclohexanone, act as plasticizers for the film. Maintenance of film dimensional stability and property uniformity is crucial to production of media intended for high recording densities. Stability and uniformity are primarily dependent on the initial physical properties of the film. However, these properties can be significantly altered by subsequent processing steps. They generally decrease and the changes are experimentally relatable to the viscoelastic response of the film.

A large amount of viscoelastic data have been reported for PET. Stress relaxation data have been reported for both the amorphous and the spherulitically crystalline films<sup>1-3</sup> for oriented PET fibers,<sup>4</sup> and for a thick (33- $\mu\text{m}$ ) biaxially oriented film.<sup>5</sup> No information has been reported for the stress relaxation behavior of thin biaxially oriented films.

For fibers, increasing the oriented crystalline structure increases the modulus with little effect on time dependence<sup>4</sup> of the modulus. The temperature dependence is less than that of unoriented amorphous film. There is a definite interaction between the oriented crystalline structure and physical properties of PET films.<sup>6,7</sup> This is observed in the stress relaxation behavior and in nearly all physical and mechanical properties of the film.

This paper describes experimental techniques developed to measure the stress relaxation behavior of thin PET films using the du Pont 943 Thermomechanical

Analyzer (TMA) module with the stress relaxation accessory. Data are reported for a 14.5- $\mu\text{m}$  film.

## EXPERIMENTAL

Measurements of relaxation modulus were made using a du Pont 990 Thermal Analysis System with the 943 Thermomechanical Analyzer (TMA) and the stress relaxation accessory. The TMA converts from strictly a displacement sensing instrument to a force-measuring transducer by adapting a passive mechanical stress relaxation accessory to the sample clamping device. The stress relaxation accessory and the system LVDT work in conjunction to provide force transducing capability. The system uses a load cell with its spring positioned in parallel with the sample. The load cell constant is chosen so that sample stress relaxation can occur at approximately constant strain as a function of time.

All measurements were made on PET films of 14.5- $\mu\text{m}$  thickness. Physical properties were typical of those for commercially produced Mylar® of that thickness. Polymer intrinsic viscosity was 0.56, measured in 60/40 TCE/Phenol mixture at 30°C. Diethylene glycol content was 1.50 mol%, measured by gas chromatography. Biaxial orientation was achieved by stretching approximately 3.6 times in the longitudinal direction followed by stretching approximately 4.0 times in the transverse direction. The oriented films were heat set at 210°C, resulting in a density of 1.3925 g/cc.

Film samples were stored at ambient temperature (22°C) and relative humidity (50–60%) in a laboratory environment for at least 24 h prior to their use.

All measurements were for the longitudinal direction, or length direction in a roll of film. Sample dimensions were 5.2 mm wide by 6.5 mm long by 14.5  $\mu\text{m}$  thick. Figure 1 shows a sample mounted in the stress relaxation probe.

Due to the low stiffness of the thin film, alignment in the sample holder was difficult. Misalignment and nonflatness had to be minimized to obtain reproducible data. All measurements were made with the furnace and Dewar flask in place to minimize convective effects.

Even with careful mounting of the film sample, some nonflatness and misalignment always remained. It was necessary to remove the compliance due to this sample nonflatness and also a small compliance that existed in the measurement system. This was done by applying a small stress with the load cell. The applied stress was the minimum amount that produced a constant calculated value for Young's modulus at room temperature. Sample strain was less than 0.2%.

To determine the initial modulus of the film, a stress, either 13.0 or 24.7 MPa corresponding to 100- and 200-g loads on the load cell, was applied and removed rapidly. The average strain from five measurements was used to calculate the modulus. The appropriate stress, either 13.0 or 24.7 MPa, was then applied to the sample and the stress decay followed as a function of time for 100 min. The total applied stress was then removed, and the sample allowed to recover. Recovery was deemed to be complete when sample length, as indicated by the LVDT measuring system on the 990 Thermal Analyzer, remained unchanged for at least 1 h, at constant temperature. Recovery was rapid at temperatures below 80°C but required as long as 4 h at the higher temperatures. After recovery was

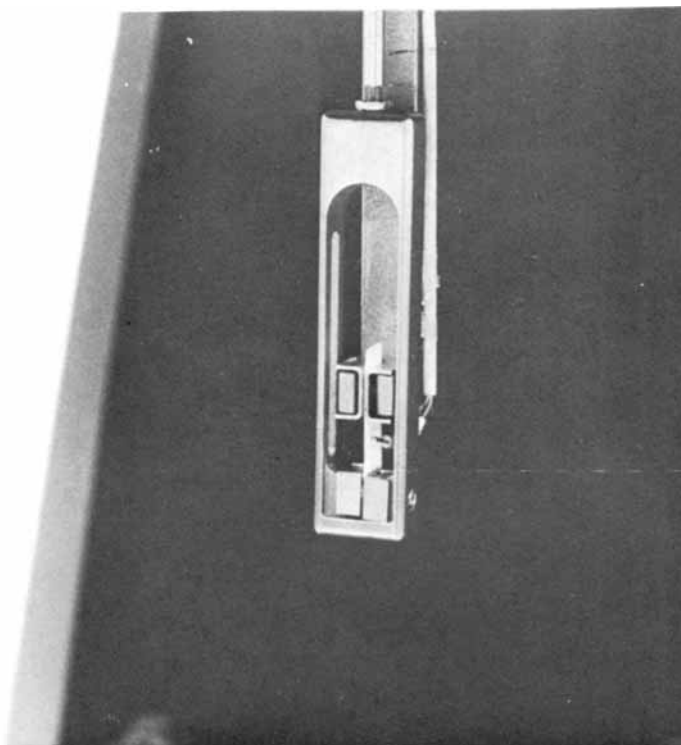


Fig. 1. Stress probe for du Pont 943 TMA.

complete, the sample was heated to the next higher temperature and the procedure repeated. No effort was made to use specific increments in temperature but control was within  $\pm 0.5^\circ\text{C}$ .

Measurements were made on three different samples at the two stress levels. The relaxation modulus was calculated from the following equation:

$$E_r T = \frac{\text{stress}}{\text{strain}} = \frac{[W - K \cdot S(t)]g}{A} \left[ \frac{S(t)}{L} \right]^{-1}$$

where  $E_r T$  = relaxation modulus (Pa),  $W$  = weight used (kg),  $L$  = length of sample (m),  $A$  = cross section area ( $\text{m}^2$ ),  $g$  = gravitational constant ( $\approx 9.8 \text{ m}\cdot\text{s}^{-2}$ ),  $K$  = force gradient of load cell (kg/m), and  $S(t)$  = displacement at time  $t$  (m).

## RESULTS AND DISCUSSION

The stress relaxation behavior of biaxially oriented semicrystalline PET film was measured at stresses of 13.0 and 24.7 MPa. The initial stress decreased as the temperature was incrementally increased to  $140^\circ\text{C}$ . Data in Table I show that only a small decrease occurred until the temperature reached  $75\text{--}80^\circ\text{C}$ . This temperature is just above the glass transition temperature (ca.  $69^\circ\text{C}$ ) of the unoriented, amorphous polymer.<sup>8</sup> The stress decayed rapidly with further increases in temperature due to much higher polymer chain mobility. While the observed effect is related to the  $T_g$ , in an oriented semicrystalline film the  $T_g$  is a function of both orientation and crystallinity. The effects are generally observed over a broad temperature range.

TABLE I  
Film Stress at 100 and 200 g Loads

Temperature (°C)	$\sigma_{100}$ (MPa)	$\sigma_{200}$ (MPa)
22	13.0	24.7
52	12.8	24.1
60	14.1	24.1
77	12.6	23.9
87	9.4	22.6
108	9.9	19.6
115	9.8	16.5
127	9.3	12.2

TABLE II  
Values of  $a_T$  Used to Superpose Stress Relaxation Data

Temperature (°C)	$\log a_T$	Temperature (°C)	$\log a_T$
22	5.42	82	0
33	4.15	87	-0.55
43	2.70	94	-1.30
52	2.00	108	-2.55
60	1.35	115	-3.25
69	0.80	128	-4.28
77	0.30	140	-5.38

The time-dependent stress relaxation data, shown in Figure 2, are typical of those obtained for the biaxially oriented, semicrystalline films. Each isothermal curve shows the effect of the initial stress loading and also the subsequent time-dependent stress relaxation. The increased rate of stress relaxation at temperatures above the polymer  $T_g$  is readily seen as the broadening of the curve spacing over the 60–108°C temperature range. The rapid flattening of these curves in the 108–128°C region is as yet unexplained.

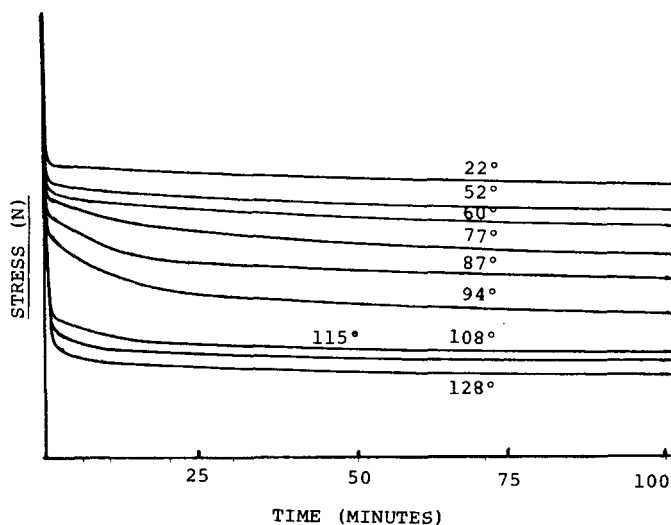


Fig. 2. Isothermal stress relaxation as a function of time.

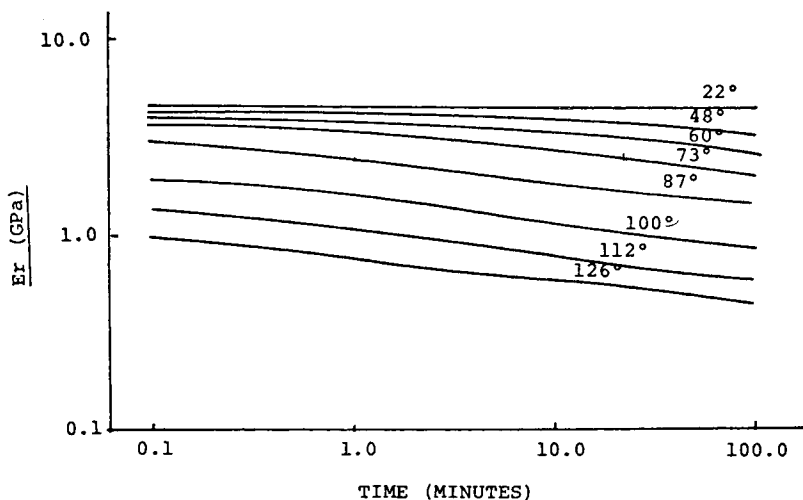


Fig. 3. Relaxation modulus as a function of time at an initial stress of 24.7 GPa.

Relaxation moduli ( $E_r$ ) were calculated. Typical results are shown in Figure 3. The magnitudes of the calculated relaxation moduli were independent of the initial stress over the range tested. Data for the same film at a 13.0-MPa stress will superimpose those in Figure 3 within experimental error. The strain in the sample resulting from these stress levels was  $\leq 0.5\%$ . At higher loads the stress-strain behavior is not linearly related.

An empirical horizontal shift of the stress relaxation modulus vs. time curves was done and the horizontal shift factors ( $\log a_T$ ) were calculated. These calculated  $\log a_T$  shift factors at 82°C are in Table II and are shown graphically vs. temperature in Figure 4. The 82°C temperature was chosen because it is about the midpoint of the temperature range over which  $T_g$  effects are seen in biaxially oriented semicrystalline PET film. The data show a linear relationship from ambient to about 45°C. At temperatures of about 90°C and higher, a second linear region of different slope is found. From 45°C to 90°C the  $\log a_T$  are

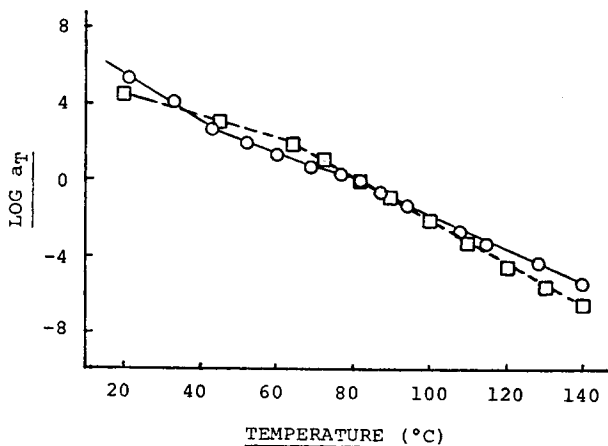


Fig. 4.  $\log a_T$  shift factors, calculated at 82°C, vs. temperature. (O) biaxially oriented film, (□)  $T = 82^\circ\text{C}$  (Murayama et al.) uniaxially oriented fiber.

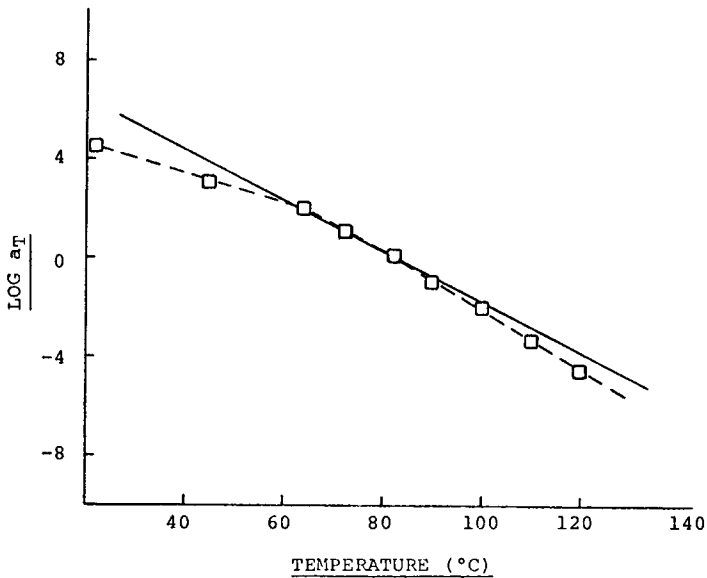


Fig. 5. Linear relationship of  $\log a_T$  vs. temperature, at  $82^\circ\text{C}$ . ( $\square$ )  $T = 82^\circ\text{C}$  (Murayama et al.).

nonlinear. This temperature range includes the glass transition temperature ( $69^\circ\text{C}$ ) for the polymer. It also is the range over which other time-dependent physical properties exhibit nonlinearity, e.g., thermal expansion.

The data of Murayama et al.<sup>4</sup> obtained from dynamic mechanical measurements on an oriented, annealed PET fiber are shown for comparison. Though generally of the same magnitude, they are very different. Both indicate a discontinuity due to  $T_g$  effects but indicate different behavior below  $T_g$  for the uniaxial orientation. Structural differences between oriented fibers and films have been reported by others<sup>9</sup> from low angle X-ray scattering studies.

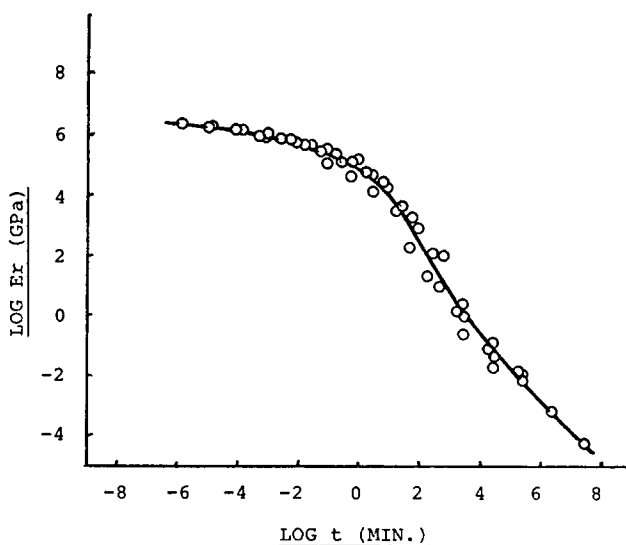


Fig. 6. Superposed data from the linear  $\log a_T$  vs. temperature relationship.

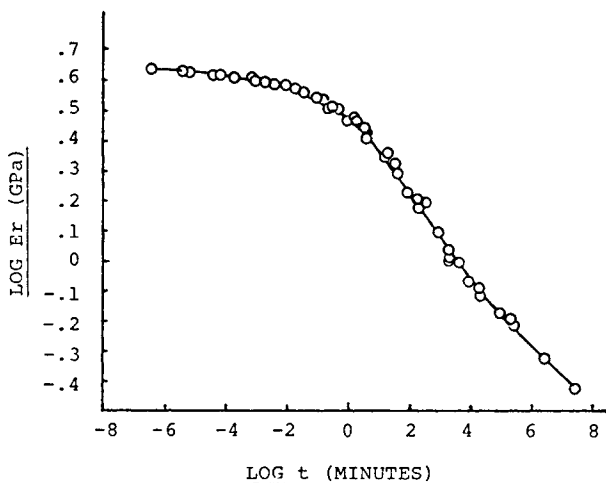


Fig. 7. Superposed data from the calculated  $\log a_T$  shift factors at 82°C.

Forcing the  $\log a_T$  data to the best linear relationship results in a  $\log a_T$  vs.  $T$  relationship as shown in Figure 5. The slope of the line is  $-0.088$  compared to a slope of  $-0.11$  from the data of Murayama et al.<sup>4</sup> However, Figure 6 shows that a linear fit of the  $\log a_T$  data does not result in a good fit for the superposed data. Substantial dispersion occurs in the data taken from temperatures higher than 45°C. When the calculated  $\log a_T$  shift factors from Table II are used, a smooth modulus-time curve is obtained, as shown in Figure 7.

The modulus-time curve shows that measurable losses in modulus occur at very short times. Superposition of the data at temperatures between 100 and 120°C shows that significant losses of modulus can occur over the time period and stress levels measured. These results confirm that exposure to high temperatures is a major contributor to property loss in polyester film products that have been coated or have otherwise undergone thermal treatments. The isochronal plot of  $\log E_r$  vs.  $\log T$  in Figure 8, over three decades of time, shows that,

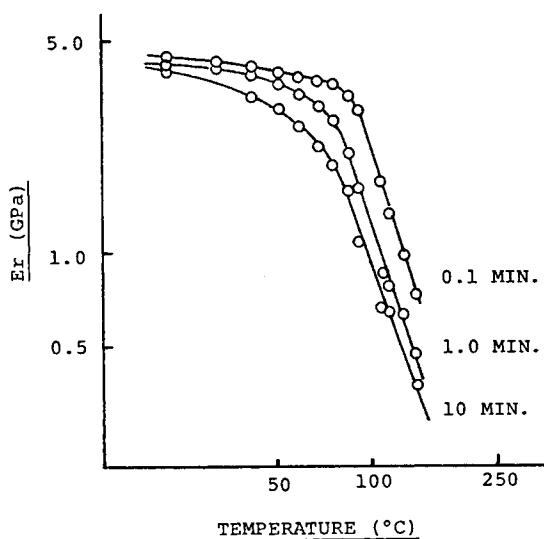


Fig. 8. Isochronous plot of  $\log E_r$  vs.  $\log T$ .

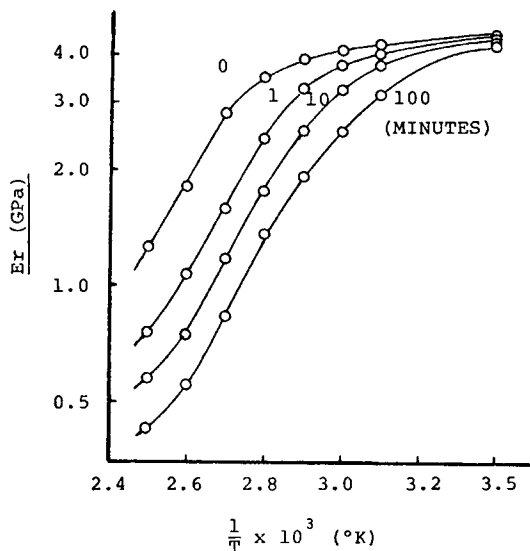


Fig. 9. Isochronous plot of relaxation modulus vs. temperature  $1/T$ .

above the temperature where  $T_g$  effects influence behavior, the rate of loss of  $\log E_r$  vs.  $\log T$  is linear and is constant with time.

An Arrhenius plot of the data as seen in Figure 9 shows that the elevated temperature data are linear over a fairly broad range of temperature (ca. 100–120°C). This region of linearity shifts to lower temperatures at long times. Calculations show an activation energy of 8.0 Kcal/mol, suggesting chain segmental motion in the amorphous regions of the structure as the dominant relaxation mechanism.

The viscoelastic behavior of biaxially oriented films is complex. These data confirm the utility of TMA as a viable technique to study stress relaxation. From stress relaxation measurements, the behavior of the modulus as a function of time and temperature was defined and shown to be nonlinear over a broad temperature range about the  $T_g$ .

Increased uniplanar orientation causes a reduction of both the magnitude and rate of stress relaxation.<sup>10</sup> Further definition of the quantitative effects of orientation and the influence of oriented crystallinity will be studied.

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