

Pulse Propagation in Polyester-Solvent Systems

H.-D. WEIGMANN and A. S. RIBNICK, *Textile Research Institute, Princeton, New Jersey 08540*

Synopsis

The propagation of sonic pulses through solvent-swollen polyester yarns has been investigated. A discontinuity is observed in the temperature dependence of the pulse transit time which has been associated with the onset of the glass transition of the polyester-solvent system. Good agreement is reached for several systems with an extrapolated zero shrinkage temperature obtained from dynamic shrinkage determination of the filament in the appropriate solvent. The agreement between the two methods suggests that an interaction parameter for the polyester-solvent system is measured which must be associated with the onset of its glass transition.

INTRODUCTION

One of the most obvious manifestations of the interactions between organic solvents and drawn polyester yarns is the longitudinal shrinkage that these yarns undergo upon exposure to a number of organic solvents. It is believed that these solvents cause the breakdown of intermolecular cohesive forces, thereby increasing segmental mobility in the polymer, allowing relaxation of orientational stresses that were introduced during the spinning and drawing processes. These events may be associated with a simultaneous or subsequent recrystallization process. An investigation of the shrinkage phenomenon under isothermal conditions led to the observation that the equilibrium shrinkage in a particular solvent shows a linear temperature dependence over a considerable temperature range.¹ Equilibrium shrinkage is here defined as the final shrinkage of the yarn after reaching equilibrium sorption of the solvent at a particular temperature. It was further shown that the temperature dependence of the equilibrium shrinkage could be used as an indication of the plasticizing capability of the solvent.

Based on these observations, a new experimental approach to the investigation of interactions between solvents and polyester was developed. The new method has been called dynamic shrinkage, and consists of continuous recording of the shrinkage of yarns immersed in solvents as they are heated at programmed rates.² It appears that with this method a rapid and accurate determination of the onset of the glass transition of a polyester-solvent system can be obtained, thereby providing a quantitative measure of the plasticizing capability of a particular solvent for polyester.

The dynamic shrinkage method establishes the linear temperature dependence of equilibrium shrinkage and then extrapolates to a zero shrinkage temperature which, in turn, may be associated with the onset of the glass

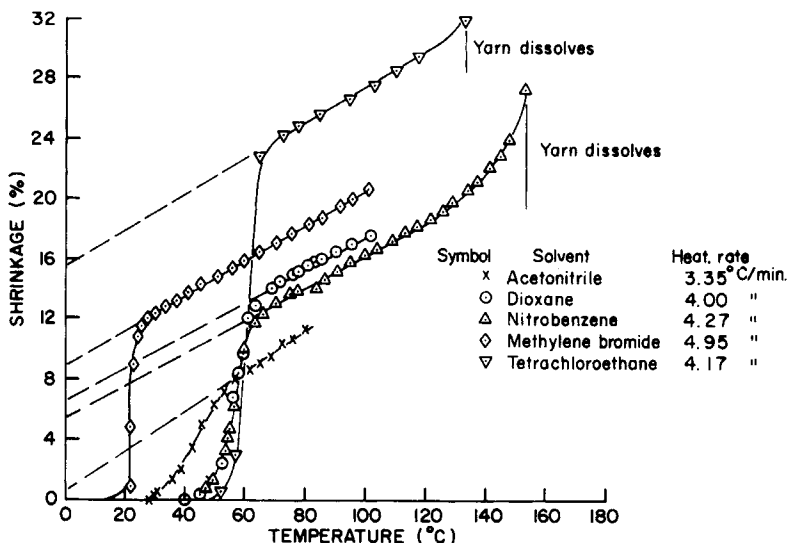


Fig. 1. Dynamic shrinkage curves for polyester yarns in various solvents at heating rates ranging from 3.4° to 5.0°C/min at constant stress (6.57×10^{-4} g/d).²

transition of the fiber-solvent system. Typical dynamic shrinkage curves for a polyester yarn in several organic solvents are shown in Figure 1. For strongly interacting solvents, these zero shrinkage temperatures are well below room temperature and require extrapolation over a considerable temperature range. It appeared desirable, therefore, to confirm the values of some of these characteristic temperatures of polyester-solvent systems by an independent method.

EXPERIMENTAL APPROACH

The polyester filaments were taken from the commercial continuous filament yarn supplied by the E. I. du Pont de Nemours and Company, Inc., of Wilmington, Delaware, which has been characterized previously.³

It was decided to characterize the fiber-solvent systems by determining the temperature dependence of dynamic properties of filaments that had been equilibrated in the organic solvent. The transit time of a sonic pulse ($\sim 10^4$ cycles per sec) through the solvent-swollen filament was measured as a function of temperature. For this purpose, the method of Moseley⁴ was adapted using a modification of the pulse propagation meter of the H. M. Morgan Company. The apparatus, containing the brass solvent cell in which the filament is submerged, is shown in Figure 2. As indicated, the filament is held below the surface of the solvent by the two transducers T_1 and T_2 , which in this experiment are in a fixed position. The transducer T_2 , however, can be moved into different positions by the external push-rod R. The solvent level in the solvent tray S is held constant by a solvent-leveling bulb F. Cooling and heating of the solvent is achieved by means of a thermoelectric module M (Melcor) with a capacity of about 50 W. The solvent cell is attached to the thermoelectric module with thermal conducting grease. The system that was

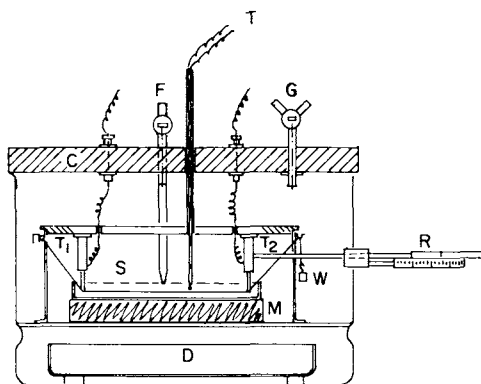


Fig. 2. Apparatus used for the determination of pulse transit time in solvent-swollen fiber systems.

used in this apparatus can cover a temperature range from -20° to $+150^{\circ}\text{C}$. The apparatus can be evacuated (G) and filled with dry air or nitrogen, and moisture levels can be controlled by appropriate salt solutions or drying agents in the bottom tray D.

After the filament has been equilibrated with the solvent under temperature-time conditions that establish equilibrium shrinkage levels, the temperature dependence of the pulse transit time is determined at decreasing and increasing temperatures below the temperature of the equilibration. The rate of temperature change is manually controlled and is kept constant at about 2°C per min. Temperature determinations are made by means of a thermocouple in the solvent tray. Several temperature scans are made for each filament at increasing and decreasing temperatures. The filaments are held under a constant load W of 1.5 g.

RESULTS AND DISCUSSION

In earlier attempts to utilize the pulse propagation method for characterizing fiber-solvent interactions, the temperature dependence of the pulse transit time was determined immediately after the yarn had been immersed in the solvent. As a result, the kinetic effects of solvent diffusion and structural changes obscured the temperature dependence of the pulse transit time under equilibrium conditions. In contrast to this approach, the current investigation establishes an equilibrium absorption condition at higher temperature and then determines the temperature dependence of the pulse transit time of the fiber-solvent system below this temperature. Thus, no further irreversible structural changes and shrinkage phenomena can interfere with this determination. In other words, the scan covers only the temperature range where the transit time of the pulse reflects the segmental mobility of the solvent-swollen polymer, and a discontinuity in the temperature dependence of the pulse transit time would be expected at the onset of the glass transition. The pulse transit time is, of course, inversely related to the velocity of pulse propagation, which in turn is related to the dynamic modulus of the particular polyester-solvent system at the experimental frequency of

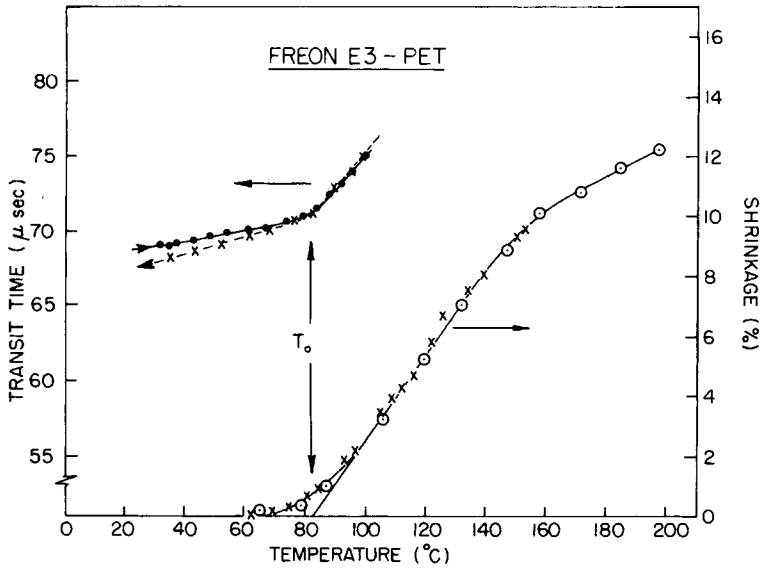


Fig. 3. Temperature dependence of the pulse transit time and dynamic shrinkage curve for polyester yarn in Freon-E3 (x) and in air (o): (●-●) increasing temp.; (x-x) decreasing temp.

10,000 cycles per sec. No effort has been made to transform pulse transit time data into dynamic moduli, since this investigation concerns itself only with the temperature dependence of the pulse transit time and the temperature of the observed discontinuity rather than with absolute values of dynamic modulus of polyester-solvent systems. Since the experiment deals with an equilibrium state of the fiber-solvent system when structural changes are not taking place, the temperature dependence of the pulse transit time should be

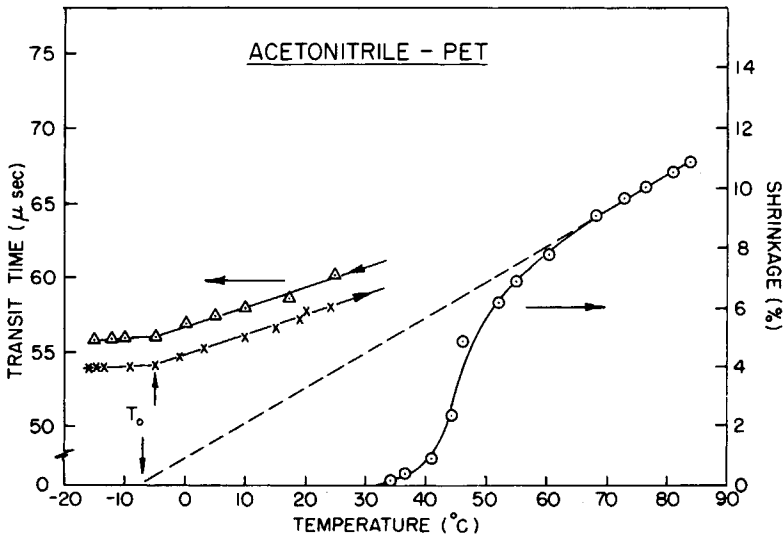


Fig. 4. Temperature dependence of pulse transit time and dynamic shrinkage curve for polyester yarn in acetonitrile: (x-x) increasing temp.; (Δ-Δ) decreasing temp.

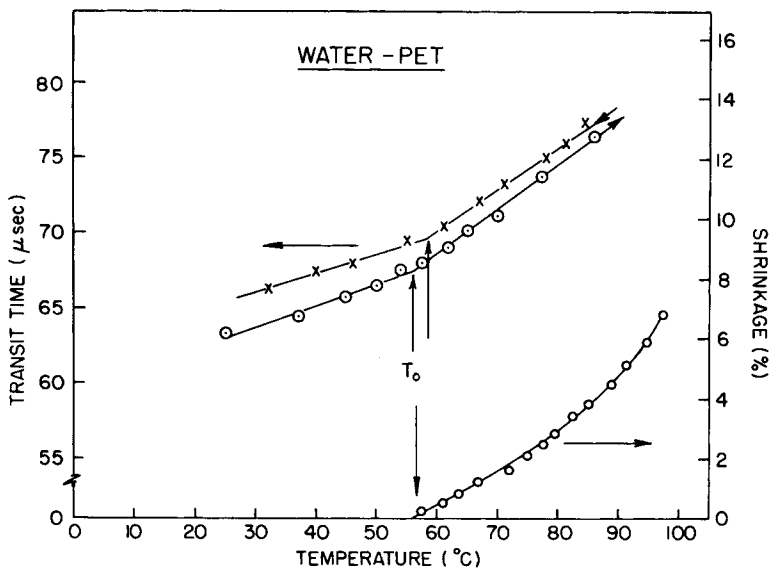


Fig. 5. Temperature dependence of pulse transit time and dynamic shrinkage curve for polyester yarn in water: (O-O) increasing temp.; (x-x) decreasing temp.

completely reversible, and the discontinuity at the onset of the glass transition would therefore be expected to be reproducible in sequential experiments at increasing or decreasing temperatures.

This method differs from the conventional methods of determining glass transition temperatures in that it establishes the onset of the temperature range in which dispersion effects occur and not the temperature at which loss phenomena, such as $\tan \delta$ or the loss modulus, reach a maximum. The temperature discontinuity of the pulse transit time is relatively sharp, as can be seen in Figures 3-5. This is in contrast to the behavior of drawn semicrystalline PET fibers measured with the Rheovibron.⁵ It should be emphasized, however, that during Rheovibron measurements on drawn PET fibers, shrinkage and orientational and structural changes occur which drastically affect the temperature dependence of the modulus. Since a broad spectrum of order and orientation exists in the polymer, ranging from completely amorphous to highly oriented chains, the onset of this transition is not as sharp as in an unoriented, undrawn PET fiber.⁵ In sharp contrast to the procedure during the determination of the temperature dependence of the dynamic modulus with the Rheovibron, the experimental procedure discussed here determines the temperature dependence of the pulse transit time or the sonic modulus in the absence of orientational changes. As pointed out above, any irreversible orientational and structural changes that could interfere with the determination of the temperature dependence of the pulse transit time have occurred prior to the experiment. The pulse transit time is, therefore, a direct reflection of changes in segmental mobility of the polymer; and at the onset of the glass transition, a rather sharp discontinuity would be expected similar to the behavior of an undrawn PET sample as shown in the investigation of Dumbleton and Murayama.⁵ Thompson and Woods⁶ have shown that, at least for amorphous PET, the temperature at which a discontinuity

occurs in the temperature dependence of the dynamic modulus shows only small dependence on the frequency used in the measurement, including frequencies up to 10^4 cps. It would, therefore, be expected that the discontinuity observed in the temperature dependence of the pulse transit time coincides with the extrapolated zero shrinkage temperature of semicrystalline drawn PET fibers, since both temperatures are reflections of the first onset of segmental mobility in the polymer.

As a first attempt, the temperature dependence of the pulse transit time of a single filament was determined in a noninteracting solvent, where the solvent essentially acts only as a heat transfer medium. Under these conditions, it would be expected that a discontinuity in the temperature dependence of the pulse transit time would occur at the onset of the glass transition of the dry polymer. The solvent selected for use with polyester filament is a perfluorinated ether of relatively high molecular weight obtained from the Du Pont Company under the trade name of Freon E3. The noninteracting nature of Freon E3 was established by the fact that the dynamic shrinkage curve for polyester in the solvent is completely identical with the dynamic shrinkage curve in air (Fig. 3). After the filament was heated to 100°C and held at this temperature for 10 min, the temperature dependence of the pulse transit time with decreasing and increasing temperature was determined. The results are shown in Figure 3 and indicate a discontinuity in the temperature dependence at about 82° to 83°C , which agrees well with the temperature obtained by extrapolating the linear portion of the dynamic shrinkage curve in air to zero shrinkage, i.e., the temperature at which the glass transition begins.

The acetonitrile-polyester system was chosen as a system involving a solvent that interacts quite strongly with polyester. The temperature dependence of the pulse transit time is shown in Figure 4 for decreasing and increasing temperatures after the filament was heated in acetonitrile at 50° for 10 min. A discontinuity in the temperature dependence is observed at a temperature of approximately -5°C , which agrees well with the extrapolated temperature of -7°C obtained from dynamic shrinkage experiments as indicated in Figure 4. It is suggested that this temperature reflects the onset of the glass transition of this polyester fiber-solvent system.

The dynamic shrinkage behavior of polyester in water reflects the unique position that this solvent assumes with regard to its plasticizing capabilities for polyester. While most solvents show a definite differentiation between the diffusion-dependent nonequilibrium phase of the shrinkage curve and the equilibrium shrinkage phase with its linear temperature dependence, water shows a dynamic shrinkage behavior which is essentially independent of the heating rate and shows no linearity in the temperature dependence of its equilibrium shrinkage. This behavior may be attributed to the fast diffusion of the small water molecules resulting in disordering of regions with relatively low order and consequently low shrinkage values. Because of the absence of a diffusion-controlled nonequilibrium phase, it was concluded that the onset of shrinkage at approximately 55°C meant that this was the onset of the glass transition of the polyester-water system. In an attempt to verify this value, polyester filaments were heated in water at 95°C for 10 min, and subsequently the temperature dependence of the pulse transit time of the filaments in

water was established at decreasing and increasing temperatures. As shown in Figure 5, a discontinuity in the temperature dependence of the pulse transit time occurs at a temperature of approximately 57°C, in good agreement with the temperature obtained in the dynamic shrinkage experiment.

These results indicate that the temperature dependence of the pulse transit time in solvent-swollen polyester filaments under equilibrium conditions provides a means of determining the onset of the glass transition of fiber-solvent systems. Furthermore, the results confirm the values for the extrapolated zero shrinkage temperatures obtained with the dynamic shrinkage technique by an independent method and strengthen the argument that these temperatures reflect the onset of the glass transition of the appropriate polyester fiber-solvent system.

References

1. A. S. Ribnick, H.-D. Weigmann, and L. Rebenfeld, *Text. Res. J.*, **43**, 176 (1973).
2. A. S. Ribnick and H.-D. Weigmann, *Text. Res. J.*, **43**, 316 (1973).
3. A. S. Ribnick, H.-D. Weigmann, and L. Rebenfeld, *Text. Res. J.*, **42**, 720 (1972).
4. W. W. Moseley, *J. Appl. Polym. Sci.*, **3**, 266 (1960).
5. J. H. Dumbleton and T. Murayama, *Kolloid-Z. Z. Polym.*, **220**, 41 (1967).
6. Thompson, A. B. and Woods, D., *Trans. Faraday Soc.*, **52**, 1382 (1956).

Received November 1, 1974

Revised October 24, 1975