Heat Setting of Oriented Poly(ethylene Terephthalate): Effects of Deformation Mode, Strain Level, and Heating Medium

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Synopsis

We continue a previous study of the α and α' mechanical relaxation processes in oriented poly(ethylene terephthalate) by means of heat-setting experiments on drawn filaments between room temperature and the melting region. Both processes were exhibited in both torsion and bending deformations, but heat setting was found consistently to be greater in bending than in torsion: this was accounted for by the known anisotropy of the α relaxation. In both modes of deformation, increasing strain level gave reduced recovery, and results suggested this arose from high stresses activating at room temperature the stress relaxation mechanisms, which at low stresses occurred only at elevated temperatures (α if as-drawn, α' if preset). Results were found to be independent of whether blown air or stirred oil was used as heat transfer medium, in contrast to some previous reports in the literature; the reason lay in differences in the precise sequences of deformation and temperature employed.

INTRODUCTION

Heat-setting experiments are of importance in two respects. First, they provide a method of obtaining meaningful measurements on mechanical relaxation processes in temperature regions where a polymer is structurally unstable. The thermal history associated with each data point is well defined. Second, they provide a model in the laboratory of industrial heat-setting processes. These are a particular feature of the manufacture of products from oriented poly(ethylene terephthalate) (PET) fibers or film.

In a previous article[1] we exploited heat-setting experiments in investigating the high-temperature viscoelasticity of oriented PET in the temperature regime where crystallization and other structural evolution take place during mechanical tests. Drawn PET filaments were deformed in small strain torsion, heat set, cooled, and released. Measurements of fractional recovery (the fraction of strain induced that was recovered on release) revealed the viscoelasticity of PET *above* the glass transition to be governed by another time-dependent relaxation process, distinct from the glass transition (α) process; and it was labeled α'. The characteristic features were highly sensitive to the microstructural state of the polymer. Specifically, the center of the α' process moved to longer relaxation times and higher temperatures with increasing crystallization. It was suggested that the origin of the process is the slipping of stressed entanglements by molecular diffusion, in a polymer network that is incompletely crosslinked by crystals.

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BUCKLEY AND SALEM

The purpose of this work is to report further details of the α and α' processes in PET as revealed by heat-setting experiments. The additional parameters considered are the mode of deformation (torsion vs. bending), strain level, and heating medium.

Previous studies of heat setting of PET in extension,[2,3] torsion,[4,5] and bending[4] have been reported in the literature, but it is now necessary to reexamine the phenomenon in light of the discovery of the α' relaxation.

EXPERIMENTAL DETAILS

The oriented PET monofilament used in this work had been prepared at UMIST by melt extrusion, followed by drawing ×5 at 80°C. It had a density of 1381 kg/m^3 and a diameter of 51 μm. A new specimen was cut from the filament for each experiment. Further details of the material were given in the previous article,[1] including microstructural details.

A schematic diagram of the main elements of the heat-setting experiment is given in Figure 1. In the present work the following conditions were kept constant: $T_0 = 20°C$, $t_A = 60$ s, $t_C - t_B = 60$ s, $t_D - t_C = 300$ s. The mode of deformation was either torsion of the filament about its own axis or bending of the filament around a cylinder. All results shown here refer to a heat-setting time $t_s = 120$ s. Other experimental variables were the temperature of heat setting T_s, the maximum (skin) shear strain of the twisted filament (in torsion) γ_0, or the maximum tensile/compressive strain at the outer edge of the filament (in bending) ϵ_0, and the temperature of any thermal pretreatment of the filament
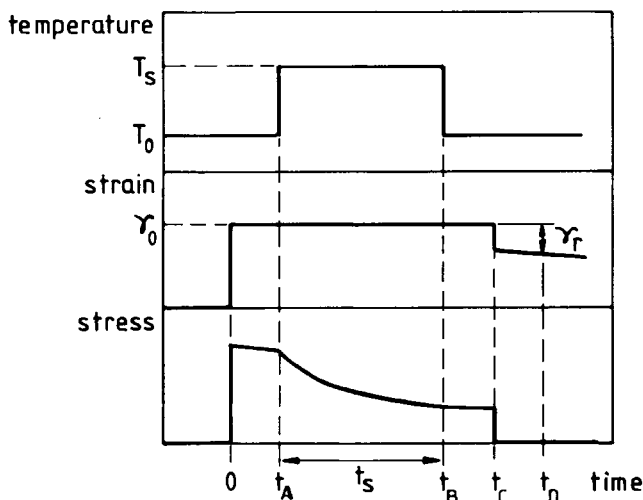

Fig. 1.   Schematic diagram of a heat-setting experiment in torsion: the specimen was (a) at zero time, twisted to maximum shear strain γ_0; (b) at time t_A, heated to temperature T_s; (c) at time t_B, cooled to temperature T_0; (d) at time t_C, released. Recovery strain γ_r was measured at time t_D. Fractional recovery was defined $f = \gamma_r/\gamma_0$. For heat setting in bending a similar sequence was followed, with bending deformation replacing twisting. Strain level was specified through the maximum tensile/compressive strain at the outer edge of the filament: ϵ_0 for strain induced, ϵ_r for strain recovered; in this case $f = \epsilon_r/\epsilon_0$.

T_p. (In this paper, shear strain in a twisted filament is expressed as the tangent of the shear angle.)

The experimental procedure for heat-setting filaments in torsion was described before.[1] A summary of the experimental sequence for filaments heat set in bending is given in the following paragraphs.

Deformation

For strains $\epsilon_0 < 0.1$, the filament was wound one turn around a Tufnol cylinder of the appropriate diameter and held in a screw clamp. For $\epsilon_0 > 0.1$, the filament was bent around a glass rod and secured in a clamp. Details of the apparatus used are given elsewhere.[6]

Heat

The filament, clamped at constant length on the cylinder or rod was immersed in a bath of stirred, thermostatically controlled silicone oil at the required temperature T_s for the required time t_s. T_s was held constant to ± 0.1 K. Alternatively (for heat setting in air), the clamped filament was heated in a forced-air furnace (details follow).

Cool

The filament was removed from the oil and quenched in stirred silicone oil at 20°C. Alternatively, filaments heated in the forced-air furnace were brought to room temperature by forcing cold air through the furnace.

Release

For $\epsilon_0 < 0.1$, the filament was released from the Tufnol cylinder and placed in a petri dish containing a thin layer of silicone oil, which ensured minimal frictional resistance to recovery. For $\epsilon_0 > 0.1$, the filament was released from the glass rod and placed on a microscope slide with a thin layer of silicone oil.

Measurement

For $\epsilon_0 < 0.1$, a camera with extension tube was mounted above the petri dish and focused on the circularly deformed filament. Beneath the dish was placed a measuring grid. From a magnified photographic negative of the filament, the recovered radius of curvature of the filament was measured. For $\epsilon_0 > 0.1$, a photomicrograph was taken of the deformed filament. Since the recovered filament usually formed less than half a circle, it was not possible to take a diameter measurement directly from the photomicrograph negative. Therefore, with the aid of a digitizing table, the coordinates of three points along the filament curve were obtained from magnified negatives, and the equation of the circle was solved to obtain the recovered radius of curvature.

Fractional recovery f was determined as the fraction of applied curvature (reciprocal radius of curvature) that was recovered on release (see Fig. 1). The random measuring error in f, as determined from repeat experiments, was found to be 0.01 in torsion and in low-strain bending tests and 0.03 in high-strain bending tests.

Some specimens were thermally preset prior to heat setting. They were held undeformed at constant length and immersed in thermostatically controlled silicone oil at the required presetting temperature T_p, for a time t_p. Following quenching in silicone oil at 20°C, they were subjected to heat-setting sequences in the usual way, as described here and in Ref. 1. In the experiments reported here, the presetting time was held constant at $t_p = 2100$ s.

Forced-air Furnace

A forced-air furnace was designed for the rapid heating and cooling of fibers in air. To heat the specimen, compressed air was forced through a coil of copper pipe submerged in hot, stirred silicone oil, from where it was directed into a chamber containing the specimen (see Fig. 2).

The specimen chamber (Fig. 3) consisted of a stainless steel outer cylinder (diameter 96 mm, height 72 mm) and an inner cylinder (diameter 65 mm, height 56 mm) that, to minimize thermal mass and maximize heating uniformity, consisted of aluminum foil, wrapped around a light stainless steel frame. The gap between inner and outer walls was filled with insulating material. A small hole through the wall of the chamber accommodated the thermocouple of a digital thermometer. Hot air passed through the 15-mm pipe at the bottom of the chamber and was exhausted through a funnel of equal diameter in the lid. In order to spread the air uniformly throughout the chamber a baffle of aluminum foil (Fig. 3) was fixed just above the hot-air inlet pipe. This also created turbulence, to enhance the rate of heat transfer to the specimen.

To cool the specimen, compressed air entered from the side of the chamber, directed via a U-shaped cooling tube submerged in a vacuum flask of crushed ice and water.

The heating and cooling cycles were activated by three remote-controlled solenoid valves. For example, the direction of air flow through the valves (Fig. 2) and the flow sequence for a typical setting experiment was as follows.
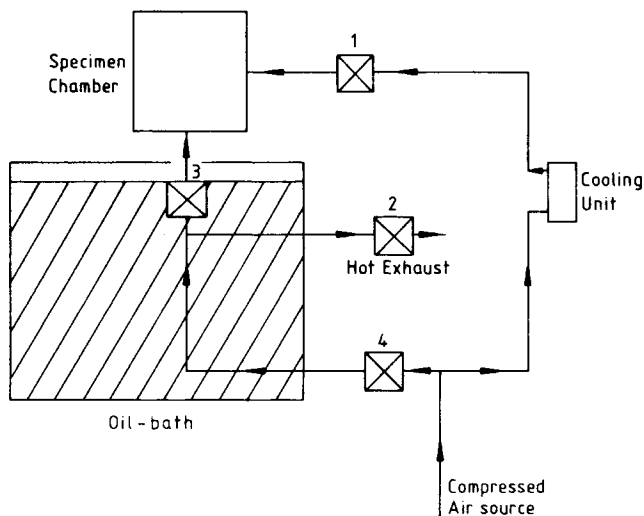

Fig. 2.   Diagram showing main elements of the hot-air furnace used for heat-setting specimen in air.
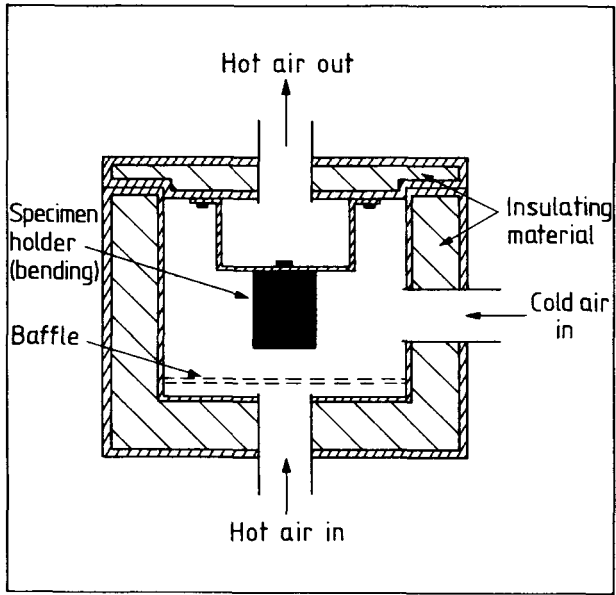
Fig. 3. Section through the specimen chamber of the hot-air furnace outlined in Figure 2.

(a) Valves 1 and 2 open, valve 3 closed: cold air entered the chamber via valve 1 to maintain the specimen at a constant initial temperature; hot air passing through the heating coil went to exhaust via valve 2.

(b) Valves 1 and 2 closed, valve 3 open: cold air was shut off from the chamber at valve 1; hot air was prevented from going to exhaust by
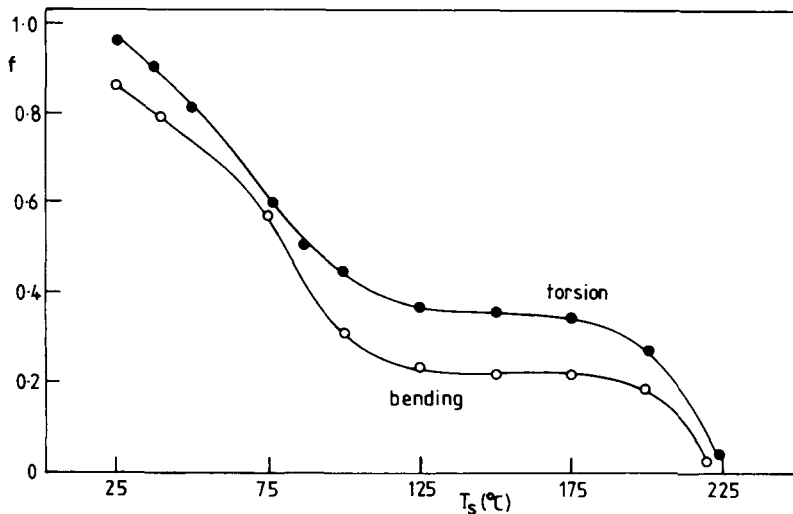

Fig. 4. Fractional recovery from low-strain heat setting in torsion ($\gamma_0 = 0.006$) and bending ($\epsilon_0 = 0.005$). Specimens had been preset at 200°C. In both modes of deformation α and α' relaxation processes are visible as maxima in the gradient of f versus T_s.
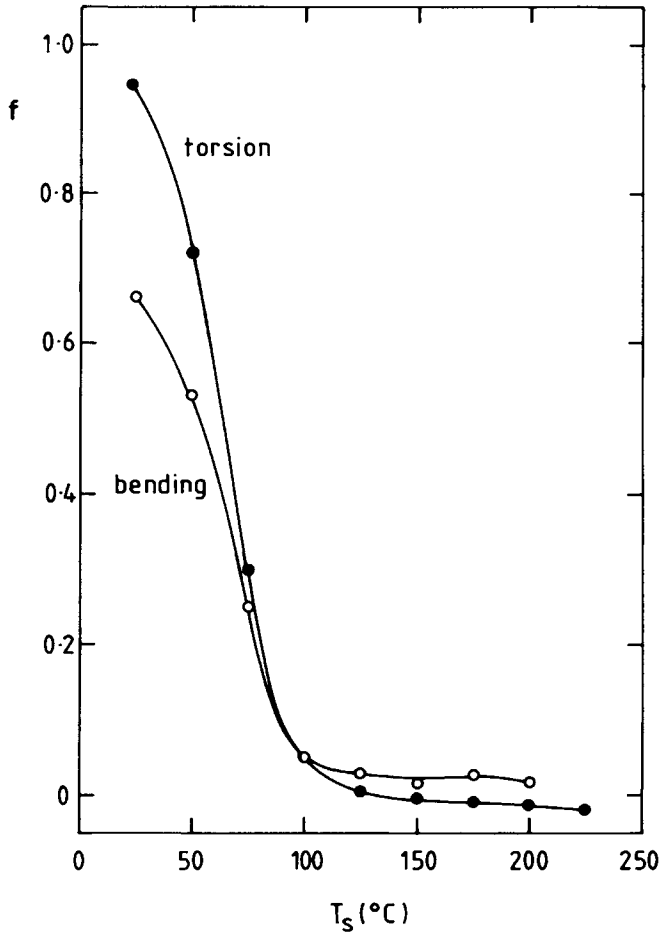
Fig. 5.   Fractional recovery from heat setting in torsion ($\gamma_0 = 0.06$) and bending ($\epsilon_0 = 0.06$) for specimens that were as-drawn. Only one relaxation process (α) is visible.

valve 2 and instead entered the chamber via valve 3 and exhausted through the funnel in the lid.

(c) Valves 1 and 2 open, valve 3 closed: as (a).

Adjustment of the hand-operated valve 4 allowed the cold air flow rate during phases (a) and (b) to be varied.

This system was designed to achieve high rates of change of the air temperature so that step changes in temperature required by the ideal heat-setting experiment (Fig. 1) could be closely approximated. Thus when heating and cooling between ambient and temperatures in the range 125–250°C, the rate of heating of the air in the chamber was greater than 40 K/s, and the rate of cooling was greater than 73 K/s.

RESULTS AND DISCUSSION

Deformation Mode

Results presented in Figures 4–6 compare the variations in fractional recovery f with T_s for bending and torsional modes of deformation. In each case the
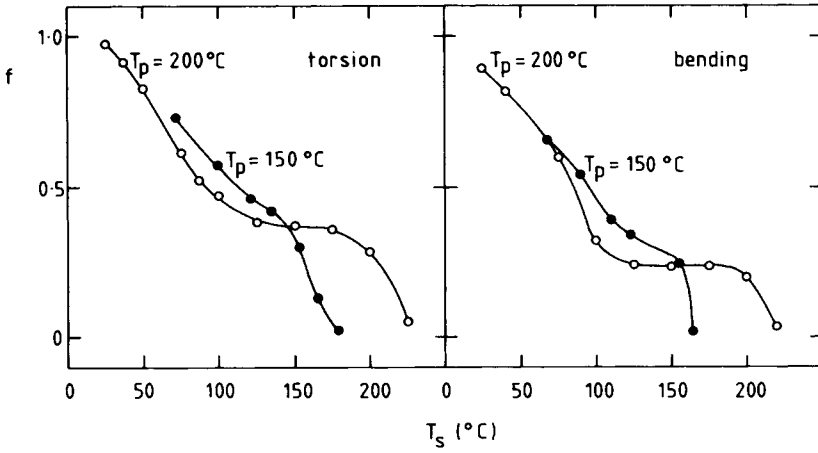
Fig. 6. Effects of varying presetting temperature T_p on the fractional recovery f following heat setting at temperature T_s in torsion ($\gamma_0 = 0.006$) and bending ($\epsilon_0 = 0.005$).
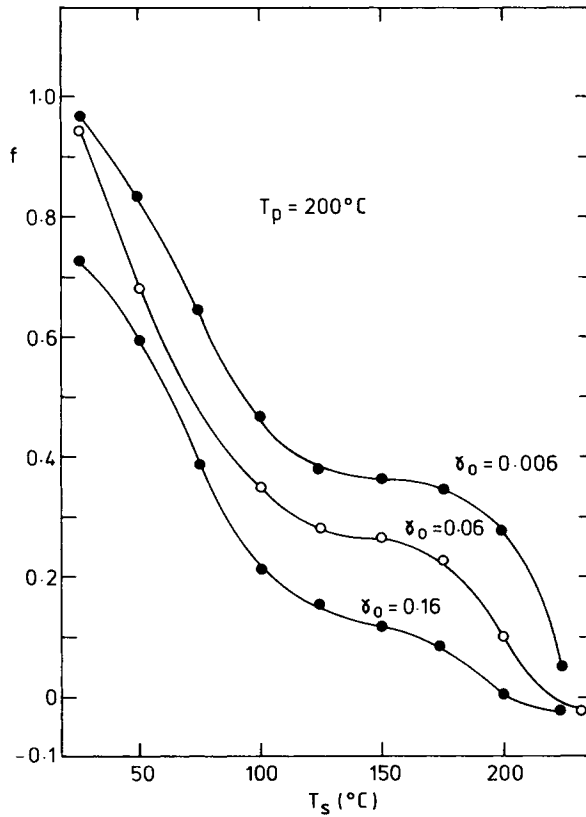

Fig. 7. Effects of varying strain level γ_0 on fractional recovery following heat setting in torsion. Specimens had been preset at $T_p = 200°C$.
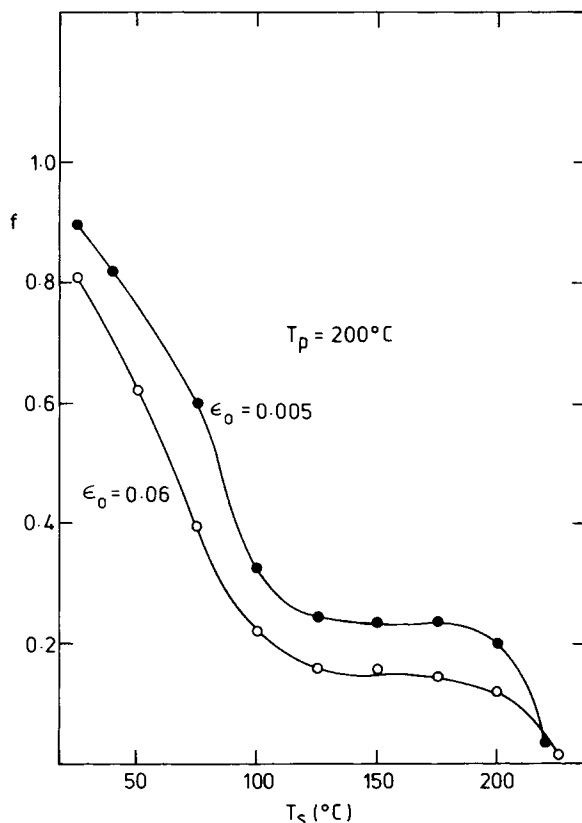
Fig. 8.   Effects of varying strain level ϵ_0 on fractional recovery following heat setting in bending. Specimens had been preset at T_p = 200°C.

pattern is clearly the same. The α and α' relaxations are evident as maxima in the gradients of f versus T_s plots. In as-drawn specimens only the glass transition (α) mechanism is apparent (Fig. 5), but in preset specimens both α and the higher temperature α' mechanisms are clearly visible. Increasing presetting temperature T_p shifts the center of α' to higher T_s (Fig. 6). As reported previously,[1] this phenomenon was explored in some detail for low-strain heat setting in torsion and was found to reflect an increase in relaxation times of the time-dependent α' process, presumed to be due to the crystallization occurring during presetting. The clear message of these results is that both α and α' processes are operative in both torsional and bending deformations, and that their time/temperature behavior is the same, irrespective of the mode of deformation. It is clear from Figures 4–6, however, that heat setting in the two modes does not produce identical results. In all cases it was found that the magnitude of f was greater for heat setting in torsion than in bending: that is, a greater degree of set was achieved in bending than in torsion.

For the as-drawn specimens deformed in torsion, the slight negative recovery (overtwist) at $T > 125°C$ has been observed before[4,5] and is believed to arise from a small contribution from the anisotropy of thermal expansion combined with the helical anisotropy of the filaments after twisting.[5,7] Such an effect
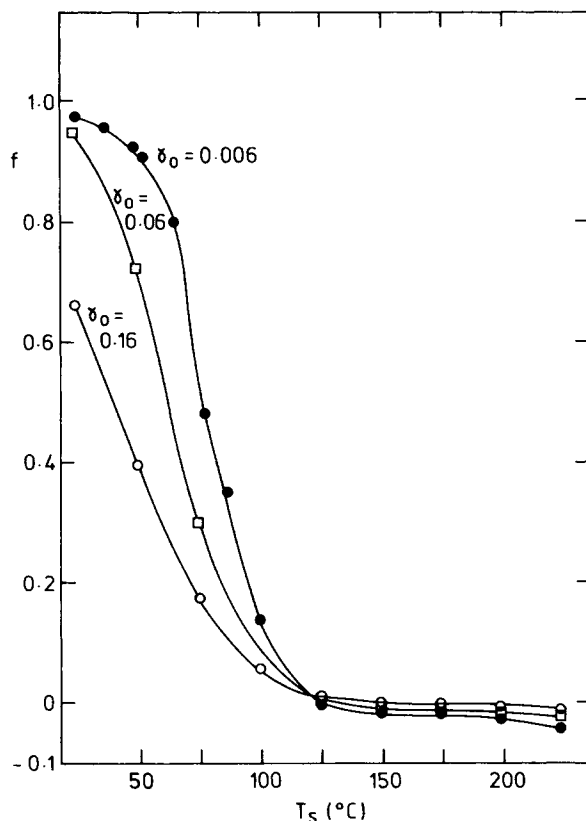
Fig. 9. Effects of varying strain level γ_0 on fractional recovery following heat setting in torsion for specimens that were as-drawn.

would not be expected to the same degree in bending, and indeed it was not observed (Fig. 5).

The present work did not include heat setting in pure extension, but close examination of the data obtained in such a study by Lunn et al.[2] suggests that α' relaxation was evident in their data for oriented, annealed PET but was overlooked. Since bending deformation of a filament occurs by axial extension and compression strains, the occurrence of the α' relaxation in extension would be expected in view of the present results for heat setting in bending.

To interpret the results of heat-setting experiments it is helpful to employ the methods of nonisothermal viscoelasticity. Fractional recovery f is then seen to correspond approximately to the stress relaxation modulus applying to time t_s and temperature T_s of setting, normalized with respect to the modulus at T_0.[1] It follows that if f is lower for heat setting in bending than in torsion, the fall in axial tensile modulus with rise in temperature in the region considered must be greater than that in axial shear modulus.

Evidence that this is indeed so can be found in the dynamic mechanical study by Davies and Ward of anisotropy of the α relaxation in annealed, oriented PET.[8] Tan δ (at 250–300 Hz) was measured with tensile stress at angles 0°, 45°, and 90° to the orientation direction (OD). In both materials studied—
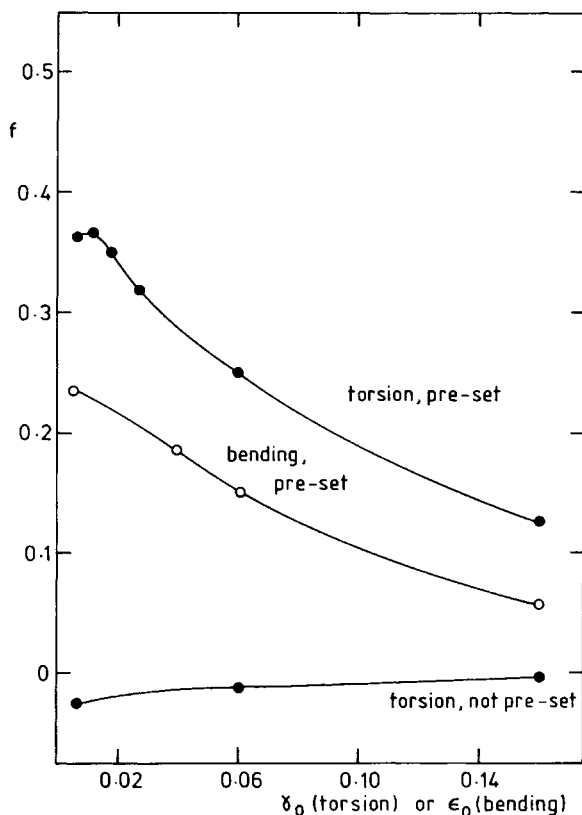
Fig. 10.   Comparison of the strain dependence of fractional recovery in torsion and bending for specimens preset at $T_p = 150°C$ and then heat set at $T_s = 200°C$. The lower curve is for as-drawn specimens deformed in torsion.

hydrostatically extruded rod and film drawn at constant width—it was found that

$$\tan \delta_0 > \tan \delta_{45}$$

throughout the α region of temperature. The ratio of peak heights ($\tan \delta_0$: $\tan \delta_{45}$) was 1 : 0.73 and 1 : 0.79 in the two cases, respectively. Since tensile deformation in these materials at 45° to OD would be dominated by axial shear, the results are consistent with the anisotropy of heat setting observed in the present work.

   The explanation for the anisotropy lies in the anisotropy of mechanical coupling of the external stress to the amorphous fraction, the relaxing element of the microstructure in the glass transition (α) process. The structure of an annealed oriented semicrystalline polymer, such as PET under tensile stress parallel to OD, provides approximately series coupling to the amorphous fraction, as first shown quantitatively by Buckley et al.[9] Series coupling produces maximum strain energy density in the low modulus (amorphous) fraction and hence yields maximum $\tan \delta$ and fractional drop in modulus at the glass transition.
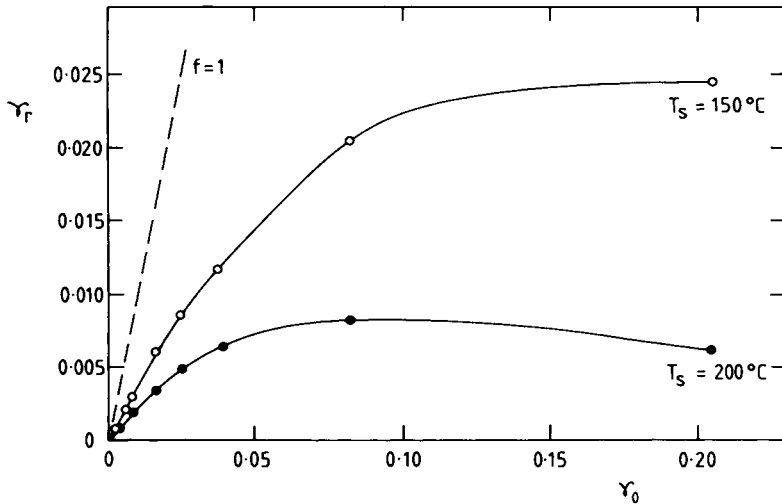
Fig. 11. Recovered shear strain γ_r versus induced shear strain γ_0 for torsional heat setting of preset specimens at setting temperatures T_s is shown. Presetting temperature was $T_p = 200°C$. Nonlinearity is clearly apparent.

The practical situation where heat setting of oriented PET filaments in torsion and bending is of vital importance is the false-twist texturing process. As the yarn is first twist set, individual filaments within it are heat set rapidly into a helical shape, involving both bending and torsional deformations. The yarn is then de-twisted, causing each filament to adopt a buckled or "crimped" shape. Research on the kinetics of this process has shown clearly that the rate at which it can be carried out is limited by the time-dependent setting mechanism within the filaments of the yarn.[10] To examine the effects of varying degree of set in torsion and bending, an approximate analytical model of the crimp shape was solved as part of the present study.[6] The level of crimp was defined (somewhat arbitrarily, but comparably to methods used in practice) as the force to hold the textured yarn at 15% contraction from its twist-set length. The effects of varying f in bending and torsion were examined by calculation. It was found that the level of crimp achieved is dominated by the degree of set in bending, while the effect of degree of set in torsion is almost negligible.

Strain Level

For preset specimens deformed in either torsion (Fig. 7) or bending (Fig. 8), the effect of increasing the applied strain level was to reduce f (i.e., to increase the degree of set) at all values of T_s. The same was true for as-drawn specimens at temperatures below 125°C, but at higher temperatures (in the region of negative f) increasing γ_0 led to lower overtwist, as predicted by theory[5] (Fig. 9).

Figure 10 compares the dependence of f on strain level for preset fibers with $T_p = 200°C$, set at $T_s = 150°C$ (i.e., in the plateau region) in bending or torsion. It is clear that fibers deformed in bending display lower recovery f at
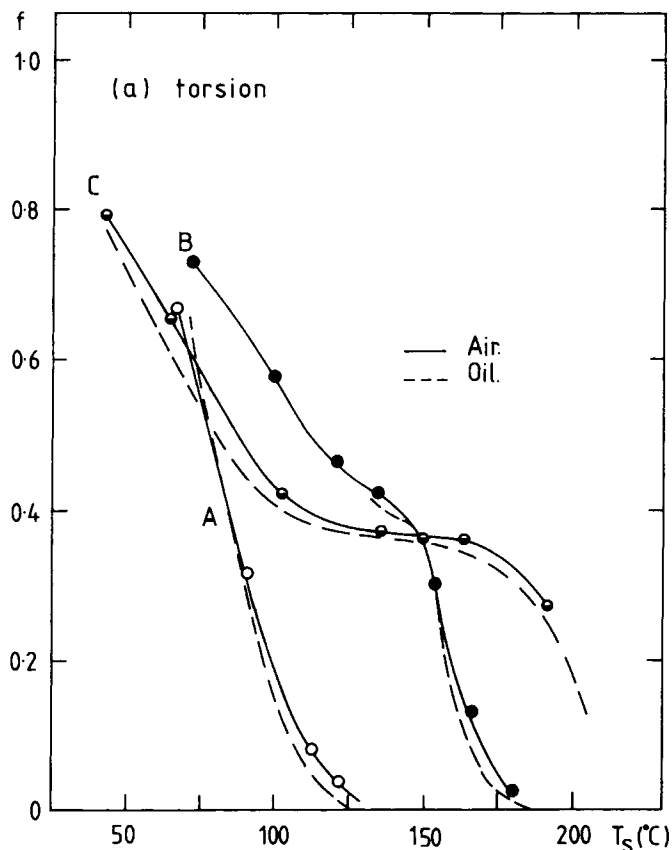
Fig. 12. Fractional recovery f versus setting temperature T_s for specimens heat set *in air* in torsion or in bending. Dashed lines show corresponding curves for specimens heat set in silicone oil. The effect of varying the heating medium is shown to be insignificant. Labels on curves indicate (A) as-drawn specimens; (B) preset at $T_p = 150°C$; (C) preset at $T_p = 200°C$. Strain levels were $\gamma_0 = 0.006$, $\epsilon_0 = 0.005$.

all strain levels explored. From the torsional data in Figure 10, it is also apparent that the effect on f of varying γ_0 becomes measurable at a strain level in the region of 0.02. This is a manifestation of nonlinearity in thermoviscoelastic behavior and is represented differently in Figure 11, where the recovered strain γ_r is plotted versus γ_0 for heat setting in torsion at two temperatures. The point of measurable departure from linearity can be seen to occur at an applied strain of approximately $\gamma_0 = 0.016$ in both cases.

It is a well-known feature of the nonlinear viscoelastic deformation of polymers that with increase in applied strain level the proportion of unrecovered strain increases on any given time or temperature scale. This was apparent, for example, in the torsional heat-setting data of Buckley et al.[5] and the extensional data of Lunn et al.[2] The present results, however, reveal an interesting difference between specimens that have or have not been preset. In preset specimens the reduction in f with increase in strain appears independent of T_s up to the plateau region separating α and α' regimes (Figs. 7 and 8), showing
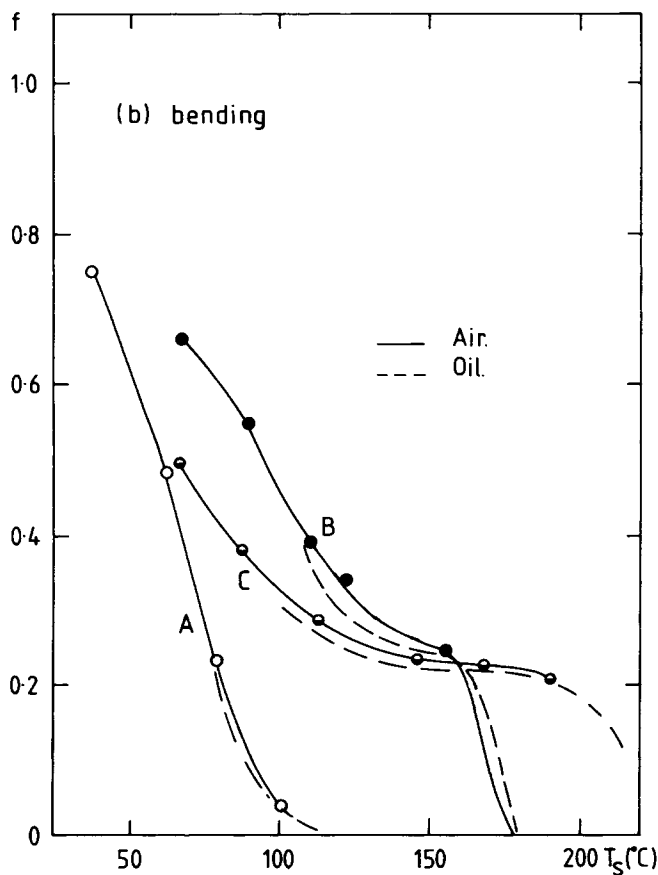
Fig. 12.   (*Continued from the previous page.*)

that it is associated with stress relaxation by the α' process. The suggestion made previously was that the α' mechanism consists of entanglement slippage.[1] If this is so, the new results provide evidence for entanglement slip even during room temperature deformation, when strains are sufficiently large. In the case of as-drawn specimens, however, the reduction in f with increase in strain appears to be associated with the α process (Fig. 9), although in these specimens this may be overlapped by α'.

Heating Medium

Figure 12 demonstrates that fractional recovery from heat setting does not depend on whether the heating medium is oil or air. For both torsion and bending, fractional recovery from heat setting in the hot-air furnace was found to be the same, to within experimental error, as that obtained in silicone oil, other conditions being the same.

This point is of interest in view of the scattered reports in the literature of major differences in thermal shrinkage and microstructure in annealed oriented PET, caused by use of different heat transfer media; see, for example, Wilson.[11]

The fact that even inert fluids such as air and silicone oil can give large differences in behavior is readily explained by the heat transfer coefficient being the critical parameter, through its control of heating rate. Wilson's work showed that the origin of such effects is competition between the kinetics of thermal shrinkage on the one hand and crystallization on the other. When the latter takes place in a drawn filament, it tends to stabilize the oriented state and hence to reduce subsequent shrinkage. Faster heating allows more shrinkage to occur in advance of crystallization, and hence gives rise to greater shrinkage and amorphous disorientation at the temperatures above ca. 100°C where crystallization occurs in PET. This explanation of events is consistent with the present results. All heat setting was carried out at constant specimen geometry, merely by means of stress relaxation at the setting temperature. There was therefore no *simultaneous* deformation and crystallization involved, and the results would be expected to be independent of the precise value of heating rate and hence of the heat transfer medium employed.

CONCLUSIONS

This work has shown the pattern of heat-setting behavior discovered by us previously, in small-strain torsional setting of oriented PET filaments, to extend to bending deformations and to larger strains in the nonlinear viscoelastic regime. In as-drawn specimens there is a single relaxation process in the glass transition (α process) region. Preset specimens, however, exhibit both the α and α' relaxation processes.

In all cases explored, magnitudes of fractional recovery were found to be lower for bending than for torsional deformation, for given presetting conditions, setting time and temperature, and maximum strain level. This result is of practical importance in that yarn crimp developed in the false-twist texturing process is more sensitive to the degree of set in bending than in torsion.

Increasing the strain level leads to decreasing fractional recovery for both torsion and bending, and in both as-drawn and preset specimens. In terms of the suggested mechanism of α' relaxation, the results for both modes of deformation suggest that this effect is due in preset specimens to entanglement slippage occurring in room temperature deformation, when strains are sufficiently high.

Comparison of results obtained with blown air or stirred silicone oil as heat transfer media showed no significant differences, in contrast to some previous reports in the literature. The reason is that the present experiments were designed to avoid concurrent deformation and crystallization, so results were not so sensitive to competition between deformation and crystallization kinetics and hence to the precise heating rates employed.

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