Fiber Recovery

H. BRODY, *Imperial Chemical Industries Limited, Fibres Division,
Harrogate, North Yorkshire, England*

Synopsis

The recovery portions of the stress–strain cycles of poly(ethylene terephthalate), poly(tetramethylene terephthalate), nylon 66, poly(vinyl chloride), and rayon were analyzed and shown to be superposable if appropriate horizontal and vertical shifts are made. The recovery curves are postulated to represent the stress–strain behavior of an elastomeric portion of the fiber which controls recovery, and the scaling factors necessary for superposition are interpreted as indicating changes in the "length" and "modulus" of the elastomer. The elastomer modulus correlates very well with the slope of the stress–strain curve, showing that the elastomer governs the fiber stress during extension. Temporary set is assumed to be due to a temporary localized ordering of the elastomer which disappears when stress is completely removed. This local ordering lowers the elastomer modulus, which leads to yield points in the stress–strain curves. Permanent set is initiated just before the temporary set approaches a constant value and increases at almost the same rate as the rate of extension. It is completely recovered by heating to near the T_g.

INTRODUCTION

Recent work by Ward et al.[1–3] has shed new light on the molecular processes that occur during extension of poly(n-methylene terephthalate) fibers to high strains. In 4GT [poly(tetramethylene) terephthalate], a crystal transition takes place due to gauche-to-trans changes as chains are straightened. The new crystal form is not thermodynamically stable and needs the energy input of the stress to maintain equilibrium. When the stress is removed, the crystal reverts to its initial form and the fiber recovers. The recovery mechanism is assumed to be entropic, that is, rubber-like, as gauche configurations are reattained.

This paper presents evidence of a general principle for all fibers which postulates that stress during extension leads to straightening of kinks and jogs that revert to their initial state on removal of stress by a rubber-like elasticity. As with 4GT, some new crystal state or enhanced level of "localized ordering" may be induced by the closer register of molecular segments on extension. This induced ordering would have varying degrees of permanence which would affect the extent and rate of recovery.

The T_g of fibers is usually above ambient temperature, which is not consistent with rubbery behavior. This paradox can be resolved by postulating that extension leads to an increase in free volume. The experience with "hard" elastomers where considerable free volume occurs on extension[4] suggests that such a possiblity exists.

The concept of elastomeric recovery is considerably supported by the shape of recovery curves after extension, the return phase of a stress–strain cycle. These curves closely resemble the stress–strain curves of elastomers. They are very steep initially when the stress is first being reduced. For an elastomer to have a stress–strain curve similar in shape, the extension would have to be very high, for example, 400–700%. The use of a simple series model[5] of high-com-

Journal of Applied Polymer Science, Vol. 22, 1631–1641 (1978)
0021-8995/78/0022-1631$01.00

pliance (elastomeric) and low-compliance (nonelastomeric) phases leads to the conclusion that only a small fraction of the length of a fiber can be elastomeric. For instance, to equate a recovery of 3% with an elastomeric extension of 500%, the total "length" of the elastomer would have to be only 0.6% of the fiber length.

This result has the additional attraction of leading to a much more reasonable appreciation of what determines the modulus of a fiber. Although an elastomer has a typical modulus value of 5 MN/m^2, a polymer crystal modulus may be 100 GN/m^2, but the fiber modulus may still be typically only 3 GN/m^2. Use of a series summation of these moduli, weighted according to 0.5% elastomer and 99.5% crystal, would give a fiber modulus of about 1 GN/m^2.

It has been found that considerable information about the elastomeric structure responsible for recovery can be extracted from these recovery curves, which are usually discarded. A method of manipulating these curves has been devised which enables such information to be obtained.

EXPERIMENTAL

Materials

The fibers used were 2GT [Terylene, poly(ethylene terephthalate)], 4GT [poly(tetramethylene terephthalate)], nylon 66, PVC, [poly(vinyl chloride)], and rayon. The fibers were in the form of continuous filaments.

Instron Cycle

The cycle used is shown in Figure 1(a). Stress relaxation was for 2 min. Cycles were also performed with no stress relaxation, but the curves were not used for the work presented in this paper, except as a comparison in the case of nylon 66. The gauge length for all fibers was 10 cm, and the rate of extension was 1 cm/min. Fibers were conditioned at 18°–20°C and 75°–80% R.H. for 24 hr before testing. When the Instron jaws had been returned to the original gauge length, a time of 3 min was allowed before reextending to determine the permanent set. The permanent set continued to decrease slowly with time.

Dynamic Modulus

A Transfer Function Analyser, made by Servomex, was used to measure the loss tangent of the fibers. A description of the use of this instrument is given in a previous publication.[6] It was found that the load cells became nonelastic above a certain load, leading to losses from the cell itself, so that the load had to be kept below a maximum level. This level was determined by gradual extension of a steel spring in the instrument. The spring had no inherent loss, so that when the instrument began to display a loss, it was known that the load cell was overloaded. Unfortunately, this occurred at rather small loads, and it was only possible to use about six filaments, depending on the fiber, in order to keep the load below the safe level at high fiber extensions. The load cell capacity used was ±450 g. The frequency of vibration was 0.2 cycles/sec and the amplitude of oscillation was 0.3 mm for a fiber length of 5 cm.

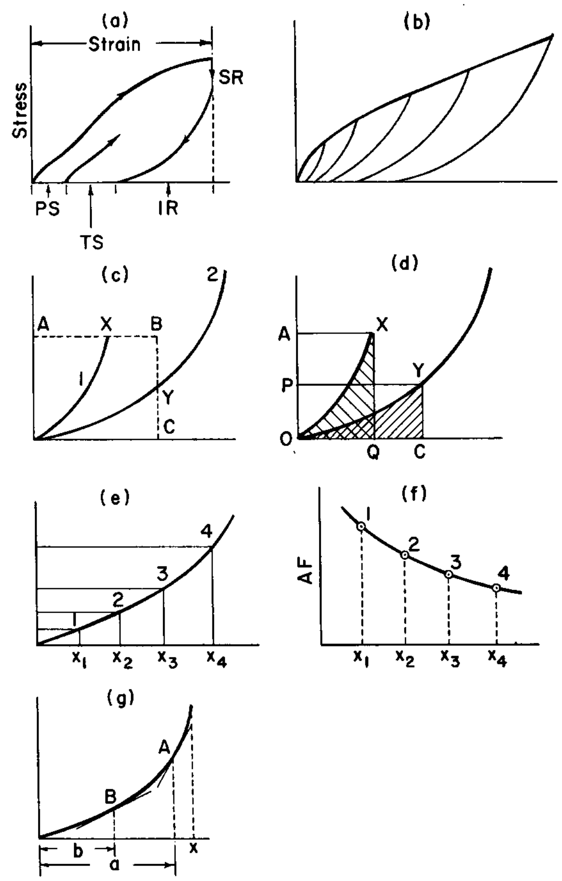

Fig. 1. Superposition technique. (a) SR = stress relaxation; PS = permanent set; TS = temporary set; IR = immediate recovery; (f) AF = area fraction; (g) $a = 0.9x$; $b = 0.5x$.

Fiber strain was measured with a cathetometer. The measurement of dynamic modulus was essentially on a "relaxed" fiber, since it took about 5 min for the instrument to equilibrate after each increase in strain.

Thermal Treatment of Fibers with Permanent Set

A specially made small bath was attached to the lower jaw of the Instron. This bath was well insulated against heat losses and was connected to a larger thermostatted bath. Silicone oil at constant temperature was circulated between the two baths by a peristaltic pump. A very long fiber yarn bundle, 50 cm, was used in order to amplify small changes in strain. The fiber was strained at 1 cm/min to the desired strain and then stress relaxed for 2 min. The jaws were then brought together at 20 cm/min until they just touched. The slack loop of fiber produced was immersed in the small bath on the lower jaw. This bath was specially designed to have a projecting lip touching the jaws so that practically all of the fiber between the jaws could be immersed. The time of heating was 3 min, after which the fiber was reextended at 20 cm/min to the original gauge length. The fiber was then further extended at 1 cm/min and the residue of permanent set determined.

SUPERPOSITION TECHNIQUE

It is assumed that the rate of Instron jaw closure is slow enough for full "elastomer" retraction, so that the maximum stress corresponding to an elastomer extension is always obtained. Examination of recovery curves shows that they are similar in shape but that they fan out, as shown in Figure 1(b). It therefore appears that during fiber extension certainly the "length" of the elastomeric portion, and most likely the "modulus," must change. If the recovery curves are plotted from the same origin, as shown for two curves in Figure 1(c), then (i) increase in "length" of the elastomeric portion would give a higher strain for the same stress, while (ii) increase in "modulus" would need a higher stress for the same strain.

It is postulated that during extension of the fiber, both these changes could occur, although they could increase or decrease. At any given fiber extension the shape of the recovery curve will contain information about the "length" and "modulus" of the elastomer. A relative estimate of these factors can be obtained by comparison with a master recovery curve, as shown in Figure 1(c). It is assumed that curve 1 will lie on the master curve 2 in such a way that the curves coincide exactly if point X moves to point Y. Scaling factors can then be used to relate curve 1 to curve 2. The length of elastomer in curve 1, referred to curve 2, will be AX/AB, while the modulus, also referred to curve 2, will be CB/CY. If the master curve is assigned the arbitrary value of unity for both properties, these factors represent the elastomer length and elastomer modulus, respectively.

The curve matching can be done by the use of area fractions, as shown in Figure 1(d). Points X and Y will coincide if area fraction OQX/AOQX = area fraction OCY/POCY. The area fraction of the master curve is determined at distances $x, x_2, \ldots$ from the origin, as shown in Figure 1(e) and plotted as a function of x in Figure 1(f). The area fraction of the smaller curve to be transposed is measured and the appropriate value of x found from Figure 1(f). This fixes point Y in Figure 1(c) and also immediately fixes the elastomer length and therefore point B. The value of the elastomer modulus can then be obtained. The elastomer length and modulus can be greater or smaller than unity, depending on the relationship with the master curve. Since area fraction decreases with x, the master curve should be chosen which has the lowest area fraction so that it embraces all other curves.

A further geometric test was made to demonstrate that curves having the same area fraction do indeed have the same shape. The shape of the curves was characterized by the ratios of the slopes of two tangents, A/B, as shown in Figure 1(g). Figure 2 shows the situation in a typical case, nylon 66. There is a unique relationship between shape and area fraction for a range of fiber strains, relaxed and nonrelaxed. This is not a rigid proof of curve similarity but was considered good justification for the superposition procedure used.

RESULTS AND DISCUSSION

Values of the elastomer modulus and length calculated from recovery curves after 2 min of relaxation are given in Figure 3 together with the fiber stress–strain curves and measured values of TS (temporary set) and PS (permanent set). The elastomer parameters have been normalized on different arbitrary scales, so no numerical values are given on the ordinates. Superposition could not be made with sufficient accuracy below a fiber strain of about 2%.

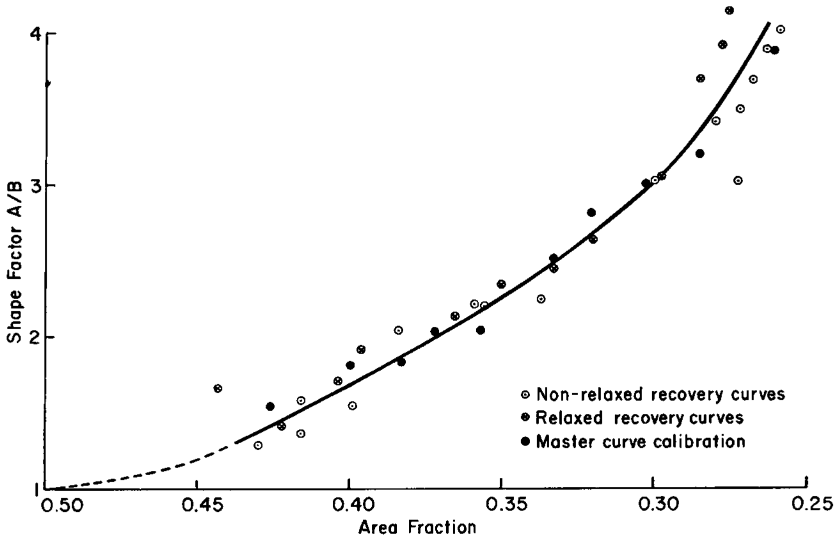

Fig. 2. Relationship between shape and area fraction of recovery curves for nylon 66.

For each stress–strain curve the slope has been determined as a function of strain, and the results also normalized on an arbitrary scale and superimposed on the elastomer modulus curves. By suitable adjustment of the ordinate scales it was possible to obtain a remarkable similarity between the shapes of these two curves. This similarity has no simple geometric basis since the elastomer modulus is only obtained after derivation of the completely independent elastomer length, and Figure 3 shows that the elastomer length curves have complex, irregular shapes. The recovery curves must therefore contain basic information about the mechanism of fiber deformation.

There is apparently a direct relationship between the postulated modulus concept of the vertical shift factor, the elastomer modulus, and the incremental stress per unit extension of the fiber, at a particular strain. This is not so surprising when it is considered that the noncrystalline modulus will dominate in a series summation if it is very much lower than that of the crystalline material. The fiber deformation is therefore mainly borne by the "rubbery" amorphous regions. This identification of a particular high-compliance phase which undergoes most of the strain is implicit in the proposed analogy of comparing the recovery curves to highly extended elastomers.

The similarity of the stress–strain slope and elastomer modulus curves was found to be very much better using recovery curves after stress relaxation has taken place rather than on immediate recovery. This provides an important clue to the nature of the relaxation process which can also be linked with the stress–strain curve. Stress in an extended elastomer can be reduced by crystallization. It is therefore proposed that during stress relaxation localized ordering of appropriate extended segments occurs, given sufficient time at a fixed strain. The recovery curve then represents the behavior of this "fixed" state. If there is no time for ordering, the segments will only maintain their relative register at a given fiber strain by maintenance of a stress. The state after relaxation is therefore representative of the stress-biased state, that is, directly related to extension during a stress–strain cycle.

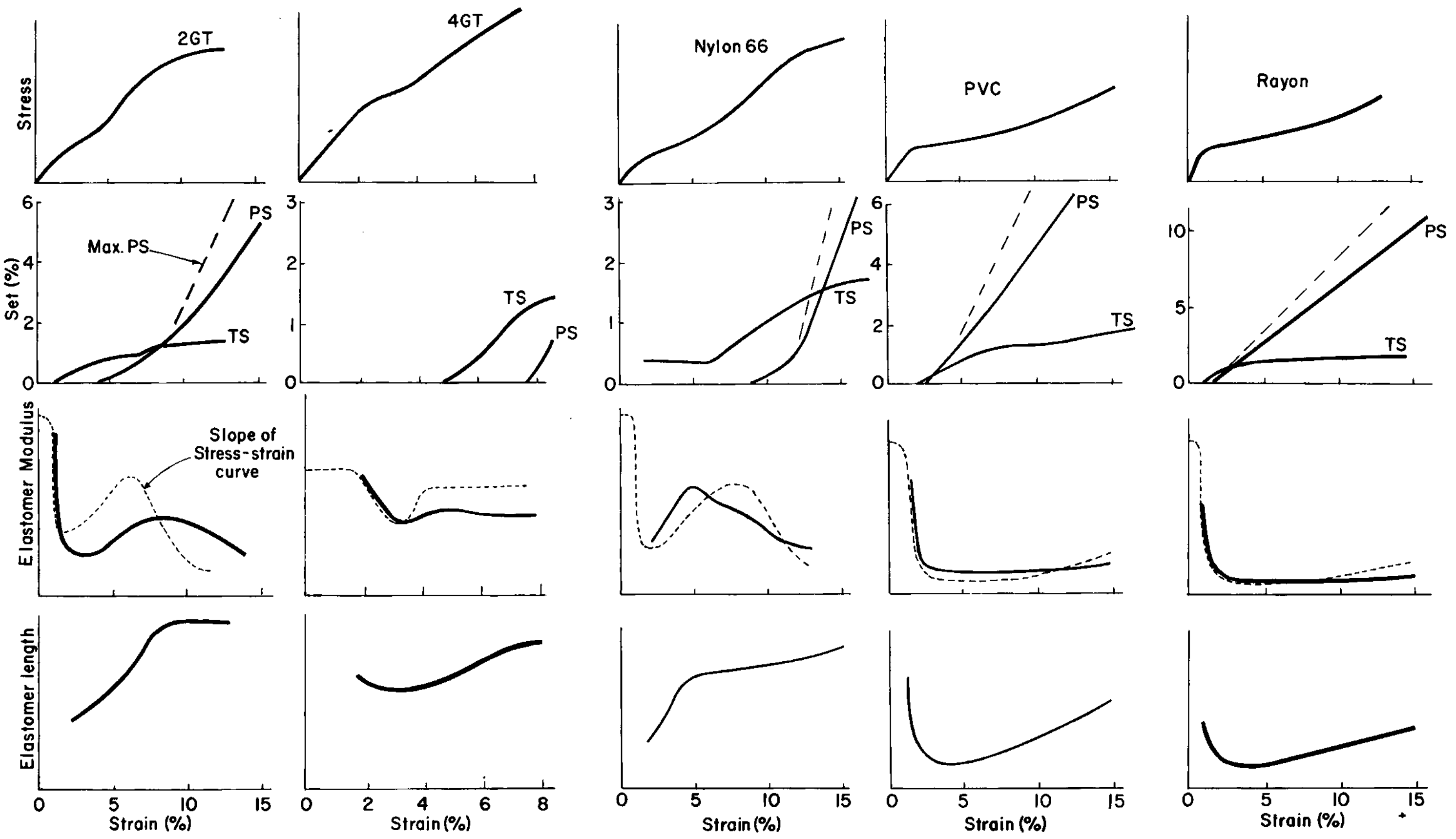

Fig. 3. Permanent set (PS), temporary set (TS), elastomer modulus, elastomer length, and slope of stress–strain curve (- - -) as function of strain for 2GT, 4GT, nylon 66, PVC, and rayon. Maximum permanent set (PS— —) is equal to the rate of increase of strain.

This reasoning explains the temporary nature of this form of set. Reduction of stress to zero removes any possible stress bias, and segmental motion rapidly destroys local order. It is necessary to assume that the ordered state does not change as the Instron jaws are brought together and the stress is gradually reduced. Put another way, the assumption is that even a small stress bias can prevent localized disordering in a short period of time.

Figure 3 shows that for all the fibers except 4GT, the temporary set (TS) is initiated at the strain which corresponds to the first yield in the stress–strain curve. The large fall in the elastomer modulus at this point is the factor that produces the apparent "yield." The explanation for this follows from the previous discussion of stress relaxation. Fiber extension produces localized ordering as elastomer chains are straightened, and when this happens the stress in the elastomer is considerably reduced.

It has been shown that a crystal transition is initiated in 4GT at about 4% strain, and complete conversion to the new crystal form is completed at about 12% strain.[1,2] The transition involves gauche to trans configurational changes. Figure 3 shows that the elastomer modulus is reduced at the primary yield, but the localized ordering that is responsible is not permanent enough, presumably because there is a strong driving force back to the first crystal form. Because of this, TS does not occur until a much higher strain is reached.

2GT, nylon 66, and to some extent 4GT, exhibit a secondary process after the primary yield which increases the slope of the stress–strain curve and also the values of elastomer modulus, followed by a second yield. Figure 3 shows that this is associated with an increase in the elastomer length, which suggests that new elastomer must be generated past a critical strain. The molecular disruption produced breaks local "crystallites." Eventually, the increased length of elastomer is sufficiently extended for localized ordering to again occur, and this leads to a second yield. For PVC and rayon there is only one yield, although there is subsequently some increase in elastomer modulus and length.

The permanent set (PS) begins when the TS approaches a constant value. The coincidence of these two events can be related to the point where the greatest extension of the kinked chains is possible. The maximum number of chain segments are aligned locally, and the TS cannot increase any more. Fiber extension can now only occur by a more severe chain slippage. Figure 3 shows that for all fibers the rate of increase of PS is almost equivalent to the rate of increase of imposed strain (referred to the point where the extrapolated PS meets the strain axis).

There will be a competition between chain slippage and chain breakage at this point, which depends on cohesive forces.[7] Electron paramagnetic resonance measurements do indeed show that the breakage of nylon 6 molecules is initiated just before the secondary yield.[8] The generation of new elastomer after the primary yield is presumably due to low molecular cohesion.

There was actually very little increase in either TS or PS during stress relaxation for any of the fibers studied. Typical results for nylon 66 are shown in Figure 4. This is an important result since it shows that it is the stress bias during extension which creates most of the temporary ordering and also more permanent slippage. The additional small amount of ordering during stress relaxation "fixes" the stress-biased state at that strain. The elastomer modulus before stress relaxation is usually larger as would be expected from consideration of the crystallization of elastomers.

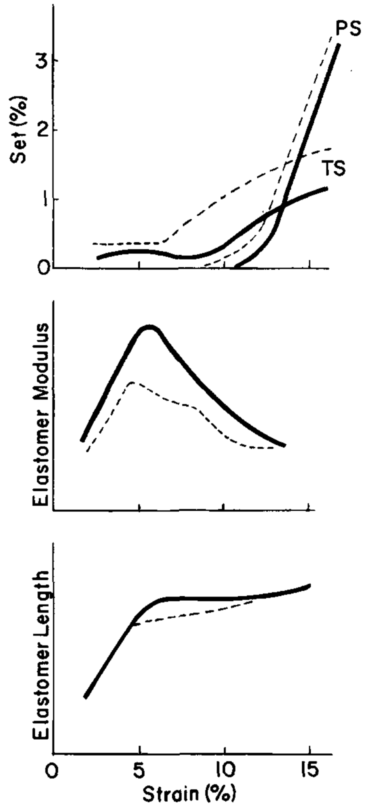

Fig. 4. Effect of stress relaxation for nylon 66: (——) without relaxation; (- - -) with relaxation.

The effect of strain on tan δ is shown in Figure 5. All fibers have an increase of tan δ which reaches a constant value at about the primary yield point. This could arise from an increase in free volume at yield, as has been proposed before.[9] Certainly, the loss processes would be expected to arise from increased molecular motion. Under these circumstances the T_g of the elastomer would effectively be lowered, which would explain why entropic rubbery forces could be present to produce recovery.

Figure 6 shows that a highly prestrained fiber in which permanent set has been produced is equivalent, in terms of the value of tan δ, to holding a fiber under stress past its yield point. If these are equivalent states, then prestrained fibers offer a convenient method for stress-free studies of loss and other processes (e.g., free volume) occurring at yield.

Some work was done to gain some understanding of the permanent set. A thermal treatment was used in which a fiber with a PS was heated in a relaxed state in silicone oil. The decrease in PS with temperature is shown in Figure 7. The PS is reduced to zero at the temperature at which the unstrained fiber itself begins to shrink. This temperature is close to the T_g. Thereafter the behavior of the unstrained and prestrained fibers is similar. A fiber with PS must have a different structure from the original fiber or the situation shown in Figure 8 would occur. The production of PS is therefore not equivalent to a slightly higher draw ratio. In addition, the PS decreases smoothly and does not disap-

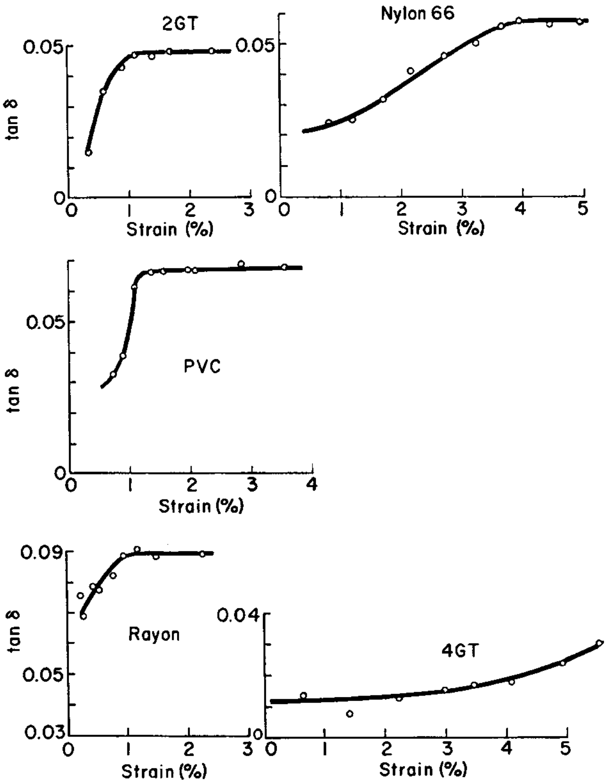

Fig. 5. Dynamic modulus measurements.

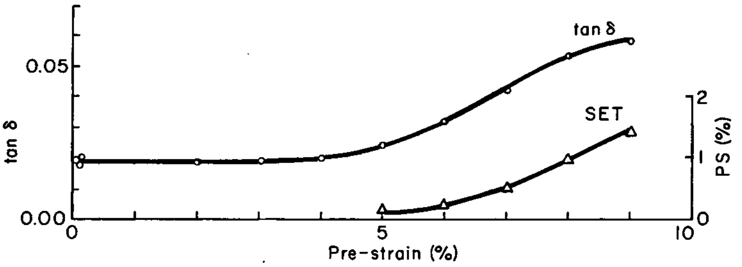

Fig. 6. Tan δ of poly(ethylene terephthalate) after prestrain.

pear over a narrow temperature range, which suggests there is a spectrum of slippage mechanisms. The fact that the PS can be completely recovered suggests that it is produced by a deformable long-range network.

CONCLUSIONS

The recovery of fibers from extensional strain is due to an entropic rubber-like elasticity of elastomeric portions of the fiber. The recovery curves of stress–strain cycles contain valuable information about this elastomer. These curves can be superposed after suitable horizontal and vertical transpositions, showing that the rubbery component is similar in nature over the range of extensional strains possible. The scaling factors can be used to calculate the relative "modulus" and "length" of this elastomer as it varies with fiber strain.

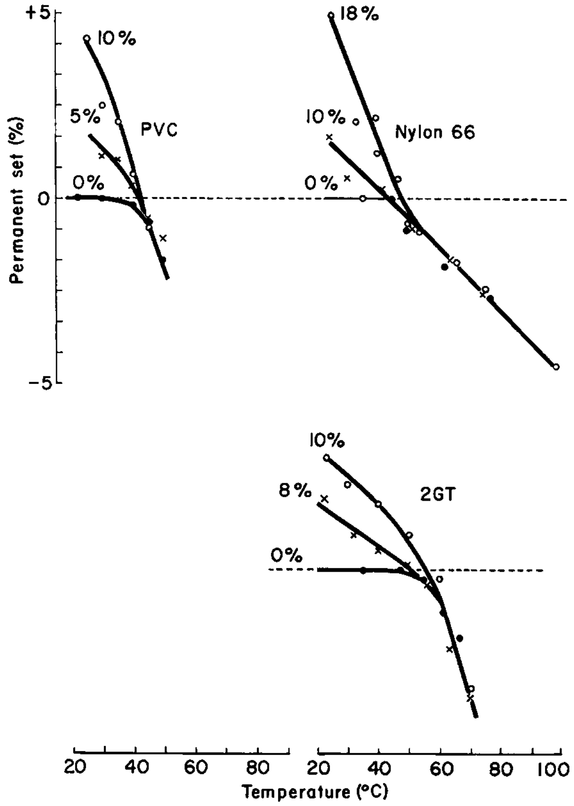

Fig. 7. Effect of heat on permanent set. Amounts of prestrain are shown as percentages.

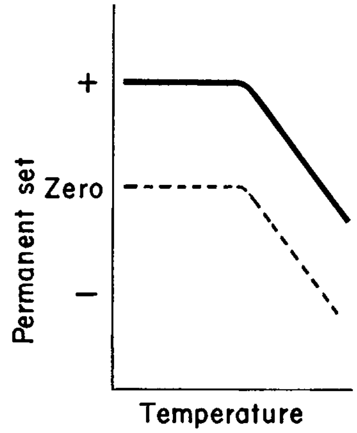

Fig. 8. Hypothetical case where prestrain just extends fiber but does not change the structure: (- - -) original fiber; (——) prestrained fiber.

The elastomer modulus, after stress relaxation, correlates very well with the slope of the stress–strain curve, showing that it is this rubbery modulus which controls extension. There is much better correlation after stress relaxation because temporary localized ordering occurs which is similar to a stress-biased ordering during extension. The temporary set is impermanent because this local register of molecular segments cannot be retained when the stress is reduced to zero.

The strain at which the temporary set is initiated corresponds to the primary yield. At this strain, localized ordering lowers the stress in the elastomer. Also at this strain the tan δ reaches a maximum, suggesting that the temporary set is initiated when sufficient molecular mobility has been generated, for example, by an increase in free volume. In the case of 2GT, 4GT, and nylon 66 more elastomer is generated after the primary yield until a secondary yield is reached. For PVC and rayon there is only a primary yield.

The permanent set is initiated just before the temporary set approaches a constant value. At this point the elastomeric chains are almost fully extended and maximum localized ordering has taken place. For PVC and rayon this occurs near the primary yield, but for 2GT, 4GT, and nylon 66 it is near the second yield. Once initiated, the rate of increase of permanent set is almost the same as the rate of increase of strain. It is fully recoverable on heating to near the T_g, showing that there is a long-range network.

The author wishes to thank Professor I. M. Ward for helpful comments and I.C.I. Fibres for permission to publish.

References

1. R. Jakeways, I. M. Ward, M. A. Wilding, I. H. Hall, I. J. Desborough, and M. G. Pass, *J. Polym. Sci., Polym. Phys. Ed.*, **13,** 799 (1975).
2. I. M. Ward, M. A. Wilding, and H. Brody, *J. Polym. Sci., Polym. Phys. Ed.*, **4,** 263 (1976).
3. R. Jakeways, T. Smith, I. M. Ward, and M. A. Wilding, *J. Polym. Sci. Lett.*, **14,** 41 (1976).
4. R. G. Quynn, and H. Brody, *J. Macromol. Sci. Phys.*, **B5,** 721 (1971).
5. M. Takayanagi, K. Imada, and T. Kajiyama, *J. Polym. Sci.*, **C15,** 263 (1966).
6. P. R. Pinnock, and I. M. Ward, *Polymer,* **7,** 255 (1966).
7. J. Becht, and H. Fischer, *Kolloid-Z. Z. Polym.*, **240,** 766 (1970).
8. J. B. Park, W. O. Statton, and K. L. De Vries, *Diss. Abstr. Int. B,* **32,** 4822 (1972).
9. G. M. Bryant, *Text. Res. J.*, **31,** 399 (1961).

Received November 9, 1976
Revised March 18, 1977