

Structure–Property Relationship in Heat-Set Poly(ethylene Terephthalate) Fibers. IV. Recovery Behavior

V. B. GUPTA, C. RAMESH, and A. K. GUPTA, *Department of Textile Technology and Centre for Materials Science and Technology, Indian Institute of Technology, Delhi, New Delhi-110016, India*

Synopsis

This study describes the recovery behavior from tensile strains of up to 0.15, of oriented poly(ethylene terephthalate) (PET) fibers, which were heat-set at different temperatures while free to relax and when held taut at constant length at room temperature. The taut annealed samples showed superior recovery behavior over the strain range studied. From structural studies on these samples, and also from FTIR studies of structural changes during deformation on similar shapes, it is concluded that, while the recovery behavior in the free-annealed samples is dominated by the amorphous phase, both the crystalline and the amorphous phases influence the recovery behavior of the taut-annealed samples.

INTRODUCTION

Textile fibers are subjected to considerable strains during their lifetime and therefore to ensure dimensional stability, it is necessary to design fibers with good recovery characteristics. An understanding of the structural features which influence recovery is therefore needed. There have, however, been only a limited number of studies to meet this objective, particularly for PET fibers.^{1,2} Ward et al.¹ compared the recovery behavior of poly(ethylene terephthalate) (2 GT, or PET in our notation), poly(trimethylene terephthalate) (3 GT) and poly(tetramethylene terephthalate) (4 GT) fibers. The relatively poor recovery shown by 2 GT fibers compared to 3 GT and 4 GT fibers was attributed to the dominance of the amorphous phase in controlling recovery in 2 GT fibers while, in 3 GT and 4 GT fibers, the crystallites also played an important role in determining the recovery behavior. Brody² analyzed the recovery data for a number of fibers including PET and concluded that recovery could be attributed to the elastomeric nature of the amorphous phase.

Extensive studies on the structure–property correlations have been previously reported^{3–10} on PET multifilament yarns heat-set over a range of temperature while free to relax and when held taut at constant length. The free-annealed and taut-annealed samples show considerable differences in structure and morphology. The taut-annealed samples have higher amorphous orientation⁴ and a higher degree of parallel coupling between the crystalline and amorphous phases^{6,8} compared to the free-annealed samples. Their mechanical properties, like elastic modulus,⁵ viscoelastic properties,⁶ load-elongation behavior,⁷ and stress–relaxation characteristics¹⁰ also show considerable differences. Unlike the control and the taut annealed samples,

the free annealed samples show⁷ two yield points and relatively large elongation to break. The free-annealed samples have lower modulus⁵ and lower strength⁷ compared to the taut-annealed samples. The stress-relaxation studies¹⁰ showed that the free-annealed samples had a higher degree of viscoelasticity. The structural changes taking place during tensile deformation¹¹ of free-annealed and taut-annealed films showed that, up to 15% strain, the predominant mechanism of deformation was chain uncoiling in the free-annealed samples while in the taut-annealed samples very early during its deformation chain unfolding occurs, indicating that there is deformation of the crystallites in this sample within the strain range studied. Thus it was considered worthwhile to study the recovery characteristics of these fibers with the hope of identifying the structural and morphological features which govern the recovery behavior of PET fibers. This hope was justified for the studies reported in this paper suggested that while the recovery behavior of the free-annealed samples was dominated by the amorphous phase, in the taut-annealed samples, the crystalline phase could also be contributing to their relatively superior recovery behavior.

EXPERIMENTAL

Sample Preparation

The starting material was a drawn (draw ratio 3.92) commercial multifilament PET yarn 76/36/0, i.e., 76 denier, 36 filaments, and zero twist. This sample will be referred to as the control. The yarn was heat-set in a silicone oil bath maintained at a fixed temperature to within $\pm 2^\circ\text{C}$. The heat-setting was done at 100, 140, 160, 180, and 220°C under two conditions, viz., when the yarn was (i) held taut at constant length designated (TA or taut-annealed) and (ii) free to relax (FA or free-annealed) at each of the above temperatures for 5 min. The samples were taken out of the bath after heat setting and then allowed to reach the ambient temperature; they were blotted, and then given a wash in carbon tetrachloride and allowed to dry in air.

Mechanical Testing

Load-Elongation Behavior

The load-elongation characteristics of the PET multifilament yarn samples of gauge length 5 cm were first obtained on an Instron Tensile Tester (Model 1112) at 100%/min rate of extension at room temperature. From the load-elongation curves, stress-strain curves were constructed, and the initial modulus, yield strain, strain at failure, and tenacity or breaking stress were computed using standard procedures.^{7,12}

Recovery Behavior

For studying the recovery behavior, the following two types of experiments were conducted on the Instron Tensile Tester.

Continuous Cyclic Tests. The Instron was set to extension cyclic mode and the multifilament PET yarn 10 cm gauge length was cycled from zero strain to fixed strains of between 3 and 15% at 100% min for about 20 cycles. From the cyclic loading-unloading curves, the fractional energy dissipated per cycle was calculated as the ratio of the energy dissipated to the total energy per cycle. Also the percent work recovery was calculated using standard procedures.¹² It may be stated that the fractional energy dissipated per cycle and percentage work recovery are complementary parameters.

Discontinuous Cyclic Tests. This test cycle was similar to that used by Ward et al.¹ and Brody.² PET multifilament yarn sample of 10 cm gauge length was initially extended in an Instron tensile testing machine to a constant strain of between 2 and 15% at an extension rate of 100%/min and then held at that strain for 2 min during which stress-relaxation takes place; after this the crosshead was returned to its original position. After a further 5 min, the filament is then reextended. From this the 2 min stress-relaxation, the immediate recovery, total recovery, and permanent set were determined, as illustrated in Figure 1.

Shrinkage Measurements

The changes in length of 40 cm of each yarn sample, after immersion in boiling water for 30 min, were measured, care being taken to allow free shrinkage.

RESULTS AND DISCUSSION

The room temperature stress-strain properties of taut-annealed and free-annealed samples have been reported earlier.⁷ However, for the present

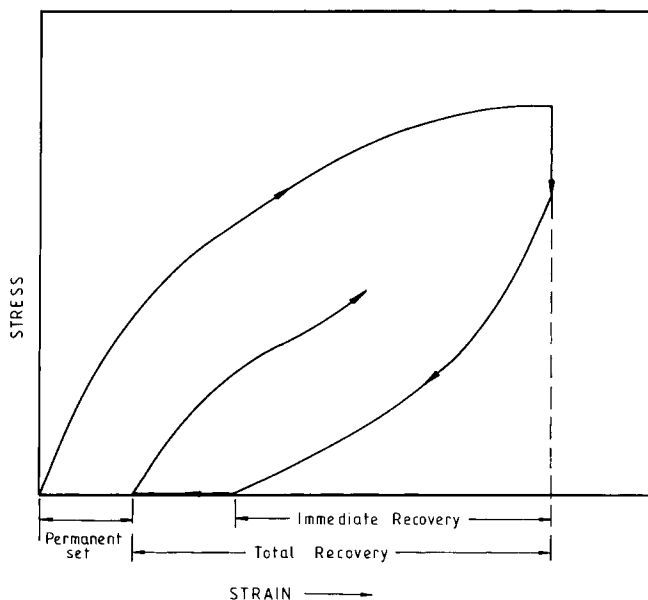


Fig. 1. The recovery cycle and definition of terms.

studies on recovery behavior, fresh samples had to be prepared from another batch of material, and therefore their stress-strain characteristics were also studied. Broadly speaking, the stress-strain curves of the fresh samples show features very similar to those reported for the earlier samples, but there are some differences when the data are examined in detail; the curves for the fresh samples are therefore included in Figure 2. The data have also been included for one other reason, viz., that, in the interpretation of the recovery data for strains up to 15%, the stress-strain curves give useful background information and thus provide the correct perspective. The taut-annealed samples show characteristics close to the control sample while the free-annealed samples have lower moduli, two yield points, and larger elongation to break compared to the control and the taut-annealed samples; the values of some of the mechanical parameters extracted from these curves are shown in Table I. The general features of the stress-strain curves,⁷ the elastic modulus,⁵ and their viscoelastic behavior⁶ have been previously discussed in detail; no further comments on these features will therefore be made.

Now the results obtained from continuous cyclic tests will be presented and discussed. The fractional energy dissipated per cycle, as stated earlier, is the ratio of the energy dissipated to the total energy expended during one loading-unloading cycle and is shown for some of the free-annealed and taut-annealed samples as a function of the number of cycles in Figure 3 for 5% and 15% strain levels. There are two points worth noting from these data: first, the taut-annealed samples dissipate a smaller fraction of the total energy compared to the free annealed samples, and, second, the frac-

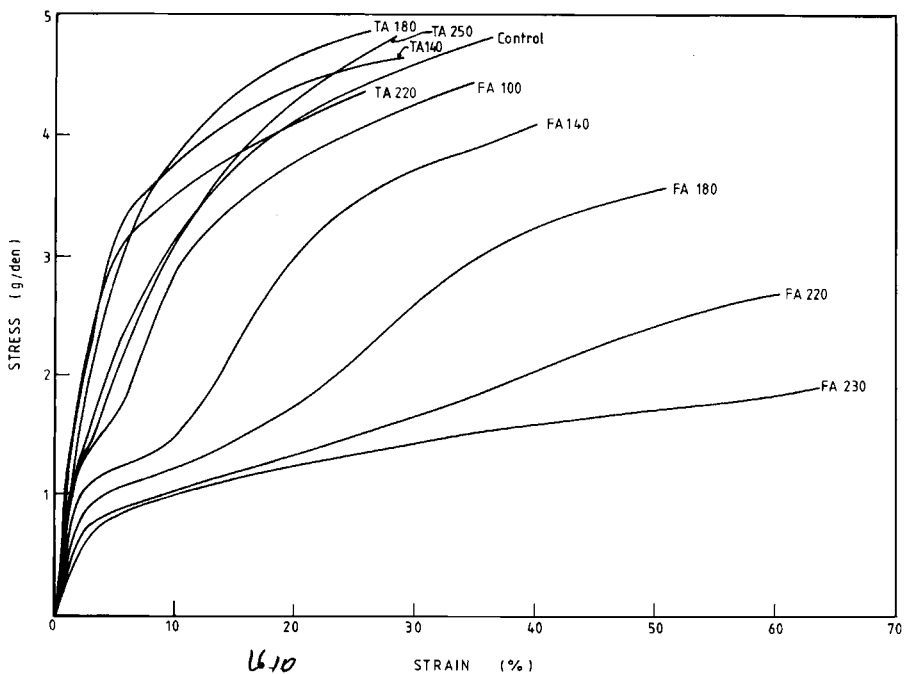


Fig. 2. Room temperature stress-strain curves for samples heat-set at different temperatures.

TABLE I
Some Mechanical Properties of the Samples

Sample	Initial modulus (g/denier)	Tenacity (g/denier)	Elongation at break (%)
Control	98.2	4.8	36.3
TA-100	94.2	4.7	32.1
TA-140	95.8	4.7	31.7
TA-180	93.8	4.9	26.6
TA-220	74.5	4.3	26.2
TA-250	78.3	4.7	27.5
FA-100	73.1	4.5	35.4
FA-140	60.8	4.1	40.9
FA-160	54.1	4.2	45.9
FA-180	41.1	3.6	48.9
FA-220	30.8	2.7	62.9
FA-230	27.5	1.9	63.8

tional energy dissipated reaches a nearly constant value for the taut-annealed samples after 5–10 cycles while, for free-annealed samples, it becomes nearly constant after 10–15 cycles. Both these features point out to the higher degree of viscoelasticity in the free-annealed samples.

The work recovery data for the first and the 20th cycles for some samples are presented in Figure 4. As stated earlier, the work recovery data are complementary to the fractional energy dissipation data and show the superior work recovery characteristics of the taut-annealed samples, as expected.

The results from the discontinuous cyclic tests will next be presented. First, the percentage stress relaxed during the 2-min stress-relaxation at a fixed strain is shown as a function of strain in Figure 5. For the taut-annealed samples, the higher the strain, the greater the stress-relaxation, indicating that the sample is more viscoelastic at higher strains, as expected. For free-annealed samples, a similar behavior is observed except at higher strains when there is a slight reduction of percentage stress relaxed.

An examination of the stress-strain curves (Fig. 2) shows that the strain range, over which this downward trend in stress-relaxation occurs, coincides with the strain region in which strain hardening shown by these samples between the two yield points occurs. It may again be noted that the free-annealed samples are more viscoelastic as they show greater stress-relaxation over the strain range examined. It is worthwhile pointing out at this stage that a similar conclusion was reached when more detailed stress-relaxation studies were made¹⁰ on these samples over a range of temperature.

The immediate and total recovery, as defined in Figure 1, are shown as a function of strain for some of the samples studied in Figure 6. The broad features shown by these two figures are similar, viz., that the taut-annealed samples show considerably superior recovery characteristics. An interesting feature worth noting on these figures is that, in the case of free-annealed samples, the higher the annealing temperature, the poorer the recovery

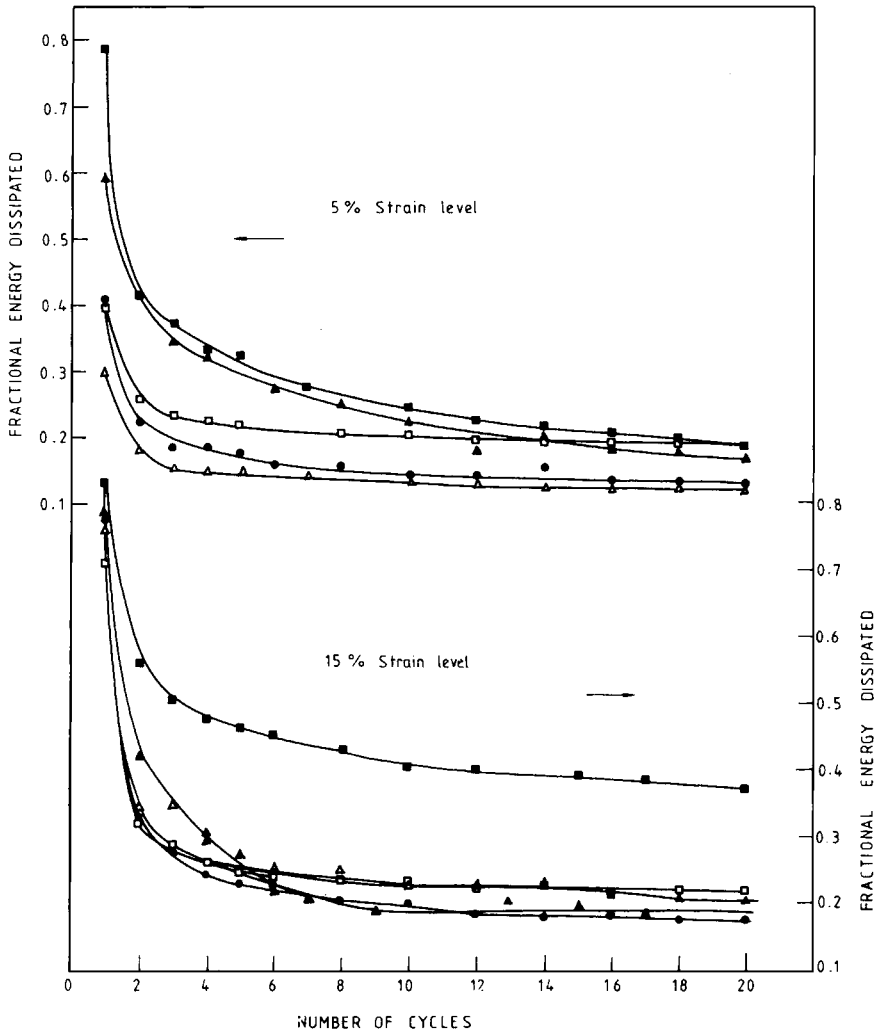


Fig. 3. Fractional energy dissipated per cycle as a function of number of cycles at 5% and 15% strain levels for some of the samples: (●) control; (▲) FA-180; (■) FA-220; (△) TA-180; (□) TA-220.

characteristics. For the taut-annealed samples, the situation is the opposite of this, viz., samples heat-set at higher temperatures show better recovery. To look at this interesting feature more clearly, the data relating to immediate recovery are replotted as a function of the heat-setting temperature for three strain levels, viz., 4%, 7.5%, and 15%, in Figure 7. With increasing heat-setting temperature, the immediate recovery decreases in the free-annealed samples while the taut-annealed samples show the opposite behavior except at the strains of 4%. Comments on this will be made later when structural correlations of recovery behavior will be discussed. The permanent set data are presented in two forms: in Figure 8 as a function of strain and in Figure 9 as a function of heat-setting temperature. The permanent set data are complementary to the recovery data, and the su-

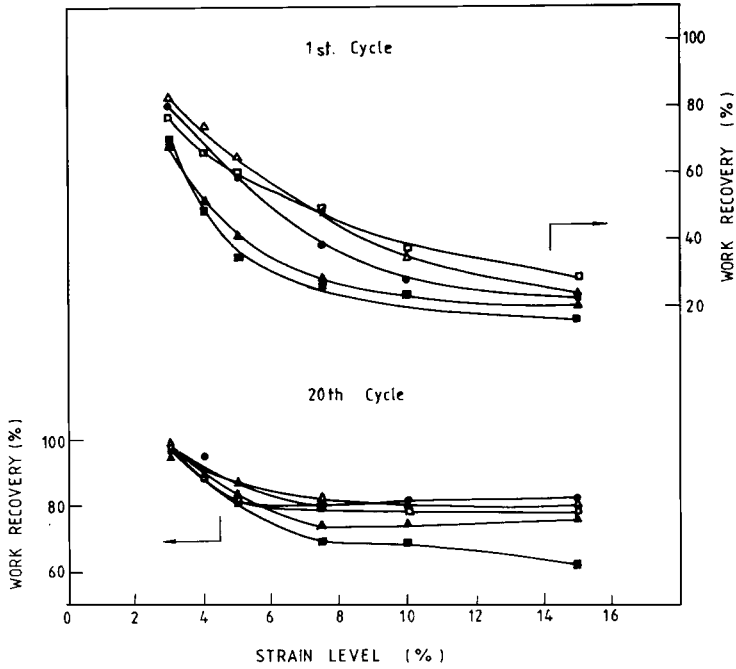


Fig. 4. Work of recovery for first and 20th cycles for some of the samples: (●) control; (▲) FA-180; (■) FA-220; (△) TA-180; (□) TA-220.

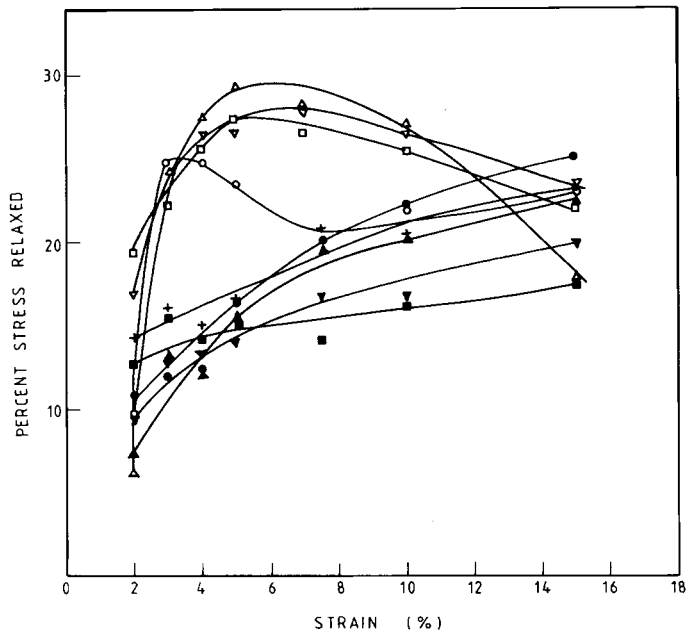


Fig. 5. Percentage stress relaxed for 2 min as a function of the prestrain during the continuous cycle test. (+) control; (●) TA-100; (▲) TA-140; (▼) TA-180; (■) TA-220; (○) FA-100; (△) FA-140; (▽) FA-180; (□) FA-220.

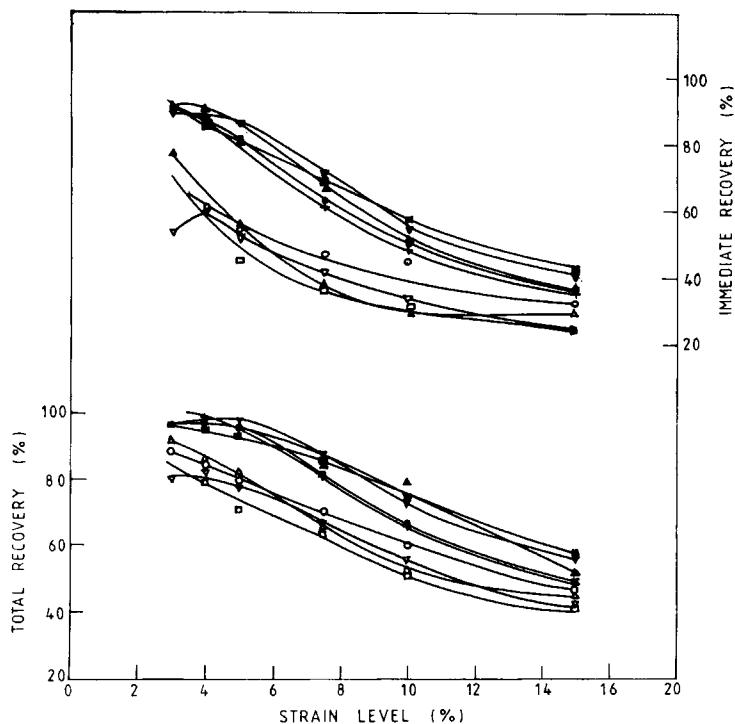


Fig. 6. Immediate recovery and total recovery as a function of strain for the control and various heat-set samples of PET fibers: (+) control; (●) TA-100; (▲) TA-140; (▼) TA-180; (■) TA-220; (○) FA-100; (△) FA-140; (▽) FA-180; (□) FA-220.

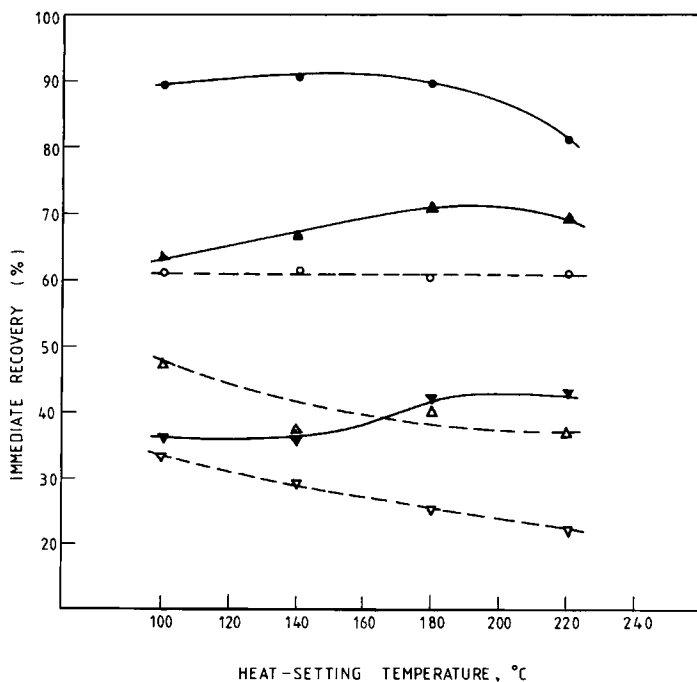


Fig. 7. Immediate recovery as a function of heat-setting temperature for free annealed (open symbols) and taut-annealed (filled symbols) samples at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

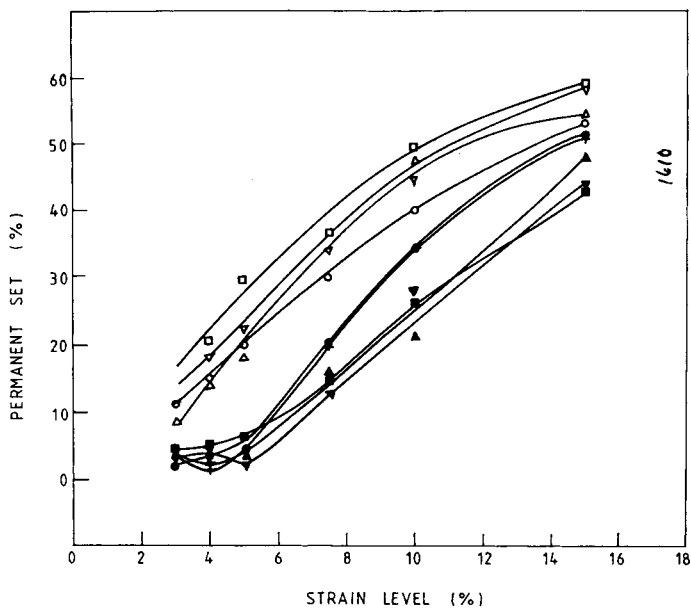


Fig. 8. Permanent set as a function of strain for control and the various heat-set samples of PET fibers. (+) control; (●) TA-100; (▲) TA-140; (▼) TA-180; (■) TA-220; (○) FA-100; (△) FA-140; (▽) FA-180; (□) FA-220.

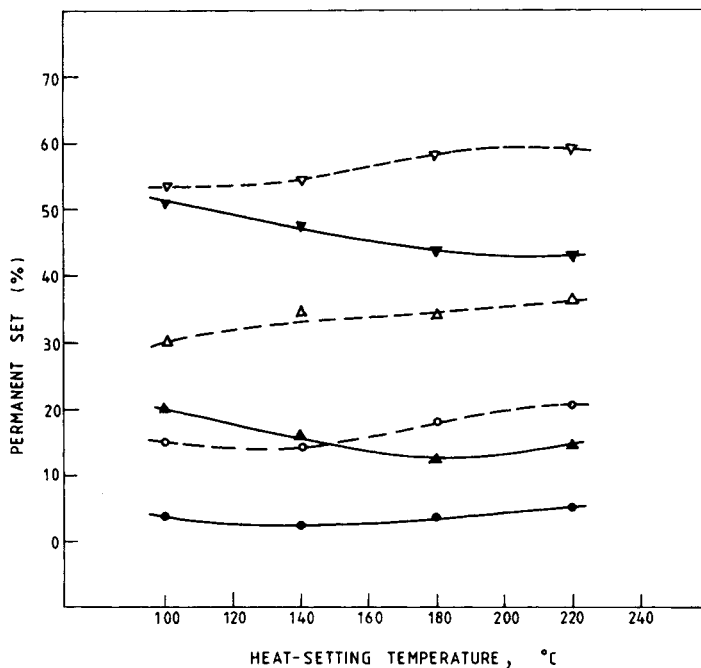


Fig. 9. Permanent set as a function of heat-setting temperature for free-annealed (open symbols) and taut-annealed (filled symbols) samples at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

periority of the taut-annealed samples in having the lower permanent set is again obvious.

The possibility of correlating the recovery characteristics with structural and morphological features will next be taken up. In this discussion, extensive use will be made of the studies made on the structures^{3,4} and morphologies^{6,8} of these fibers and also on the structural changes occurring during the tensile deformations of PET fibers¹¹ similarly prepared.

Previous work relating to structure-property correlations of PET fibers has shown that the mechanical properties of these heat-set anisotropic fibers do not correlate with crystallinity⁵⁻⁷; a fiber with low crystallinity like the control sample can have much higher modulus than the fiber free-annealed at 200°C, for example, which has a higher crystallinity. This observation is true for the recovery also; samples with the highest crystallinity are those which have been free-annealed at high temperatures and these show relatively poor recovery behavior. It may, however, be pointed out in passing that the recovery of crimped or textured PET yarns has been shown¹³ to correlate with crystallinity, but it should be stated that recovery in this case involves crimping back of uncrimped yarn and very little fiber stretch occurs during uncrimping.

The parameters which were found to be important in controlling mechanical properties of PET fibers from the previous work⁵⁻⁸ are (i) the amorphous orientation factor f_a , (ii) $(1-\beta)(1-f_a)$, which is a combination of the amount of amorphous phase $(1-\beta)$, where β is the degree of crystallinity, and $(1-f_a)$, a measure of the amorphous state disorientation, (iii) Δn , the sample birefringence, and (iv) the nature of the coupling between the crystalline and amorphous phases. The coupling parameters are represented⁸ by λ (series) and ϕ (parallel) obtained from the Takayanagi model.¹⁴ The immediate recovery and permanent set data will now be analyzed as a function of these parameters.

The dependence of immediate recovery on Herman's orientation factor for the amorphous phase, f_a , and on $(1-f_a)(1-\beta)$ are shown in Figures 10 and 11, respectively. It is obvious that while, in the case of free-annealed samples, there is a good correlation between immediate recovery and f_a , the same is not true of taut-annealed samples. The same situation is apparent in the permanent set data, as shown in Figures 12 and 13.

The correlations with birefringence, Δn , appear more encouraging, as shown in Figures 14 and 15 for the immediate recovery and permanent set, respectively. This would imply that the recovery behavior is governed more by average orientation rather than by amorphous orientation. It is worth pointing out that structural studies have shown^{4,8} that, with increasing heat-setting temperature, birefringence decreases for free-annealed samples and increases for taut-annealed samples, a behavior similar to that shown by the immediate recovery data presented in this paper.

The dependence of the recovery behavior on the coupling parameters for these samples will next be considered with increase in heat-setting temperature, in both taut-annealed and free-annealed samples the parallel coupling parameter ϕ decreases and the series coupling parameter λ increases.⁸ It has been shown⁸ that some mechanical properties depend on ϕ/λ , the ratio of parallel to series coupling parameters. The immediate recovery and the permanent set data are shown as function of ϕ/λ in Figures

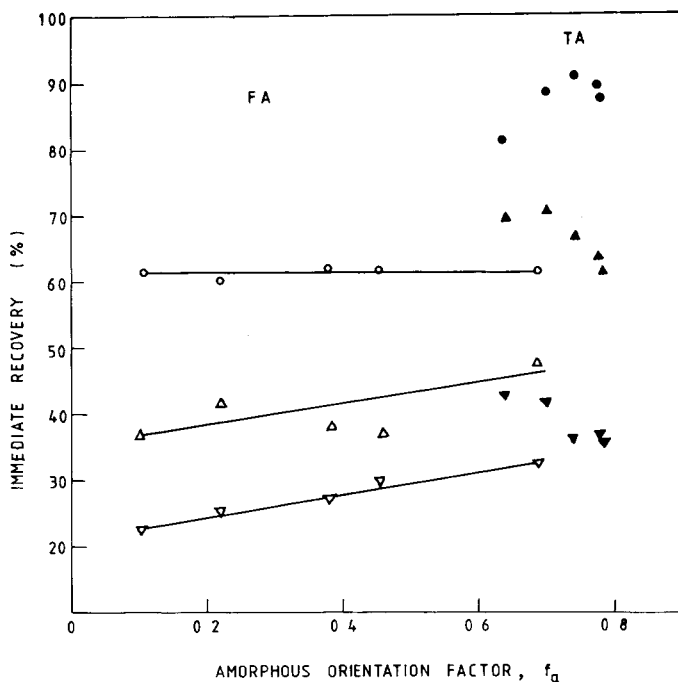


Fig. 10. Immediate recovery as a function of amorphous orientation factor, F_a , for free-annealed (open symbols) and taut-annealed (filled symbols) at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

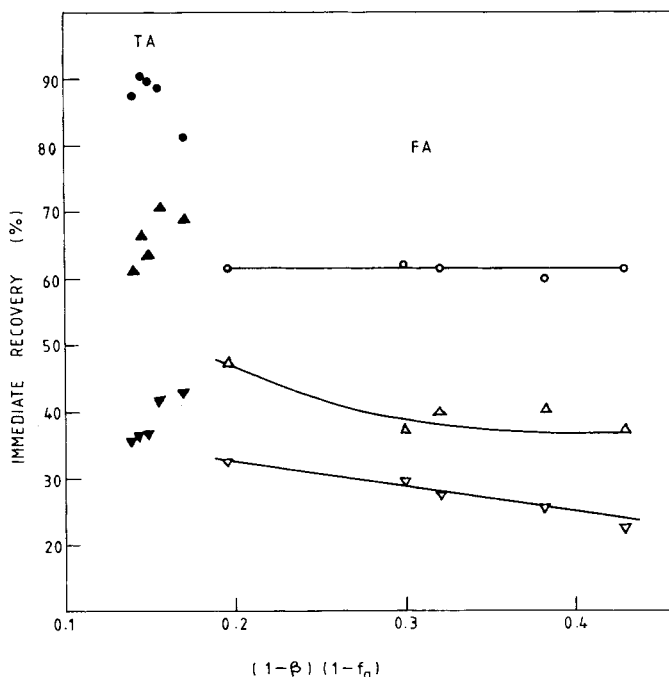


Fig. 11. Immediate recovery as a function of $(1-\beta)(1-f_a)$ for free-annealed (open symbols) and taut-annealed (filled symbols) samples at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

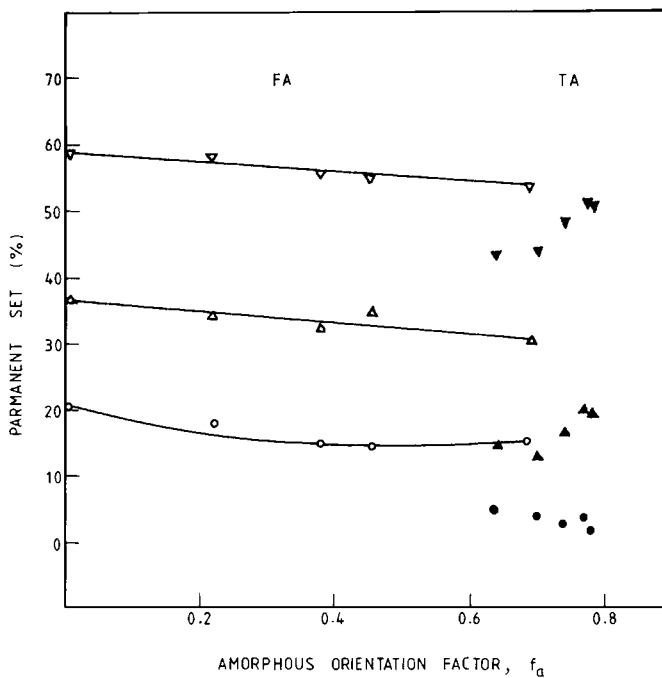


Fig. 12. Permanent set as a function of amorphous orientation factor, f_a , for free-annealed (open symbols) and taut-annealed (filled symbols) samples at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

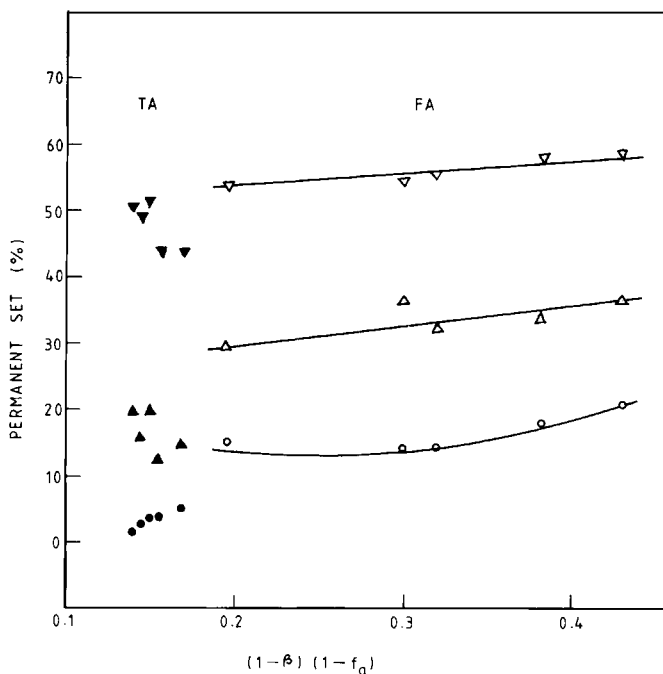


Fig. 13. Permanent set as a function of $(1-\beta)(1-f_a)$ for free-annealed (open symbols) and taut-annealed (filled symbols) samples at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

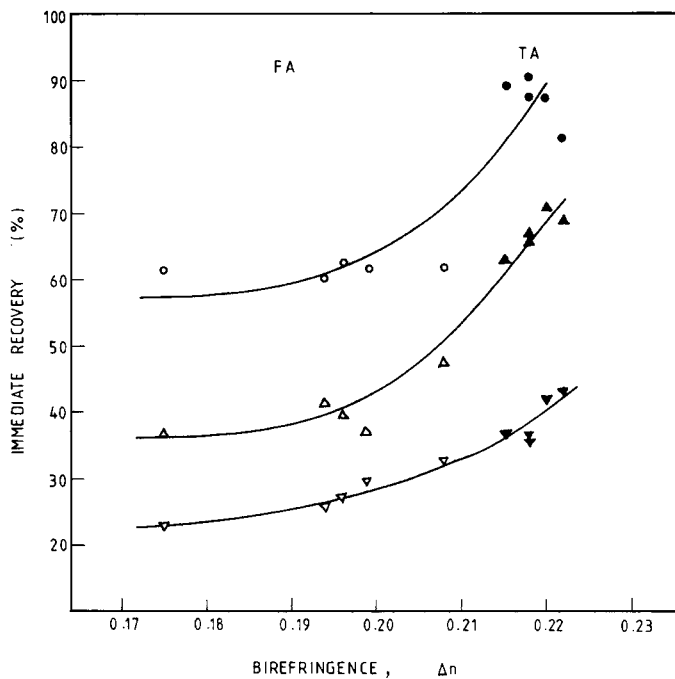


Fig. 14. Immediate recovery as a function of birefringence, Δn , for free-annealed (open symbols) and taut-annealed (filled symbols) samples at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

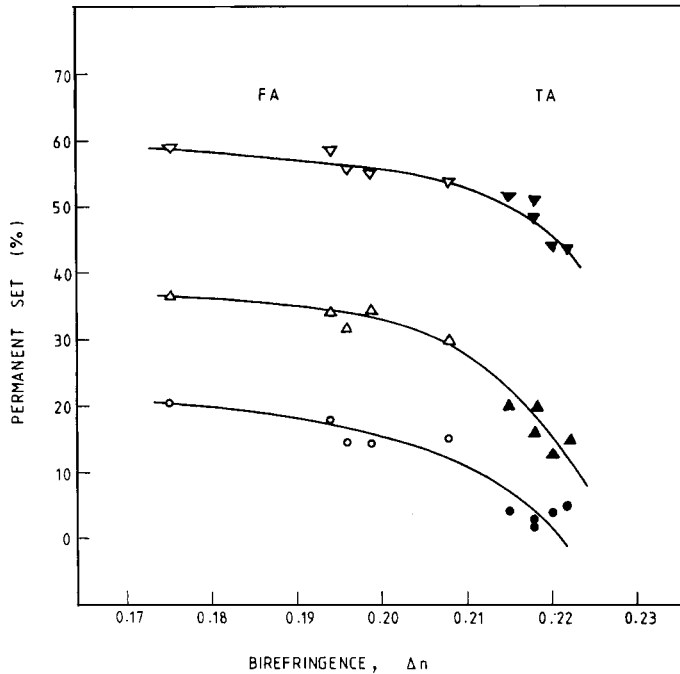


Fig. 15. Permanent set as a function of birefringence, Δn , for free annealed (open symbols) and taut-annealed (filled symbols) samples at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

16 and 17, respectively. It would intuitively be expected that with increase of parallel coupling (ϕ) and decrease of series coupling (λ), immediate recovery will improve; hence with increase in ϕ/λ recovery should be better. This appears to hold for the free-annealed samples but is not the case for taut-annealed samples, specially at higher strains.

The above attempts at seeking correlations between the recovery behavior and structural and morphological factors should not be taken to mean that recovery depends on average orientation but not on amorphous orientation or on the coupling between the amorphous or crystalline regions. All these factors will play some part in controlling the recovery behavior. However, the change of birefringence, but not the other parameters that have been considered, with heat-setting temperature shows features which have similarities with the dependence of immediate recovery on heat-setting temperature, suggesting some further examination of the dependence of recovery on this parameter. Birefringence is a composite parameter having contributions from the degree of crystallinity, crystallite orientation, and amorphous orientation. In the taut-annealed samples none of these three factors considered above can explain the recovery behavior. In the free-annealed samples, the recovery behavior, on the other hand, shows quite good correlation with amorphous orientation. Thus it might be argued that, in the taut-annealed samples, the crystallites may also be playing a role in determining the recovery behavior. Evidence that this may indeed be the case comes from FTIR studies on structural changes taking place in free-annealed and taut-annealed films when they are uniaxially stretched.¹¹ The data on films must not be taken to be entirely representative of the fiber data. Nevertheless, there will be expected to be some correspondence between the behavior shown by the film and fiber samples. The FTIR data showed¹¹ that, up to 15% strain, the predominant deformation mechanism in the free-annealed samples was chain uncoiling in the amorphous regions. In the taut-annealed samples, there was considerable chain unfolding within this strain range but no chain uncoiling. This result could be considered to indicate that the crystallites are deformed when taut-annealed samples are stretched and therefore they will play a part in the recovery process. In the free-annealed samples, on the other hand, recovery will mainly be due to the coiling back of the uncoiled chains in the amorphous regions; this will therefore necessarily be a highly viscoelastic, time-dependent process, as has been seen to be the case.

It may be recalled that at low strains the dependence of immediate recovery on heat-setting temperature is similar for the taut-annealed and free-annealed samples as shown in Figure 7, while at high strains the dependence is dissimilar. While the dominance of the amorphous phase in controlling the recovery of free-annealed samples and of both the amorphous and crystalline phases in the case of taut-annealed samples can explain the dissimilar behavior, no satisfactory explanation of the low strain behavior has yet been given. Though FTIR results indicate¹¹ that, in taut-annealed samples, chain-unfolding occurs at low strains, it is not unlikely that at low strains there is also some deformation of the amorphous phase in these samples. Indeed, this was earlier suggested⁷ to be the case to explain the stress-relaxation curves of these samples. In this context it is interesting

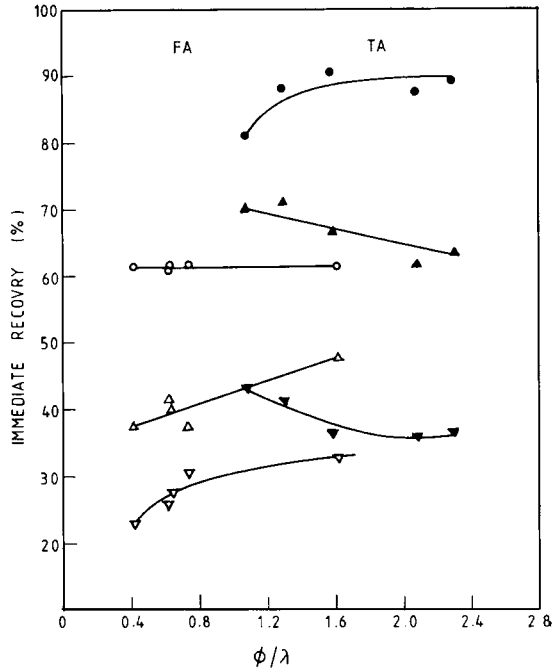


Fig. 16. Immediate recovery as a function of Φ/λ for free-annealed (open symbols) and taut-annealed (filled symbols) samples at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

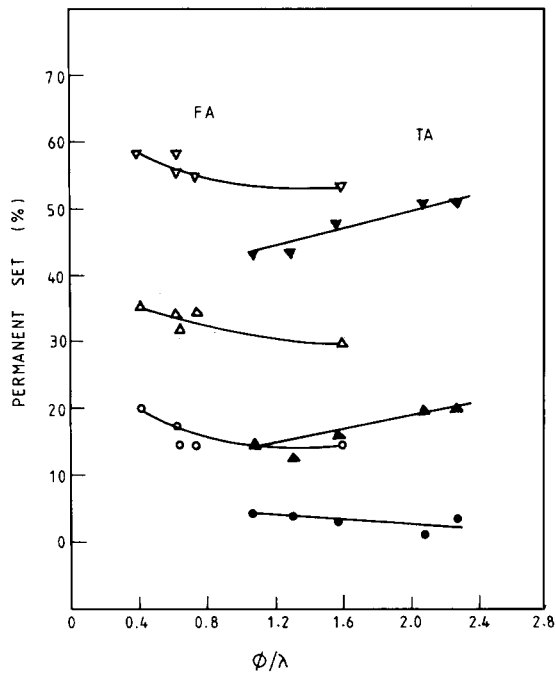


Fig. 17. Permanent set as a function of Φ/λ for free-annealed (open symbols) and taut-annealed (filled symbols) samples at various strain levels. Strain: (○, ●) 4%; (△, ▲) 7.5%; (▽, ▼) 15%.

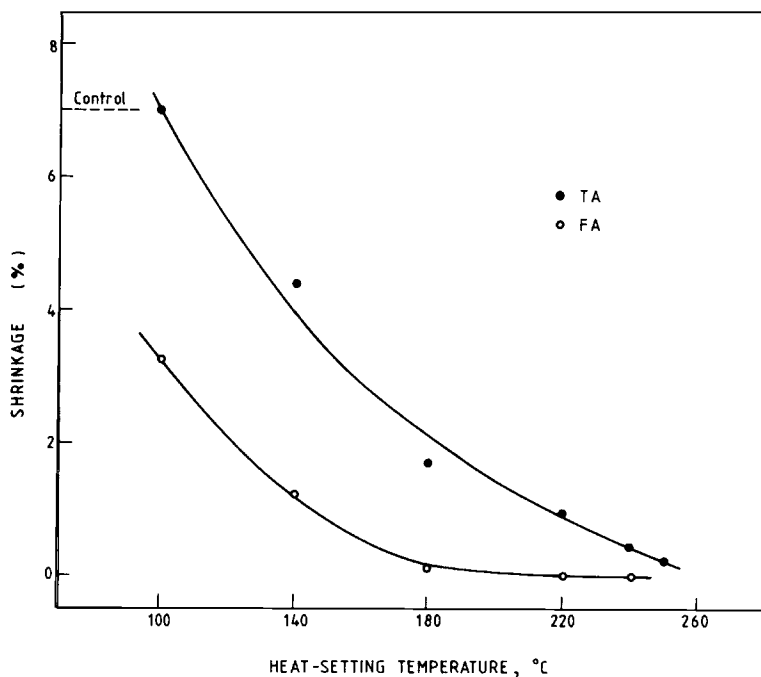


Fig. 18. Shrinkage in boiling water as a function of heat setting temperature for free-annealed (○) and taut-annealed (●) samples.

to note that Dulmage and Contois¹⁵ showed presumably for similar fibers that the strain in the crystalline regions was a factor of about 10 less than the macroscopic strain for macroscopic strain of up to 1.8%; the stress-strain behavior at these low strains must therefore be associated with the deformation of amorphous regions. It is suggested that the low strain behavior is dominated by the amorphous phase in both taut-annealed and free-annealed samples. It should, however, be remembered that the amorphous phase in the taut-annealed samples has much higher orientation to begin with and will therefore have different recovery characteristics. At higher strains in the taut-annealed samples the strain due to deformation of crystallites which is superposed on the strain in the amorphous phase will begin to play an important role and become the dominant factor controlling the recovery behavior.

The data on shrinkage in boiling water are presented in Figure 18. The free-annealed samples show the lowest shrinkage and as shown earlier, also the poorest recovery. Ward et al.¹ had noticed this similarity in their samples and commented that this was not surprising if both recovery and shrinkage involve the contraction of an extended network. No further comments on this aspect will be made at this stage.

References

1. I. M. Ward, M. A. Wilding, and H. Brody, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 263 (1976).
2. H. Brody, *J. Appl. Polym. Sci.*, **22**, 1631 (1978).
3. V. B. Gupta and S. Kumar, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1307 (1979).

4. V. B. Gupta and S. Kumar, *J. Appl. Polym. Sci.*, **26**, 1865 (1981).
5. V. B. Gupta and S. Kumar, *J. Appl. Polym. Sci.*, **26**, 1877 (1981).
6. V. B. Gupta and S. Kumar, *J. Appl. Polym. Sci.*, **26**, 1885 (1981).
7. V. B. Gupta and S. Kumar, *J. Appl. Polym. Sci.*, **26**, 1897 (1981).
8. V. B. Gupta, C. Ramesh, and A. K. Gupta, *J. Appl. Polym. Sci.*, **29**, 3115 (1984).
9. V. B. Gupta, C. Ramesh, and A. K. Gupta, *J. Appl. Polym. Sci.*, **29**, 3727 (1984).
10. V. B. Gupta, C. Ramesh, and A. K. Gupta, *J. Appl. Polym. Sci.*, **29**, 4203 (1984).
11. V. B. Gupta, C. Ramesh, and A. K. Gupta, *J. Appl. Polym. Sci., Polym. Phys. Ed.* to appear.
12. W. E. Morton and J. W. S. Hearle, *Physical Properties of Textile Fibres*, The Textile Institute and Heinemann, London, (1975).
13. V. B. Gupta, A. Ailawadi, and P. K. Ganguly, *Text. Res. J.*, Sept. (1983).
14. M. Takayanagi, *Proc. 4th Int. Cong. Rheology, Part I*, Interscience, New York, 1965, p. 161.
15. W. J. Dulmage and L. E. Contois, *J. Polym. Sci.*, **28**, 275 (1958).

Received December 20, 1983

Accepted May 1, 1984