

# **The Effect of Heat Setting on the Structure and Mechanical Properties of Poly(ethylene Terephthalate) Fiber. IV. Tensile Properties Other Than Modulus and Their Dependence on Structure**

V. B. GUPTA and SATISH KUMAR,\* *Textile Technology Department, Indian Institute of Technology, Delhi, New Delhi 110016, India*

## **Synopsis**

The stress-strain characteristics of poly(ethylene terephthalate) fibers, heat set under different conditions have been studied under tension, and mechanical properties such as tenacity, yield point, elongation at break, and work of rupture are presented and discussed. An attempt has been made to correlate these mechanical properties with structural parameters. The orientation of the molecules in the fiber and the size and distribution of the crystallites emerge as important factors controlling the tensile properties.

## **INTRODUCTION**

Though a considerable amount of work has been done on studying the stress-strain characteristics of poly(ethylene terephthalate) (PET) fibers,<sup>1-13</sup> a systematic study to assess how structure and morphology influence the shape of the stress-strain curve and the tensile properties obtained from the curve does not appear to have been made. To achieve this, PET fibers having a wide spectrum of structure and morphology were prepared by heat setting the commercial fiber under different conditions. The room-temperature load-elongation behavior of these samples was studied. From these curves, data were obtained on elastic modulus, yield point, tenacity, elongation at break, and work of rupture. The elastic modulus data have already been discussed<sup>16</sup> in part II. In this article, properties other than tensile modulus are presented and correlated with the structural parameters reported<sup>14</sup> in part I.

## **EXPERIMENTAL**

### **Sample Preparation**

Details of sample preparation appear<sup>14</sup> in part I of this series. Briefly, the commercial multifilament PET yarn was heat set in a silicone oil bath while free to relax (FA) or held taut at constant length (TA) between 100 and 220°C for times ranging from 1 to 60 min. In one case, the samples heat set for 60 min, the cooling time was also varied.

\* Present address: Polymer Research Institute, University of Massachusetts, Amherst, MA 01003.

### **Load–Elongation Behavior**

Load–elongation curves of multifilament yarn of gauge length 5 cm were obtained using an Instron Tensile Tester at an extension rate of 100%/min. From the load–elongation curves, the stress–strain curves were constructed; and from the latter, the following parameters were computed (the values reported represent an average of at least 40 measurements in each case):

#### **Elongation at Break**

This was measured in two ways, viz., by noting the percentage elongation at the first and the last fiber break.

#### **Specific Work of Rupture**

The area under the stress–strain curve gives the specific work of rupture and is reported in grams per denier.

#### **Yield Stress and Yield Strain**

The yield point was located using the Coplan construction,<sup>15</sup> and the stress and strain at the yield point were taken to represent the yield stress and yield strain, respectively.

#### **Tenacity**

The nominal and true tenacity represent, respectively, the maximum breaking load divided by the original and final denier of the yarn.

## **RESULTS AND DISCUSSION**

To illustrate the type of data obtained, the average stress–strain curves for the control and the free- and taut-annealed samples at 100, 160, and 220°C for a heat-setting time of 1 min are shown in Figure 1. The data for all other samples follow a similar trend. It may be noted that the stress–strain curves for samples annealed at constant length are quite close to one another and fall above the control. The shapes of the curves indicate closeness to brittle rather than to ductile behavior. The curves for the free-annealed samples, on the other hand, show considerable variations and fall below the control. These samples show a more distinct yield behavior and their ductility increases with increase of heat-setting temperature. The control sample shows a reasonably distinct yield point, and its behavior is intermediate between the taut-annealed and the free-annealed samples. The breaking stress of most taut-annealed samples is generally higher than that for free-annealed samples. Free-annealed samples show comparatively high elongation.

While these characteristics of the stress–strain curves will be discussed later when individual properties are discussed, it can be stated here that, as observed in the case of modulus, while the properties of the free-annealed samples show a predominant effect of the amorphous phase, in taut-annealed samples this is not so. Obviously, the presence of two distinct phases coupled in series in the

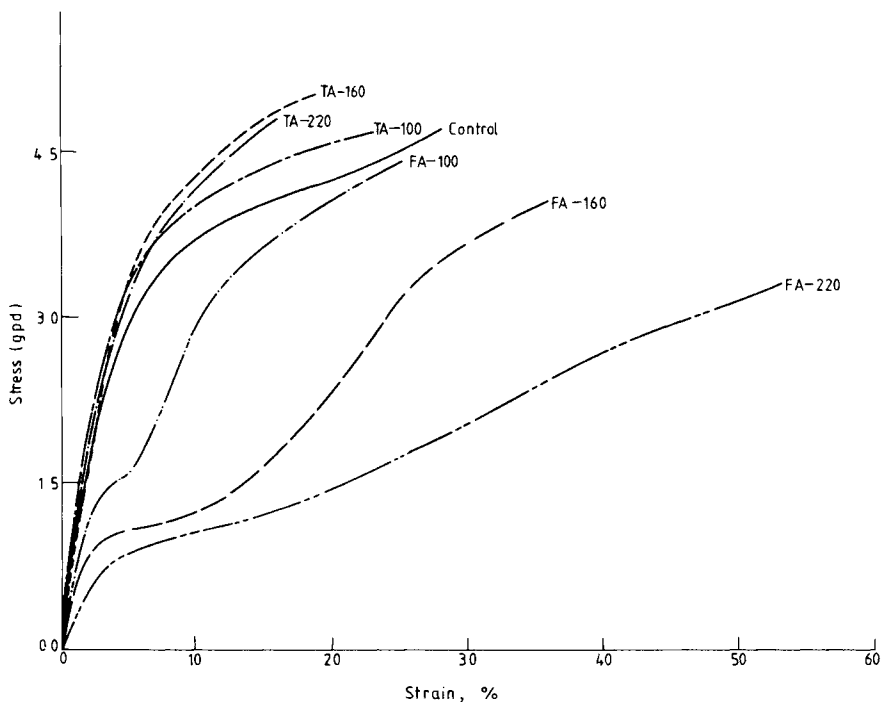


Fig. 1. Stress-strain curves for samples heat set for 1 min at 100, 160, and 200°C and for control sample (FA, free-annealed; TA, taut-annealed).

case of free-annealed samples and the two phases distributed without distinct boundaries and with no clear-cut series coupling in the case of taut-annealed samples would be expected to contribute to these differences.

### Yield Point

Examination of Figure 1 reveals that in the taut-annealed samples the yield point is quite close to the fracture point. There are two yield points in the free-annealed samples—the first in the small strain region and the second close to the fracture point. The control sample shows only one reasonably distinct yield point and has characteristics intermediate between the taut-annealed and the free-annealed samples.

The differences in the arrangement of molecules in the crystalline and amorphous regions in the free- and the taut-annealed samples have been shown schematically<sup>17</sup> in part III (Fig. 7 of part III). These figures show that while in free-annealed samples the crystalline and amorphous phases are quite distinct and are stacked in series, in taut-annealed samples there are no sharp boundaries and the crystallites are distributed within the amorphous mass. The load sharing is therefore better in the taut-annealed samples; and hence when a tensile force is applied, the material initially extends uniformly. In this region, the stress-strain curves of the control and taut-annealed samples will show a structural dependence similar to that for modulus, which has been discussed<sup>16</sup> in part II, where it was shown that the two-phase model, which is based on a series coupling between the crystalline and amorphous regions, is not very satisfactory for

taut-annealed samples. The distribution of strains being more uniform in these samples, the crystalline phase also contributes to the resistance to deformation. The initial amorphous orientation of these samples is high, and hence they offer more resistance to further extension. By the time the yield point is reached, it is likely that most of the tie molecules could have snapped and fibrillar slip could become possible, thus resulting in a bending of the curve toward the strain axis. It must be appreciated that PET is a glassy material at room temperature, and therefore such deformation can occur only to a limited extent.

In free-annealed samples, on the other hand, there is a different arrangement of the crystalline and amorphous regions, and the number of taut interlamellar ties is very small. The straight connecting molecules will be the first to take up the load. Due to their limited number, the stress concentration will be high and they will quickly snap. The initial portion of the curve and the first yield point can arise from these phenomena. After this the molecules in the interlamellar amorphous regions, which have a distribution of orientation, will start uncoiling. This will result in some amount of strain hardening. In the samples heat set at higher temperatures, the rather low amorphous orientation is quite perceptible in the form of considerable deformation at relatively low stresses. The decrease in yield stress and the increase in yield strain (relating to the first yield point) of the free-annealed samples as a function of heat-setting temperature, as shown in Figures 2(a) and 2(b) respectively, lend support to the above explanation. The second yield point will relate to the slip processes, as explained in the case of taut-annealed samples.

It has been shown<sup>18</sup> that the oriented amorphous phase or the third phase is related to the amorphous orientation factor. It will be expected that the number of taut-interconnecting chains will be less if the amorphous orientation factor is small. Therefore, yield stress and yield strain should correlate with amorphous orientation factor. The yield stress and yield strain for the first yield point in free-annealed samples are plotted as functions of amorphous orientation factor in Figures 3(a) and 3(b), respectively. A reasonably clear trend is apparent, thus

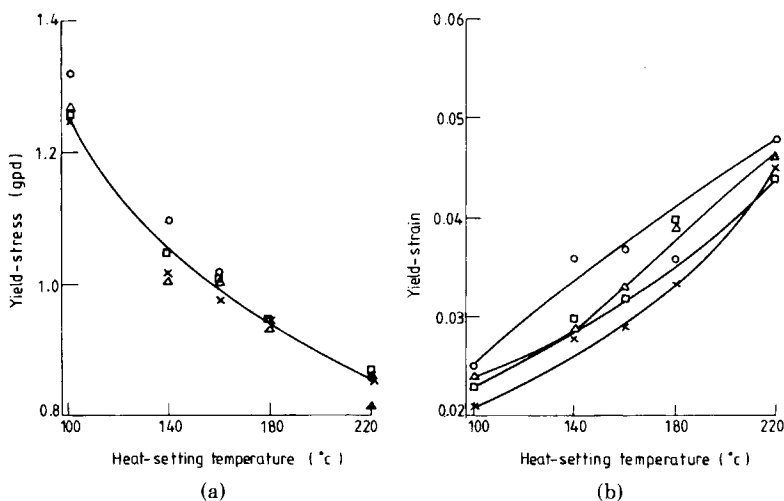


Fig. 2. Dependence of (a) yield stress and (b) yield strain on heat-setting temperature for free-annealed samples: (O) 1 min; ( $\Delta$ ) 15 min; ( $\square$ ) 30 min; (X) 60 min.

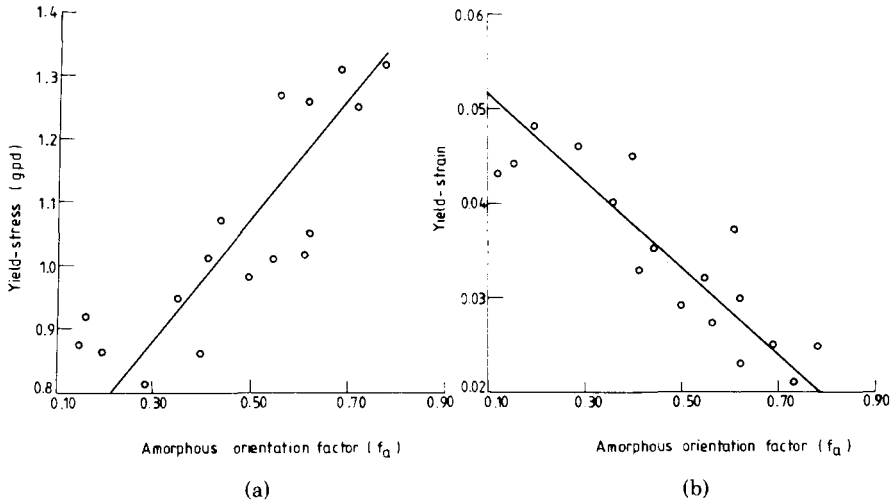


Fig. 3. Dependence of (a) yield stress and (b) yield strain on the amorphous orientation factor ( $f_a$ ) for free-annealed samples.

adding substance to the arguments presented to explain the structural dependence of the yield phenomenon.

### Elongation at Break

In the testing of multifilament yarn, all the filaments may not have the same length; some will be longer than others, and hence the stress distribution will not be uniform. The individual filaments break at different times during the stress-strain test. The data on extension at the first fiber break and at the last fiber break are presented in Figures 4(a) and 4(b), respectively, for all the samples as a function of the heat-setting temperature. They show similar trends. The discussion will be confined to the elongation at the first fiber break. The following points should be noted from Figure 4:

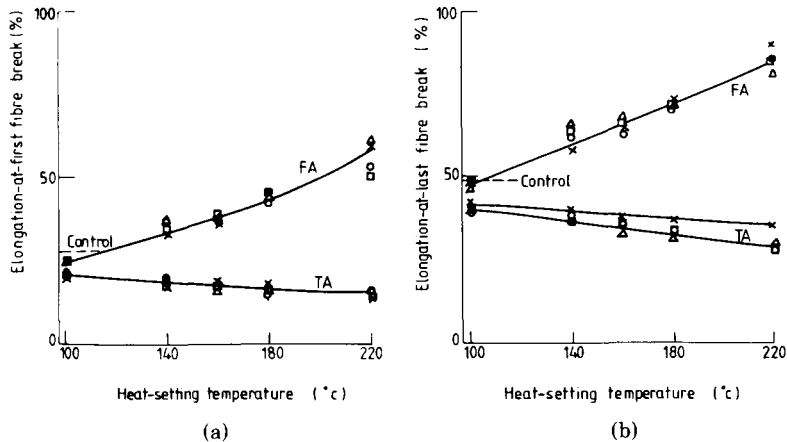


Fig. 4. Dependence of elongation at break on heat-setting temperature: (a) first fiber break; (b) last fiber break.

(1) The elongation at break for the control sample is, in general, intermediate between that of free- and taut-annealed samples.

(2) The elongation at break increases with heat-setting temperature in free-annealed samples, while it decreases in taut-annealed samples.

(3) The elongation at break of free-annealed samples is higher than that of the taut-annealed samples.

It has been shown<sup>14</sup> in part I that during heat setting there is considerable shrinkage in free-annealed samples. Due to this shrinkage, the orientation of the molecules has been shown to be reduced. When these fibers are subjected to a tensile test, it is expected that they will extend relatively more than the taut-annealed and the control samples, as is indeed the case (Fig. 4). The elongation at break is plotted as a function of birefringence in Figure 5, and there is a reasonable correlation between the two. In free-annealed samples there is a marked reduction in elongation at break with increasing birefringence, while in taut-annealed samples the effect is relatively smaller. This type of behavior, in which the slope changes, has been reported by Samuels<sup>5</sup> for isotactic polypropylene. The dependence of elongation at break on the amorphous orientation factor does not show any clear-cut trend; in fact, for taut-annealed samples the elongation at break shows a slight increase with increase in amorphous orientation factor, thus indicating that other factors such as the amount and distribution of crystallite size must also be considered.

### Tenacity

Nominal tenacity of all the heat-set samples is shown in Figure 6 as a function of heat-setting temperature. The nominal tenacity of the free-annealed samples is less than that of the control, while for the taut-annealed samples it is higher than the control. In free-annealed samples, nominal tenacity decreases with increase of heat-setting temperature, while in taut-annealed samples it increases. The nominal tenacity represents the breaking load divided by the linear density of the yarn before deformation. In free-annealed samples, since deformation is large, the linear density will decrease considerably by the time the fiber breaks, and this will increase the tenacity, if the change in denier is accounted for. According to Samuels,<sup>5</sup> when the rate of deformation is slow enough for the mole-

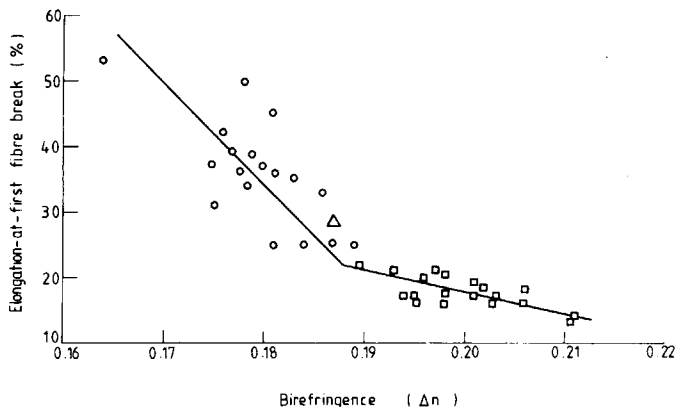


Fig. 5. Dependence of elongation at break on birefringence: (○) FA; (□) TA; (Δ) control.

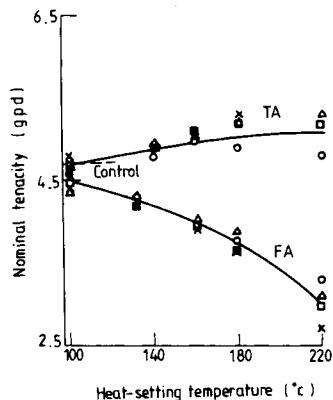


Fig. 6. Nominal tenacity vs. heat-setting temperature: (O) 1 min; (Δ) 15 min; (□) 30 min; (X) 60 min.

cules to reach the highest orientation possible before the flow mechanism predominates, the force required for failure for a given cross-sectional area of the sample is independent of the starting orientation of the sample. The reason given for this is that the molecules in all samples are equally oriented at the time of break, irrespective of the initial orientation state. True tenacity for the present set of samples, as plotted against heat-setting temperature in Figure 7, is obviously not constant. It shows a trend similar to the nominal tenacity results.

Nominal tenacity shows a reasonable correlation with amorphous orientation factor for the free-annealed samples, as shown in Figure 8. In the taut-annealed samples, such a linear dependence does not exist. In Figure 9, the nominal tenacity data for all the samples is presented as a function of birefringence. There is a reasonable correlation; it may however be noted that some taut-annealed samples with high values of birefringence show relatively low tenacity; for isotactic polypropylene, Samuels<sup>5</sup> showed a similar effect.

It was shown<sup>16</sup> in part II that the initial modulus, measured on an Instron Tester, correlates with the amorphous orientation factor for both sets of samples. This is apparently because initial modulus is a low strain property and therefore

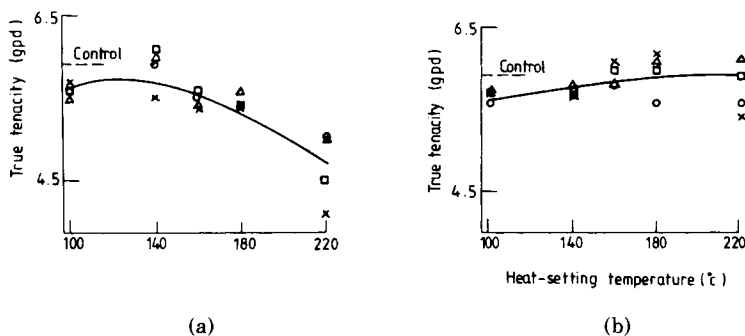


Fig. 7. True tenacity vs. heat-setting temperature: (a) FA; (b) TA; (O) 1 min; (Δ) 15 min; (□) 30 min; (X) 60 min.

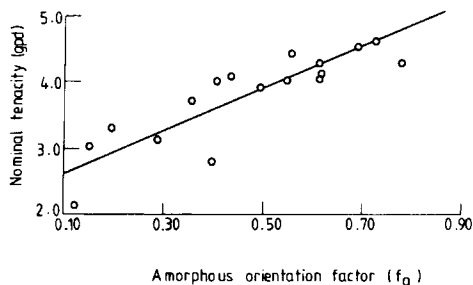


Fig. 8. Nominal tenacity vs. amorphous orientation factor for free-annealed samples.

leans heavily on the initial response of the sample to an externally applied force which will be expected to be dominated by the weaker and more compliant phase, viz., the amorphous phase. Tenacity and elongation at break, on the other hand, are large strain properties and involve, to different degrees, the deformation of both the amorphous and crystalline phases. Thus, in these cases, the average molecular orientation of the sample will determine to what extent it can be further extended or what would be the ultimate load at break, as observed experimentally.

### Work of Rupture

The work of rupture, sometimes called the toughness, is defined as the energy needed to break the fiber. It is given by the area under the load-elongation curve. The area under the stress-strain curve, on the other hand, gives the specific work of rupture. Specific work of rupture has been calculated for free- and taut-annealed samples and is shown as a function of heat-setting temperature in Figure 10 for all the heat-setting times. The free-annealed samples possess higher specific work of rupture compared to taut-annealed samples. The control sample appears to be more close to the free-annealed samples in this respect. As shown earlier, ductility shown by free-annealed samples is also reflected to some extent in the control sample, whereas the taut-annealed samples are closer to the behavior of a brittle solid. With increase in heat-setting temperatures, the specific work of rupture does not change much in free-annealed samples [Fig. 9(a)] but decreases gradually in the case of taut-annealed samples.

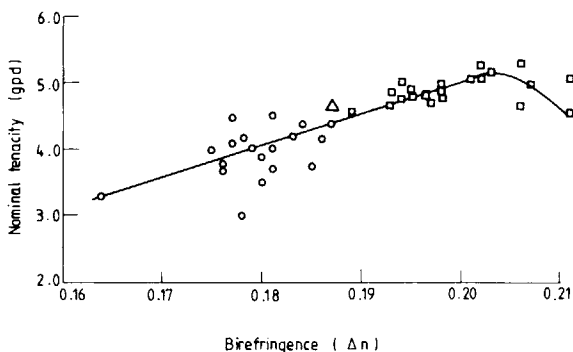


Fig. 9. Nominal tenacity vs. birefringence for all samples: (○) FA; (□) TA; (△) control.



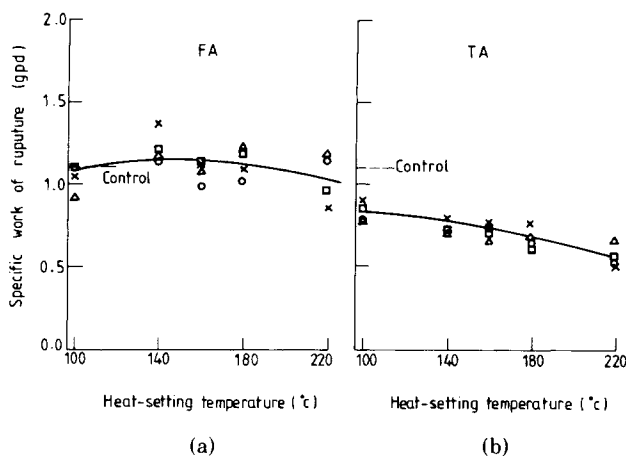


Fig. 10. Dependence of work of rupture on heat-setting temperature for (a) free- and (b) taut-annealed samples: (O) 1 min; ( $\Delta$ ) 15 min; ( $\square$ ) 30 min; (X) 60 min.

### Effect of Heat-Setting Time and Rate of Cooling

The time of heat setting and the rate of cooling have no significant influence on the tensile properties compared to that shown by temperature and tension; this is in keeping with the results presented in the other parts of this series.

### References

1. J. H. Dumbleton, *J. Polym. Sci. Part A-2*, **7**, 667 (1969).
2. A. Peterlin, *J. Macromol. Sci.-Phys.*, **86**(4), 583 (1971).
3. D. C. Prevorsek, *Int. J. Polym. Mater.*, **2**, 185 (1973).
4. W. Preston, and Jr. Denney, *Fiber Sci. Technol.*, **6**, 187 (1973).
5. R. J. Samuels, *Structured Polymer Properties*, Wiley, New York, 1974.
6. M. M. Mayeux, *Trans. ASAE*, **17**(6), 39 (1974).
7. D. C. Prevorsek, G. A. Tirpak, P. J. Marget, and A. C. Reimachuesse, *J. Macromol. Sci.-Phys.*, **B9**(4), 733 (1974).
8. K. Stersallek, *Angew. Makromol. Chem.*, **53**(1), 35 (1976).
9. D. C. Prevorsek, R. H. Butler, Y. D. Kwon, G. E. R. Lamb, and R. K. Sharma, *Text. Res. J.*, **47**, 107 (1977).
10. T. I. Sogolova, and M. I. Demina, *Mekh. Polim. (Russ.)*, **3**, 337 (1977).
11. J. O. Warwicker, and S. S. Graham, *J. Appl. Polym. Sci.*, **21**, 1137 (1977).
12. A. J. De Vries, C. Bonnebat, and J. Beautemps, *J. Polym. Sci. Part C*, **58**, 109 (1977).
13. G. M. Venkatesh, P. J. Bose, R. V. Shah, and N. E. Dweltz, *J. Appl. Polym. Sci.*, **22**, 2357 (1978).
14. V. B. Gupta, and S. Kumar, *J. Appl. Polym. Sci.*, **26**, 1865 (1981).
15. W. E. Morton, and J. W. S. Hearle, *Physical Properties of Textile Fibres*, Heinemann, London, 1975.
16. V. B. Gupta, and S. Kumar, *J. Appl. Polym. Sci.*, **26**, 1877 (1981).
17. V. B. Gupta, and S. Kumar, *J. Appl. Polym. Sci.*, **26**, 1885 (1981).
18. V. B. Gupta, and S. Kumar, *Polymer*, **14**, 953 (1978).

Received December 14, 1979

Accepted November 18, 1980