

Influence of Processing Conditions on Structure Development and Mechanical Properties of Poly(butylene Terephthalate) Filament

FU-MIN LU* and J. E. SPRUIELL, *Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee 37996*

Synopsis

A study of the relationship between the drawing and annealing conditions of melt-spun poly(butylene terephthalate) filaments and the resulting structure and mechanical properties is described. The relative amount of β -form crystal content was found to increase with increase in draw ratio and to be directly proportional to the drawing stress for a given draw ratio. As drawing stress decreases with increase of draw temperature, the β content decreases rapidly with increased draw temperature. Annealing reduces the amount of β -phase but increases the α -phase content and crystallinity. The effect of these structural variations on the mechanical properties is examined. The mechanical properties are shown to be very sensitive to the structure of the filaments and, hence, to the processing conditions.

INTRODUCTION

It is well known that poly(butylene terephthalate) (PBT) exists in two crystalline forms (α and β forms) and possesses interesting mechanical properties due to the $\alpha \rightleftharpoons \beta$ crystalline transition.¹⁻¹⁵ Although Ward et al.,¹⁻⁵ Tadokoro et al.,^{6,7} and others⁸⁻¹⁰ did extensive investigations on the structure and mechanical properties of PBT fiber and its crystalline transition induced by mechanical deformation, there have been no detailed reports dealing with the relationship between structure development and processing conditions of PBT filament. In particular, no detailed descriptions exist in the open literature of the effects of spinning, drawing, and annealing conditions on the resulting structure and mechanical properties. To help fill this gap, therefore, we present the results of a study on how processing conditions (especially drawing) influence the development of fine structure and affect the mechanical properties of PBT filament.

EXPERIMENTAL

Preparation of Samples

The poly(butylene terephthalate) used in this study was supplied in the form of chip of 0.75 IV by Celanese Plastics & Specialties Company. After drying at 120°C under vacuum for 4 h, the chips were melt spun using a Modern Plastics screw extruder. The extruder delivered the molten polymer

* Permanent address: The Beijing Institute of Chemical Fiber, He Pin Li, Northern Suburb, Beijing, People's Republic of China.

to a Zenith gear pump, which metered the polymer through a monofilament spinneret at the rate of 6.0 g/min. The spinneret capillary had a hole diameter of 1.524 mm and an $L/D = 5$. The melt-spun filaments were taken up on a bobbin at a take-up velocity of 700 m/min. A small amount of quenched fiber was also obtained by extruding it from an Instron capillary rheometer with an ice-water bath under it. The as-spun filament was subsequently drawn over a half-meter-long aluminum hot plate. Draw temperatures of 22 (room temperature), 90, 120, 160, and 190°C were used, and at each temperature samples were drawn to draw ratios (L_f/L_o) of 2, 3, or 4. The measuring head of an electronic tensiometer was placed after the hot plate prior to the draw roll to measure the tension.

A group of samples drawn at the same temperature of 120°C but different draw ratios of 2, 3, or 4, were annealed in an oven at 185°C for 13 h under slight tension at fixed length. Another set of samples was prepared by annealing the fiber drawn at 22°C and draw ratio equal to 4 at 50, 70, 90, 120, and 160°C for different periods of time under no tension.

Crystallinity Measurement

It is common that the crystallinity of polymeric materials can be correctly determined by density measurement if the densities of its crystalline and amorphous regions are known and few voids or defects are contained in the material. The sensitivity of the measurement depends on the difference between the crystalline and amorphous densities. In the case of PBT fiber, the density of the α -form crystal was calculated by Yokouchi et al.⁶ to be 1.404 g/cm³ and, independently, by Boye and Overton¹⁶ to be 1.396 g/cm³. Both values are reasonable compared with the observed density of samples having large fractions of α phase. On the other hand, the density of the β -form crystals computed from the mass and volume of the crystalline unit cell is about 1.283 g/cm³,⁶ which is very close to that of amorphous PBT reported by Boye and Overton¹⁶ of 1.278 g/cm³ or 1.282 g/cm³ reported by Stein and Misra.¹⁰ It is therefore not feasible to use the density method for determination of crystallinity of PBT fiber if the β form is prevalent. For those samples that contain predominantly the α -crystal form, the crystallinity can be estimated by the density method using the usual relation

$$X_c = \frac{d_c^\alpha (d - d_{am})}{d (d_c^\alpha - d_{am})} \quad (1)$$

where d_c^α , the α -form crystalline density, was taken to be 1.396 g/cm³ and d_{am} , the amorphous density, was taken equal to 1.2812 g/cm³. The latter value was measured in the present investigation on rapidly quenched, amorphous filaments.

Another way to determine the crystallinity of polymeric fiber is by the x-ray diffraction method. It was reported³ that although the intensity and Bragg angle of the $\bar{1}04$ and $\bar{1}06$ reflections of PBT fiber varied discontinuously with the content of α and β forms, the equatorial reflections did not show a similar behavior but appeared to shift continuously by less than 1°. Also it was found in the present work that the equatorial x-ray diffraction

scan of PBT fiber in the range of 2θ of 6–38° is analogous to that of PET fiber. Therefore, to a good approximation, Farrow's method^{17,18} for determination of crystallinity of PET fiber could be used to estimate the total crystallinity of PBT fiber. The diffraction pattern from a quenched (amorphous) sample was used as a template to determine the amorphous contribution, and the crystallinity was then calculated by the equation

$$\chi_c = \frac{I_c}{I_c + \kappa I_{am}} \quad (2)$$

where I_c is the integrated intensity of the crystalline peaks, I_{am} is the integrated intensity of amorphous scattering, and κ is a constant taken to be 0.9.

An x-ray diffractometer (Rigaku D-MAX IIIA) equipped with a fiber sample holder and goniometer was used to make all quantitative diffraction measurements. The diffractometer is also equipped with a diffracted beam graphite crystal monochromator to provide monochromatic $\text{CuK}\alpha$ radiation. The generator was operated at 40 kV and 30 mA.

Crystalline Orientation Measurement

The x-ray diffraction method was used to measure the crystalline orientation function of drawn PBT fiber. Although the crystal structure of PBT is triclinic, it is possible to proceed by analogy to the approaches that have been previously used for PET because of the similarity of equatorial reflections of both α and β forms with that of PET fiber. In particular, Farrow's method could be used; that is, the PBT triclinic crystal is approximated as pseudo-orthorhombic with respect to α , β , and γ axes. From measuring the orientation of the (100) and (010) planes,¹⁷ Herman's orientation function was obtained using the equation

$$f_c = 1 - \frac{3}{2} \overline{(\sin^2 \phi_{cz})} = 1 - \frac{3}{2} (\overline{\cos^2 \phi_{100,z}} + \overline{\cos^2 \phi_{010,z}}) \quad (3)$$

where z is the fiber axis. Although this approach is clearly an approximate method to determine the average crystalline orientation factors of both α and β forms, it seems justified on the basis that it is relatively simple to apply and provides useful results.

Measurement of the Content of α and β Phases in PBT Fiber

In order to find a feasible way to determine the content of α and β form in the fiber, a sample of as-spun fiber, annealed at 185°C for 13 h and free of tension, was used as a standard of pure α -form crystal. By stretching the fiber to an elongation of 15% and maintaining it at this elongation in the fiber sample holder, a standard of pure β form was obtained.³ Similarly, samples extended 2, 4, 8, and 10% were prepared. Meridional scans of these samples from 2θ of 20–50° were made. It was found that the $\bar{1}04$ reflection from the α phase occurring at $2\theta = 31.4^\circ$ gradually weakens without shifting

in position and the $\bar{1}04$ reflection from the β phase appears at 27.4° and gradually grows stronger. Similar, consistent changes in the intensity of other α - and β -phase reflections were also observed. These results were consistent with those reported by Brereton et al.³ Based upon the facts just described, the relative amounts of the α or β form may be calculated to a first approximation by the relation

$$\chi_\alpha = \frac{I_\alpha}{I_\alpha + \kappa I_\beta} \quad (4)$$

$$\chi_\alpha + \chi_\beta = 1 \quad (5)$$

where I_α is the peak intensity of the $\bar{1}04$ α -form reflection, I_β is the peak intensity of the $\bar{1}04$ β -form reflection, and κ is a proportionality constant equal to the ratio of the peak intensity of the $\bar{1}04$ reflection of pure α form to that of pure β form of the same sample. The $\bar{1}04$ reflections were chosen for this purpose because their peaks are more intense than those of the $\bar{1}06$ reflections. Again, the corresponding x-ray diffraction pattern of quenched fiber was used as a template for subtracting the amorphous background and then measuring the intensity of the peak.

Mechanical Property Measurement

Tensile stress-strain curves of PBT fiber were obtained using a table model Instron tensile testing machine in a conditioned room of 20°C , 65% relative humidity. A gage length of 5.08 cm and a crosshead speed of 2.54 cm/min were used.

RESULTS AND DISCUSSION

Crystallinity

Sample crystallinity results obtained by both density measurement and x-ray diffraction method are listed in Table I.

In Fig. 1, the crystallinity of PBT fibers drawn $4\times$ as a function of draw temperature is plotted. From Table I and Fig. 1, it is clear that the density and also the crystallinity of drawn PBT fiber increase with increasing the temperature at which the fiber was drawn. Moreover, the relationship between crystallinity by x-ray measurement and the drawing temperature of the fiber is almost linear. The magnitude of the crystallinity obtained by the density method is fairly close to that found by x-ray measurement in the region of drawing temperature from 160 to 190°C , where the β -form content is small compared with the α -form content. At lower draw temperatures, the densities are not reliable indicators of the crystallinity because of large fractions of β form (see next section) and because of the formation of microvoids in the fiber. These two factors make the density method unsuitable for the determination of crystallinity of PBT fiber drawn at temperatures below 160°C .

The existence of microvoids in the fiber drawn at room temperature can be inferred from its density of 1.277 g/cm^3 , which is even lower than the

TABLE I
Crystallinity of Drawn PBT Fiber

No.	Drawing temperature (°C)	Draw ratio	Density (g/cm ³)	χ_c (%) (by density)	χ_c (%) (by x-ray)
1	22	2	1.277		
2	22	3	1.288		20
3	22	4	1.288		20
4	90	2	1.298		25
5	90	3	1.298		25
6	90	4	1.299		27
7	120	2	1.305		31
8	120	3	1.305		31
8	120	3	1.305		31
9	120	4	1.305		31
10	160	2	1.316	33.0	34
11	160	3	1.318	34.7	36
12	160	4	1.320	36.0	37
13	190	2	1.325	40.8	38
14	190	3	1.327	42.6	39
15	190	4	1.329	44.3	41
16	120 (annealed 13 h at 185°C)	2	1.334	48.7	44
17	120 (annealed 13 h at 185°C)	3	1.336	50.9	46
18	120 (annealed 13 h at 185°C)	4	1.339	53.0	48

amorphous density of 1.2812 g/cm³. Another thing worth noting is that the density and the crystallinity of the fiber drawn at the same temperature do not change much with draw ratio in the range between 2× and 4×. The reason for this may relate to the fact that the same feed speed during the drawing process was used so that the effect of increased draw ratio was reduced by shortening the contact time of the fiber with the hot plate at higher take-up velocity for higher draw ratio.

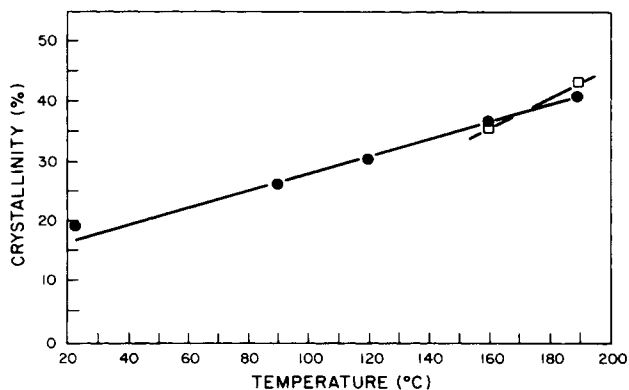


Fig. 1. Crystallinity of PBT filaments drawn 4× as a function of draw temperature.

Relative Amounts of α and β Forms in Drawn PBT Fiber

The structure of poly(butylene terephthalate) has been thoroughly investigated by many authors.^{6,12,13,19} It was found that the difference between the α and β forms of PBT crystal is mainly in the conformations of the four-methylene group sequence $[-CH_2-CH_2-CH_2-CH_2-]$, which is \overline{GGTGG} for the α form and \overline{TSTST} for the β form. The conformation of the molecule is more coiled (less extended) in the α form, which is also more stable thermodynamically, in the absence of applied stress, than is the β form. Application of stress favors extension of the chain and formation of β phase. Also well established is that the transition between the two crystalline phases is reversible upon removal of the stress only within the strain range of about 4–12%. In this strain range, the stress-strain curve of the PBT sample exhibits a characteristic plateau, with strain increasing at nearly constant stress. Beyond this point, however, as the deformation of the sample continues, higher and higher stress is required, and a smaller fraction of β form can be reverted back to α form after stress is released, as shown by Ward et al.² That is, the higher the stress or strain, the more the β -form crystalline phase will be retained in the sample.

The results obtained in the present study are quite consistent with the previous findings. In Table II are listed the contents of α - and β -crystalline phase formed in the fiber drawn at different temperatures and draw ratios.

As can be seen from Table II, the content of β form increases with increasing draw ratio, that is, strain, at the same draw temperature. The content of β form also increases with decreasing draw temperature at constant draw ratio (see Fig. 2). The reason for this behavior is easy to understand. When a PBT fiber is drawn at low temperature to high draw ratio, for example, DR 4 at room temperature, higher external force is exerted. This favors the formation of β form and also imposes a more extended conformation on molecules in the amorphous network. At tem-

TABLE II
Relative Content of α and β Forms in Drawn PBT Filaments

No.	Drawing temperature (°C)	DR	χ_α (%)	χ_β (%)	Drawing tension (GPa)
1	22	2			
2	22	3	26	74	0.092
3	22	4	8	92	0.135
4	90	2	59	41	0.027
5	90	3	40	60	0.084
6	90	4	32	68	0.128
7	120	2	68	32	0.025
8	120	3	62	38	0.073
9	120	4	45	55	0.118
10	160	2	94	6	0.017
11	160	3	92	8	0.058
12	160	4	88	12	0.099
13	190	2	95	5	0.016
14	190	3	94	6	0.055
15	190	4	95	5	0.096

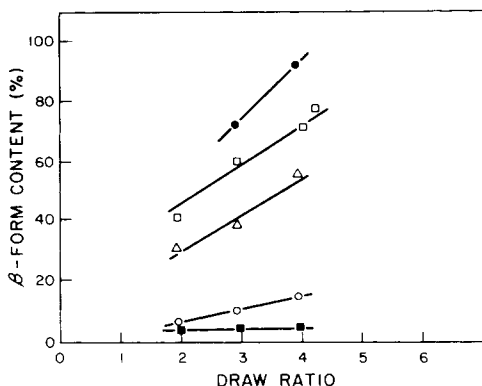


Fig. 2. β -Phase content as a function of draw ratio and draw temperature.

peratures below T_g ($\sim 40^\circ\text{C}$), these conformations are not readily relaxed even in the amorphous regions and the chains would have even less mobility in the crystalline regions. Consequently, a fiber having greater β -phase content was obtained. On the other hand, if higher draw temperature was used, for example 190°C , the force required even for DR 4 was much smaller, resulting in less β -phase formation and more relaxed conformation of molecules in the amorphous network. The higher draw temperature provides greater mobility for thermal crystallization to the α phase and hence higher crystallinity (Table I). The drawn filament exiting the draw heater is cooled rapidly under stress to room temperature. This cooling process freezes in residual stresses and stabilizes the β content. It is extremely interesting to note at this point that the plot of the external stress versus drawing temperature measured during the drawing process resembles the plot of the content of β form of fiber drawn $4\times$ versus drawing temperature. This is shown in Figs. 3 and 4. The β -form content in fibers drawn $4\times$ at different temperatures is plotted versus the applied draw stress in Fig. 5. This figure indicates that the relative content of the β -form crystalline phase of the drawn PBT fiber is linearly related to the external force, which in turn is determined by the processing conditions. From the description above, it

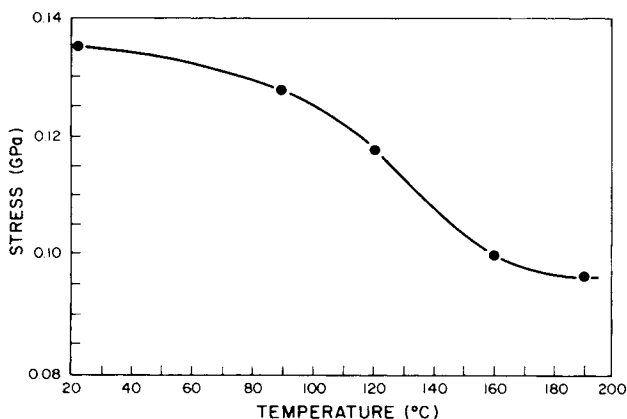


Fig. 3. Drawing stress as a function of draw temperature for PBT filaments drawn $4\times$.

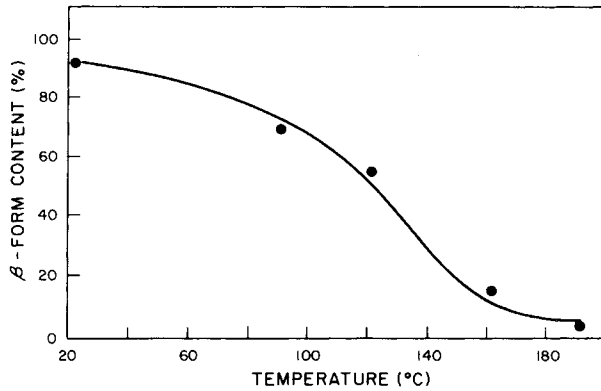


Fig. 4. β -Phase content as a function of draw temperature for PBT filaments drawn $4\times$.

may be possible that by drawing as-spun PBT fiber carefully at low enough temperature, a drawn PBT fiber containing only β -form crystals can be obtained (even though poorly crystallized).

On annealing, in the absence of stress, the β phase should spontaneously transform to the more thermodynamically stable α form. Figure 6 shows the transformation rate and extent as a function of annealing temperature and time for samples initially drawn $4\times$ at room temperature. The annealing was carried out without tension. The transformation rate increases with annealing temperature. The data seem to indicate that annealing is accompanied by large-scale disorientation of the amorphous network,^{20,21} which releases the internal stresses. This in turn allows the unstable β form to return to the α form promptly until a new equilibrium state is reached. Therefore, it is not surprisingly, as seen in Fig. 6, that not all the β -form crystalline phase in the sample can transform back to α form unless the annealing temperature is high enough, say, above 160°C (β form less than 10%).

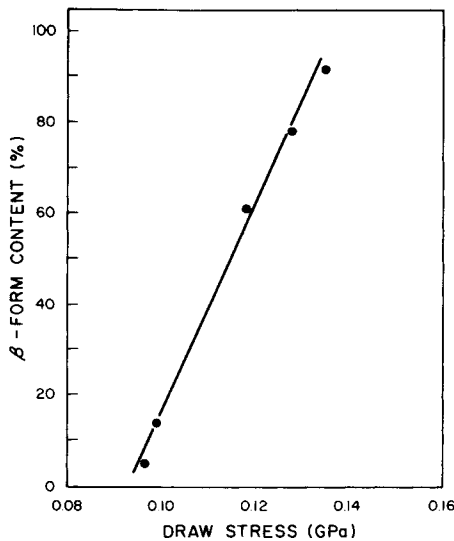


Fig. 5. Cross plot of β -phase content versus draw stress.

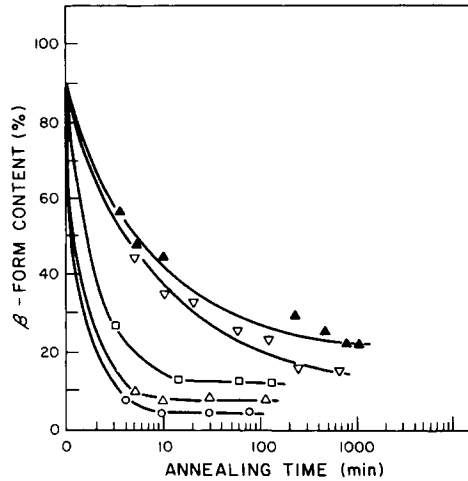


Fig. 6. β -Form content as a function of annealing temperature and time for filaments initially drawn 4 \times at room temperature.

Influence of Crystalline Orientation on Phase Transition-Related Stress-Strain Curve

As discussed by earlier investigators,^{3,7} the $\alpha \rightleftharpoons \beta$ form transition of drawn and annealed PBT fiber occurs at the stress corresponding to the plateau region of the stress-strain curve. This critical stress is also temperature dependent; that is, it varies with the temperature at which the stress-strain curve is measured. In our experiment, however, it was found that the plateau region of the stress-strain curve is also affected by the crystalline orientation of the fibers. Table III presents the basic characteristics of three samples, and Fig. 7 shows the corresponding stress-versus-elongation curves.

These three samples were all drawn at 120°C to draw ratios of 2, 3, and 4, respectively. All three samples were then annealed on the bobbins at 185°C for 13 h. This produced samples containing predominantly the α -crystal form but having different levels of crystalline orientation (Table III). These samples have almost the same initial modulus, but the critical stress in the plateau region that causes the transition of α form to β form to occur is observed to decrease in magnitude with increase in draw ratio. The initial modulus would seem to be controlled primarily by the crystal-

TABLE III
Characteristics of Three Drawn and Annealed Samples

Sample ^a	DR	χ_c (by density)	f_c (before annealing)	f_c (after annealing)	Modulus (GPa)	Critical stress (GPa)
1	2	0.49	0.70	0.73	3.2	0.07
2	3	0.51	0.80	0.85	3.28	0.061
3	4	0.53	0.88	0.93	3.3	0.046

^aSamples originally drawn at 120°C and annealed at 185°C for 13 h at constant length (on the bobbins).

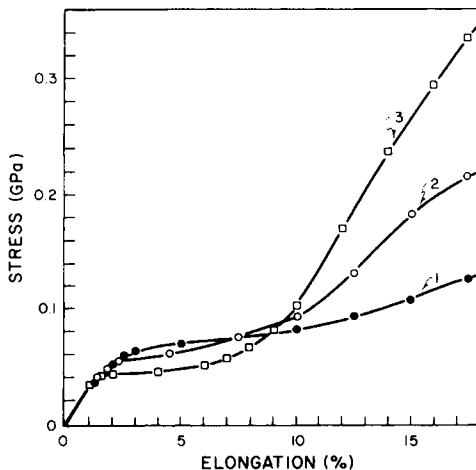


Fig. 7. Stress-versus-elongation curves for samples having different crystalline orientation.

linity level and the molecular orientation in the amorphous regions. Since the same annealing condition was applied to all three samples, the crystallinity and the relaxation of the orientation in the amorphous regions reaches nearly the same equilibrium condition. At low strains applied to the fiber the deformation can be accommodated by molecular bond angle rotation and bond bending in the amorphous phase. As a result, the initial moduli of the fibers are very nearly equal. But as the deformation continues the stress reaches a critical level needed to produce deformation of the crystalline regions, extension of the crystalline chains, and transformation to the β phase. If it is assumed necessary to have a critical force applied in the chain axis direction in order to achieve these changes, we would expect the variation in the critical stress with fiber orientation shown in Fig. 7. With the applied force acting along the fiber axis, the resolved force in the direction of the chain axes would be lower the greater the angle between the chain axis and the fiber axis. This angle increases, on the average, as the crystalline orientation decreases, thus explaining qualitatively why the crystalline orientation should affect the critical stress at the plateau region. Initial computations for the critical stress variation based on this simple model do not give quantitative agreement with the experimental data. This is not surprising but simply means that the deformation process involves complications that are not fully accounted for in this rather oversimplified model.

Structure Dependence of Mechanical Properties of PBT Fiber

Figure 8 shows the stress versus elongation curves of samples that were drawn $3\times$ at temperatures of 22, 90, and 160°C, respectively. Figure 9 shows stress versus elongation curves of two samples, both of which were drawn $3\times$ at 120°C. Sample 5 was obtained by annealing sample 4 at 185°C for 13 h. Listed in Table IV are the structural characteristics and mechanical properties of those samples whose stress versus elongation curves are shown in Figs. 8 and 9.

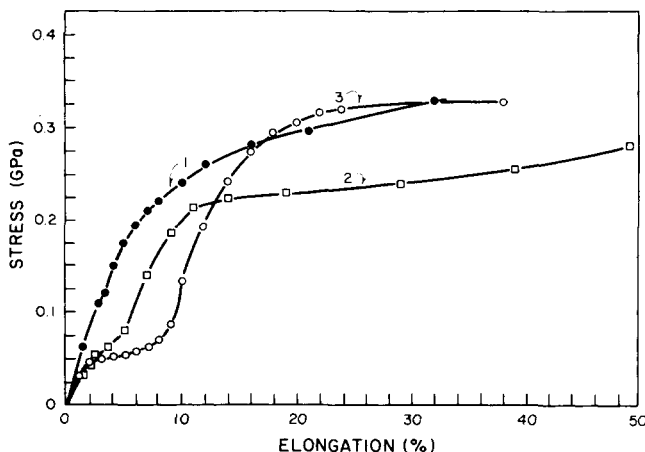


Fig. 8. Effect of draw temperature on the stress-versus-elongation curves of filaments drawn 3 \times : curve 1, drawn at 22°C; curve 2, drawn at 90°C; curve 3, drawn at 160°C.

It is seen from Fig. 8 and Table IV that the modulus of sample 1 is much higher than that of samples 2 and 3. This is true even though the crystalline orientation, determined as the average for the α and β phases, is essentially the same for all three samples because they have the same draw ratio. The reason for this is, again, the different conformations of molecules in both amorphous network and crystalline regions caused by different processing conditions. As described before, the lower the drawing temperature, the higher the drawing force, the more extended form of conformation of molecules in the fiber will be obtained. On the other hand, the modulus of sample 3 is higher than that of sample 2. This can possibly be attributed to the fact that the crystallinity of the sample increases with increasing draw temperature, thus reducing the content of the amorphous material of the sample and shortening the length of the amorphous network correspondingly. This would favor an increase of the modulus. Since the crys-

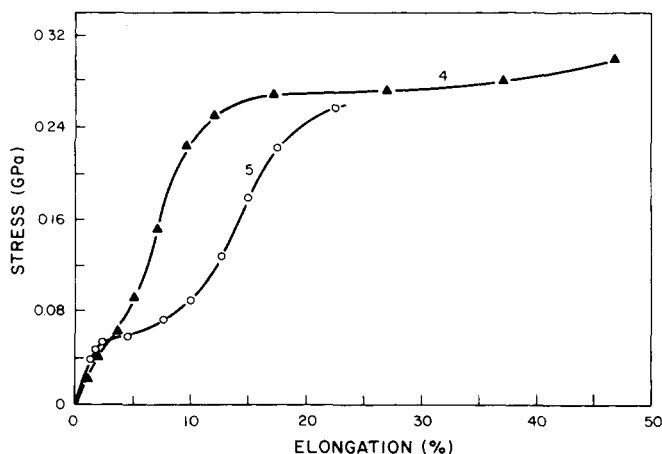


Fig. 9. Effect of annealing on stress-versus-elongation curves for filaments drawn 3 \times at 120°C; curve 4, unannealed; curve 5, annealed 13 h at 185°C.

TABLE IV
Structural Characteristics and Mechanical Properties of Selected Samples

Sample	Processing condition	f_c	χ_c (%) (by x-ray)	Modulus (GPa)	Tenacity (GPa)
1	DR 4 at 22°C	0.88	20	4.42	0.325
2	DR 4 at 90°C	0.89	27	3.2	0.278
3	DR 4 at 160°C	0.90	37	3.35	0.322
4	DR 3 at 120°C	0.80	31	2.74	0.298
5	DR 3 at 120°C Annealed at 185°C for 13 h	0.85	46	3.28	0.257

tallinity of sample 3 is greater than that of sample 2, this latter effect could explain the slightly higher initial modulus of sample 3. The same explanation applies to the relative initial moduli of samples 4 and 5.

These observations are consistent with those reported by Ward et al.² and further confirm the series model of PBT proposed by Tashiro et al.⁷ In addition, Figs. 8 and 9 show clearly that the plateau region of the stress-strain curves also varies with the processing conditions used in developing the fiber structure. Sample 1, for example, has almost no plateau at all, indicating that little α -form phase exists in the filament. But for sample 3, the plateau region extends from an elongation of 2% to about 9%. This resulted from higher crystallinity and higher content of α phase in the filament. Similarly, comparing samples 4 and 5 in Fig. 9, one can see the effect of annealing on the length of the plateau region. Therefore, higher phase transformation-induced elastic recoveries are produced by achieving higher crystallinity and more α -form crystal through drawing the PBT fiber at higher temperature (above 160°C) or drawing at lower temperature and then annealing at sufficiently high temperature.

SUMMARY AND CONCLUSIONS

This study of the effect of processing conditions on the structure development and mechanical properties of PGT filament has shown that the resulting structure and mechanical properties of PBT filaments is extraordinarily sensitive to the processing conditions used. The relative amount of β -form crystal content in the processed filament was found to increase with increases in draw ratio and to be directly proportional to the drawing stress for a given draw ratio. Draw temperature was therefore shown to be one of the most important variables in determining this quantity. By inference, increasing the draw rate should also increase the amount of β phase retained. The total crystallinity was also shown to be quite dependent on the draw temperature and also increased with subsequent annealing. Annealing reduced the amount of β phase present but increased the amount of α phase present more than would be accounted for by the reduction of β content alone. The level of crystalline orientation was most affected by draw ratio, and it was affected only slightly by draw temperature in the range studied. Annealing under tension also had little effect on crystalline orientation.

The initial (tangent) modulus of the PBT filaments seemed to increase with the orientation retained in the amorphous regions and the crystallinity of the filaments. As high drawing temperatures produced greater relaxation of the amorphous chains but higher crystallinities, the effect of draw temperature could be interpreted as a balance of these two effects. Increasing amounts of α phase (reduced β -phase content) resulted in more elongation in the plateau region of the stress-versus-elongation curve. Thus increasing the draw temperature or annealing would produce this effect on the stress-versus-elongation curve. The critical stress level corresponding to the plateau was found to be sensitive to the crystalline orientation developed in the processing. This appeared to be qualitatively explicable as a geometric effect of resolving the applied force along the chain axis direction.

Although not studied in the present investigation, it is likely that changes in the spinning conditions would significantly affect the as-spun structure. Such changes in the starting structure could produce markedly different results if subjected to the same drawing conditions described here. These effects will be the subject of a subsequent paper.

References

1. R. Jakeways, I. M. Ward, M. A. Wilding, J. 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.*, **14**, 263 (1976).
3. M. G. Brereton, G. R. Davies, R. Jakeways, T. Smith, and I. M. Ward, *Polymer*, **19**, 17 (1978).
4. I. M. Ward, *Text. Res. J.*, **31**, 650 (1961).
5. I. M. Ward, *J. Macromol. Sci. Phys.*, **B1**, 667 (1967).
6. M. Yokouchi, Y. Sakakibara, Y. Chatani, H. Tadokoro, T. Tanaka, and K. Yoda, *Macromolecules*, **9**, 266 (1976).
7. K. Tashiro, Y. Nakai, M. Kobayashi, and H. Tadokoro, *Macromolecules*, **13**, 137 (1980).
8. E. P. Chang and E. L. Slagowski, *J. Appl. Polym. Sci.*, **22**, 769 (1978).
9. W. P. Leung and C. L. Choy, *J. Appl. Polym. Sci.*, **27**, 2693 (1982).
10. R. S. Stein and A. Misra, *J. Polym. Sci., Phys. Ed.*, **18**, 327 (1980).
11. R. Jakeways, T. Smith, I. M. Ward, and M. A. Wilding, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 41 (1976).
12. Z. Mencik, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 2173 (1975).
13. I. H. Hall and M. G. Pass, *Polymer*, **17**, 807 (1976).
14. I. J. Desborough and I. H. Hall, *Polymer*, **18**, 825 (1977).
15. I. M. Ward and M. A. Wilding, *Polymer*, **18**, 327 (1977).
16. C. A. Boye, Jr., and J. R. Overton, A Reversible, Stress-Induced Solid Phase Transition in Poly(tetramethylene Terephthalate), paper presented at the ACPS meeting, Division of High Polymers, Philadelphia, March 1974.
17. G. Farrow and D. Preston, *Brit. J. Appl. Phys.*, **11**, 353 (1960).
18. G. Farrow, *Polymer*, **1**, 518 (1960).
19. B. Stambaugh, J. L. Koenig, and J. B. Lando, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1053 (1979).
20. D. Patterson and I. M. Ward, *Trans. Faraday Soc.*, **53**, 1516 (1957).
21. M. P. S. Wilson, *Polymer*, **15**, 277 (1974).

Received December 4, 1984

Accepted June 5, 1985