The Effect of Stretching Conditions on Properties of Amorphous Polyethylene Terephthalate Film

S. K. SHARMA and A. MISRA* *Centre for Materials Science & Technology, Indian Institute of Technology, Delhi, New Delhi 110016, India*

Synopsis

The effect of stretching conditions on stress-induced crystallization of amorphous polyethylene terephthalate (PET) film has been studied. Cast PET film was stretched at 85°C with stretching rates ranging from 100% per minute to 600% per minute for various stretching ratios. The stretched film samples were annealed at 140°C both under tension as well as under relaxed conditions. Tensile properties were determined using Instron Tensile Tester and results were compared. Tenacity, yield stress, and initial modulus were found to increase while elongation at break decreased with the increase in stretching rate. The degree of crystallinity was measured by x-ray diffraction as well as density methods. Birefringence and crystalline orientation factor values were determined experimentally and using these, amorphous orientation factor values were calculated. Birefringence, crystalline orientation and amorphous orientation values were found to increase with the increase in stretching rate. These studies showed that at low stretching rates a significant amount of relaxation takes place, resulting in lower orientation and strength. On the other hand, at higher stretching rates relaxation is minimized thus providing high orientation and strength. Upon annealing the crystallinity values increased as expected, however the trend of orientation and mechanical properties with respect to stretching rate was similar to those of unannealed films.

INTRODUCTION

Polyethylene terephthalate (PET) finds wide commercial application in the form of fibers and films. Amorphous PET is of little commercial importance because it has low mechanical strength, low dimensional stability, and high extensibility. The conversion of PET into commercial products such as fibers[1,2] and films[3-6] requires that the polymer be highly oriented and have a high degree of crystallinity. Amorphous PET can be thermally crystallized by heating it above its glass transition temperature. However, in the case of films and fibers, crystallinity is generally induced by a high level of strain brought about by stretching and is termed strain (or stress)-induced crystallization. This may be accompanied by some thermal crystallization either during stretching or by subsequent annealing at elevated temperatures. The structure and properties during the process of orientation are dependent upon the conditions of stretching such as temperature, rate of stretching, and the draw ratio. Hence it is important to understand the effect of stretching conditions on the properties of amorphous PET, which forms the basis of this work.

*To whom correspondence may be sent.

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The drawing behavior of PET has been studied extensively over many years and different workers have highlighted different features, from the purely mechanical aspects[7] to the structural changes which occur.[8-14] Some workers have developed relationships between structure and properties of oriented systems.[15,16] Koenig and co-workers have studied the structure developed in the amorphous as well as crystalline regions upon the drawing of amorphous PET films and fibers at different temperatures by infrared spectroscopy.[17-20] In particular they studied the chain folding of molecules[17] and concluded that uncoiling of amorphous chains occurs through the conversion of the distorted gauche to the extended *trans* isomer resulting in a slight increase in crystallinity. Annealing of the drawn film under stress produces some relief of the stress-induced alignment of the crystalline regions while considerable amount of relaxation of the orientation occurs when the films are allowed to shrink during subsequent heat treatment. They also showed that drawing of a crystalline PET film produces a minimal increase in crystallinity but a higher degree of alignment of the crystalline regions. Very little uncoiling of the amorphous chains occurs when a crystalline sample is drawn and no new crystals are produced. They further studied the effect of annealing of drawn films[17,18] and fibers[20] and explained their results on the basis of their structural model. Misra and Stein[21] investigated the deformation behavior and the superstructures formed when amorphous PET films were drawn below as well as above the glass transition temperature (T_g). They characterized their films by wide angle x-ray diffraction, small angle light scattering, density and birefringence measurements. Terada et al.[22] studied the deformation behavior of PET film at various temperatures above T_g and found that orientation of the amorphous chain segments increased considerably with decreasing stretching temperature.

In the present study the deformation behavior of PET films has been studied at 85°C by varying the stretching rate and stretching amount. Mechanical and structural properties have been determined and an attempt made to correlate them. The 85°C stretching temperature was chosen because at this temperature isothermal crystallization is negligible and hence stress-induced effects could be easily studied.

EXPERIMENTAL

A semiautomatic stretching unit was fabricated to stretch cast amorphous PET films, a photograph of which is shown in Figure 1. This unit consists of

1. A synchronous motor (50 rpm 240 V AC, torque 20 kg/cm^2) which has the capability of instant starting and stopping and is fitted with a reversible speed switch.
2. A gear system to vary the stretching rate ranging from 100% per minute to 600% per minute using the gauge length 5 cm.
3. A stretcher which is fitted to the gear system with a pin-type coupling and can be removed easily and rapidly in approximately 5 s.
4. A constant temperature-stirred silicone oil bath in which the stretcher is immersed.

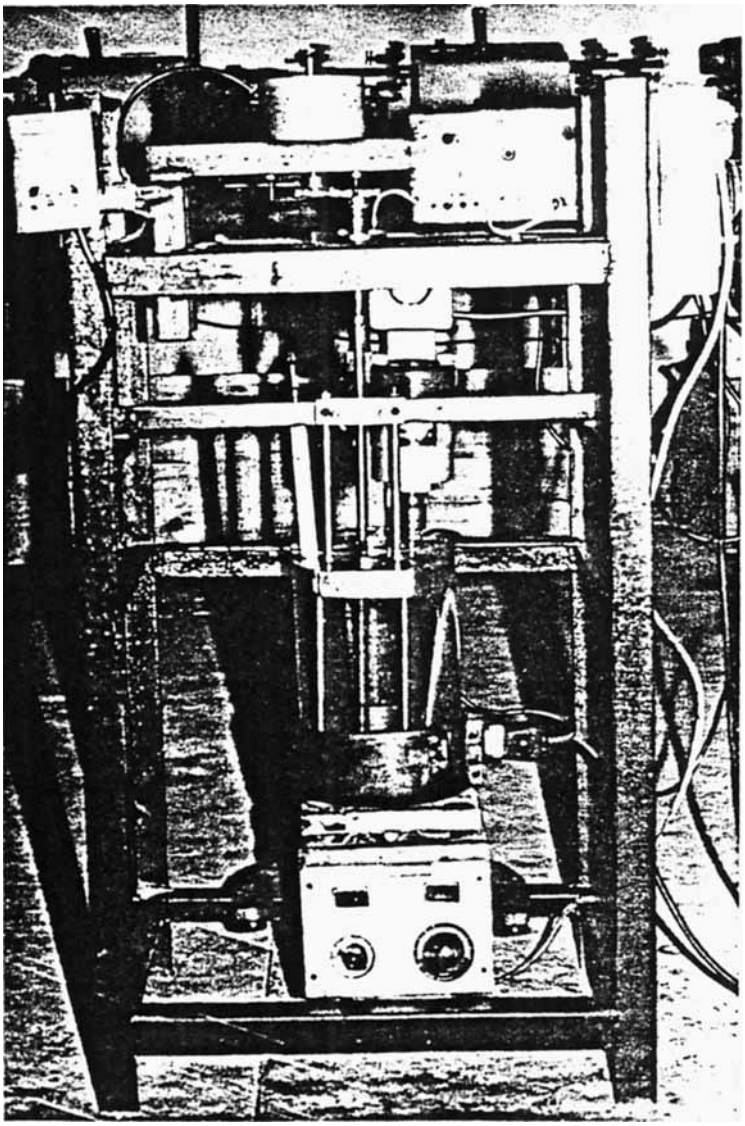

Fig. 1. Photograph of the stretching unit.

Sample Preparation

Sample strips of width 1 cm and gauge length 5 cm were prepared from cast PET film (2% crystallinity) obtained from Garware Plastics & Polyester Ltd., India. The PET film strips were fixed in the stretcher which were then immersed in the silicone oil bath maintained at 85°C and was attached to the gear system. After conditioning at 85°C for 5 minutes, the sample was stretched up to required stretching ratio at selected stretching rate. Immediately following stretching, the stretcher with the film fixed in it was

removed quickly and quenched within 5 to 10 s in a silicone oil bath at 0°C to minimize relaxation.

The stretching rates used for this study were 100%, 200%, 400%, and 600% per minute, respectively. At each stretching rate samples were stretched for stretching amounts of 50%, 100%, 200%, 300%, and 400% elongation, respectively. These stretched samples were subsequently annealed at 140°C in a silicone oil bath for 15 minutes under tension as well as under relaxed conditions.

For comparison undrawn PET film was conditioned at 85°C for 5 minutes. These undrawn PET films were also annealed at 140°C for 15 minutes after conditioning.

The exact stretching ratios were determined using a micrometer. The stretching ratios of annealed samples were measured after annealing.

Mechanical Properties

Load elongation curves were obtained for all PET samples using an Instron Universal Testing Machine (Model 1112) at 25°C with the gauge length 5 cm and cross-head speed of 5 cm/min (100% per minute). Ten specimens were taken for each sample and average values determined. Tenacity, yield stress, initial modulus, and elongation at break were calculated from the stress–strain curves.

Crystallinity

Degree of crystallinity was determined by measuring density values in a density gradient column prepared by using xylene and carbon tetrachloride mixture. The amorphous and crystalline densities of PET were taken to be 1.335 and 1.455 g/cc, respectively.[23]

Degree of crystallinity of few samples was also measured by wide angle x-ray diffractometer. Details of the method used are described elsewhere.[24]

ORIENTATION AND BIREFRINGENCE

Herman's crystalline orientation function (f_c) was determined by wide angle x-ray diffractometer using 100 and 010 diffraction planes. The birefringence (Δn) values were determined by the retardation method using a tilting compensator fitted to a polarizing microscope. Birefringence of an oriented crystalline polymer is given as

$$\Delta n = X_c f_c \Delta n_c^0 + (1 - X_c) f_a \Delta n_a^0$$

where X_c is the degree of crystallinity, f_c and f_a are the crystalline and amorphous orientation functions, respectively. Δn_c^0 and Δn_a^0 are the intrinsic birefringence values for perfectly oriented crystals and amorphous polymer, respectively. In the above equation, Δn, X_c and f_c are determined experimentally while the values of Δn_c^0 and Δn_a^0 were taken to be 0.235 and 0.275, respectively. The value of f_a was calculated using the above equation.

RESULTS

Tenacity values as a function of draw ratio for stretching rates 100%, 200%, 400%, and 600% per minute for samples stretched at 85°C, annealed under tension and relaxed conditions are plotted in Figures 2, 3, and 4, respectively. It can be clearly seen in Figure 2 that at equivalent draw ratios higher stretching rate gives higher values of tenacity. At all the stretching rates tenacity values increase with draw ratio except in the case of 100% per minute where the tenacity goes through a maximum at the draw ratio of 4.0 and then decreases. The difference in tenacity for different rates is less at low draw ratios and is large at high draw ratios. A similar trend of tenacity values is also observed when the stretched samples were annealed as can be seen in Figures 3 and 4, respectively. Annealing increases the tenacity values considerably for all cases. Tenacity shows much higher values for samples annealed under tension as compared to samples annealed under relaxed condition. Changes in yield stress with respect to draw ratio at all stretching rates for samples before and after annealing under tension are shown in Figures 5 and 6, respectively. Yield stress increases with increase in draw ratio and higher stretching rate shows higher yield stress values. In case of annealing under relaxed condition, the yield stress values are lower compared to samples annealed under tension. In general, the trend of variation of yield stress values is similar to tenacity values. Initial modulus as a function of draw ratio at all

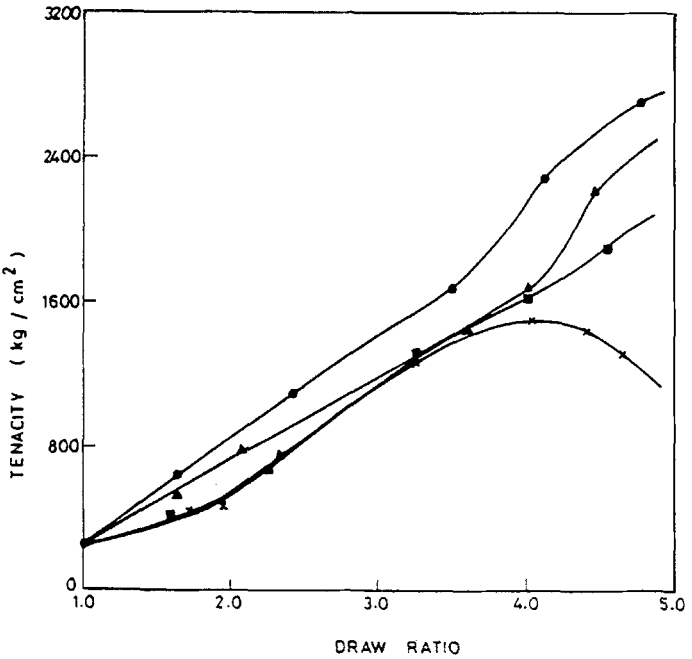

Fig. 2. Plots of tenacity versus draw ratio for amorphous PET films stretched at 85°C at different stretching rates. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

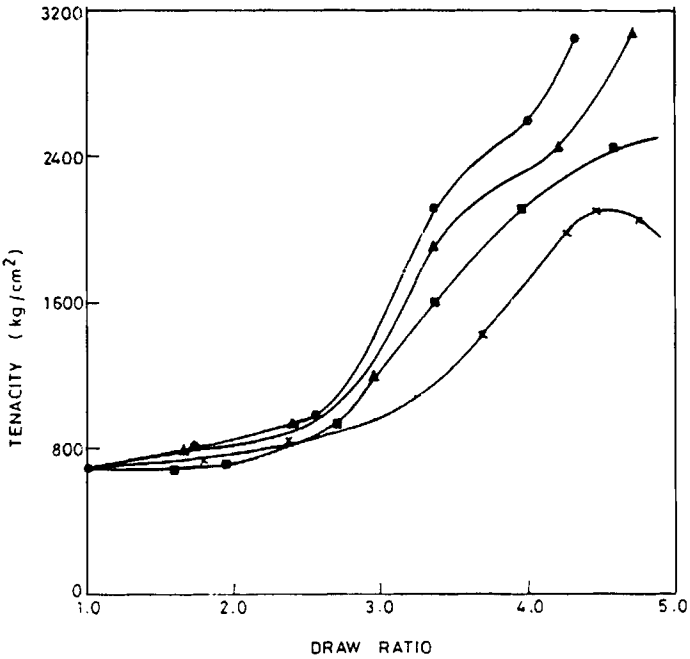

Fig. 3. Plots of tenacity versus draw ratio for stretched PET films annealed under tension at 140°C. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

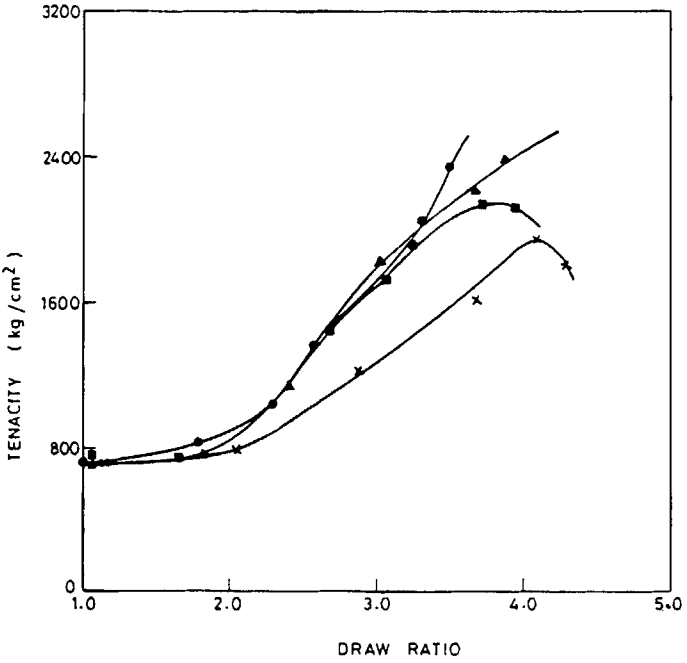

Fig. 4. Plots of tenacity versus draw ratio for stretched PET films annealed under relaxed condition at 140°C. (x) Stretching rate 100/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

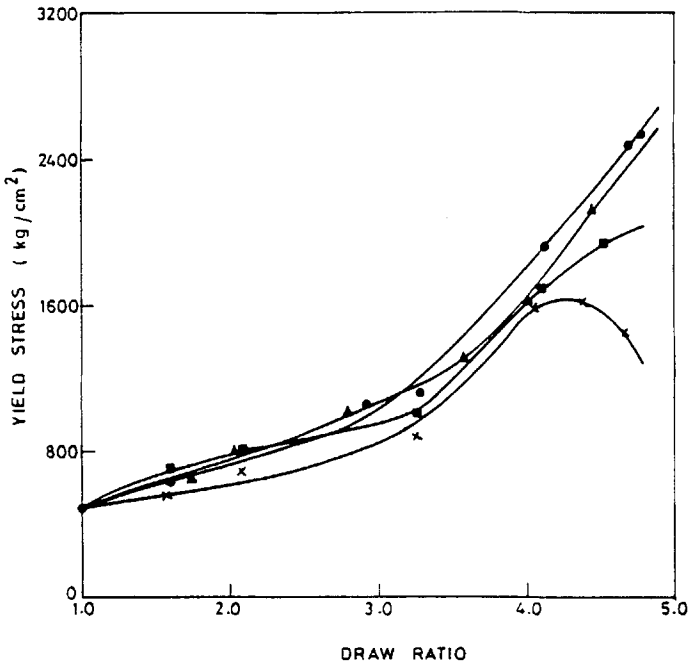

Fig. 5. Plots of yield stress versus draw ratio for amorphous PET films stretched at 85°C at different stretching rates. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

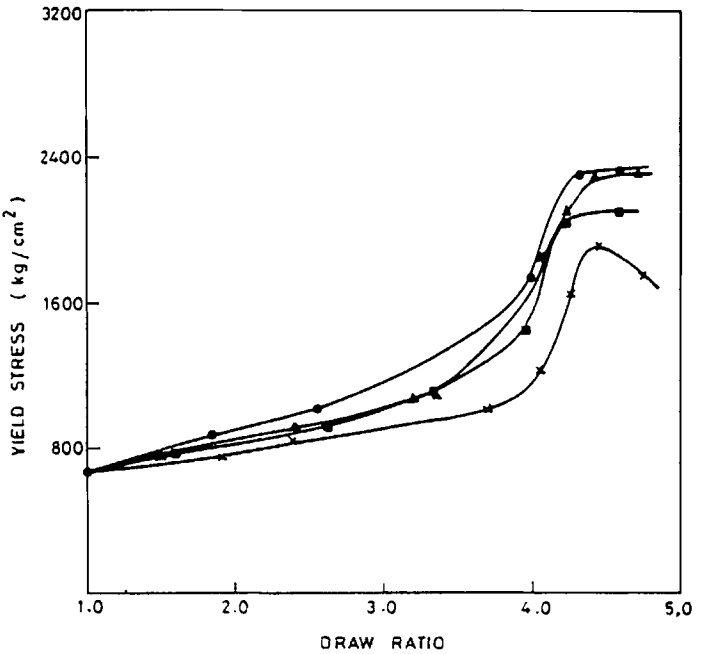

Fig. 6. Plots of yield stress versus draw ratio for stretched PET films annealed under tension at 140°C. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

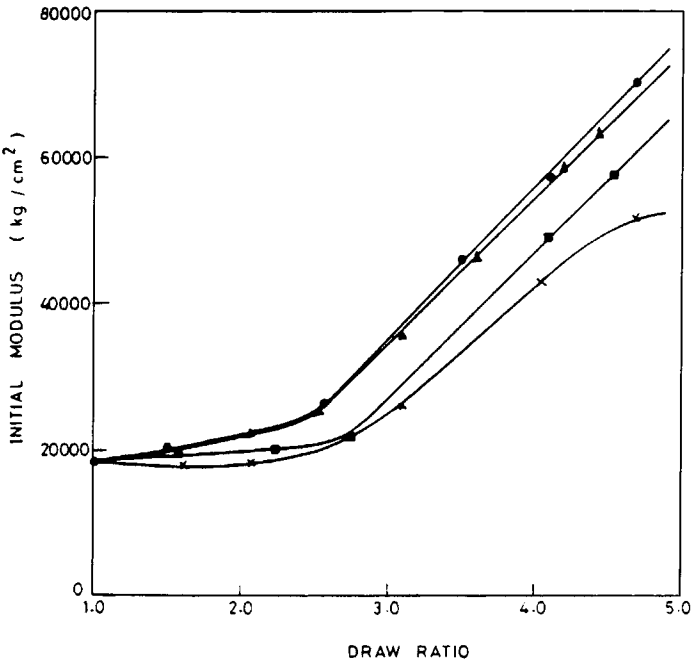

Fig. 7. Plots of initial modulus versus draw ratio for amorphous PET films stretched at 85°C at different stretching rates. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

stretching rates for samples stretched and annealed under tension are plotted in Figures 7 and 8, respectively. At low draw ratio the increase in initial modulus is relatively small while at higher draw ratio increase is considerable. At equivalent draw ratios, initial modulus is higher at higher stretching rates. However, annealed samples of 100% per minute show that the initial modulus goes through a maximum at a draw ratio of about 4.5 × and then decreases. In case of samples annealed under relaxed condition, the effect of stretching rate is much less. The trend of variation of initial modulus with the stretching rate and draw ratio supports the tenacity and yield stress results. Elongation at break as a function of draw ratio for all stretching rates for samples stretched, annealed under tension and relaxed conditions, are presented in Figures 9, 10, and 11, respectively. In case of stretched samples at high stretching rate the elongation at break decreases. This trend shows that the orientation is higher at high stretching rate and supports the tenacity, yield stress, and initial modulus values. In case of undrawn film annealed under tension (Fig. 10) the elongation at break is 5% while unannealed undrawn film shows that the elongation at break is 217%. On annealing the undrawn film the elongation at break decreases very much, which shows that on annealing PET becomes stiff. In Figure 10 it can be seen that elongation at break increases with an increase in draw ratio up to a value around 3 × and then decreases while it decreases with the increase in stretching rate. In samples annealed under relaxed condition, elongation at break shows trend similar to samples annealed under tension, but the values are higher compared to

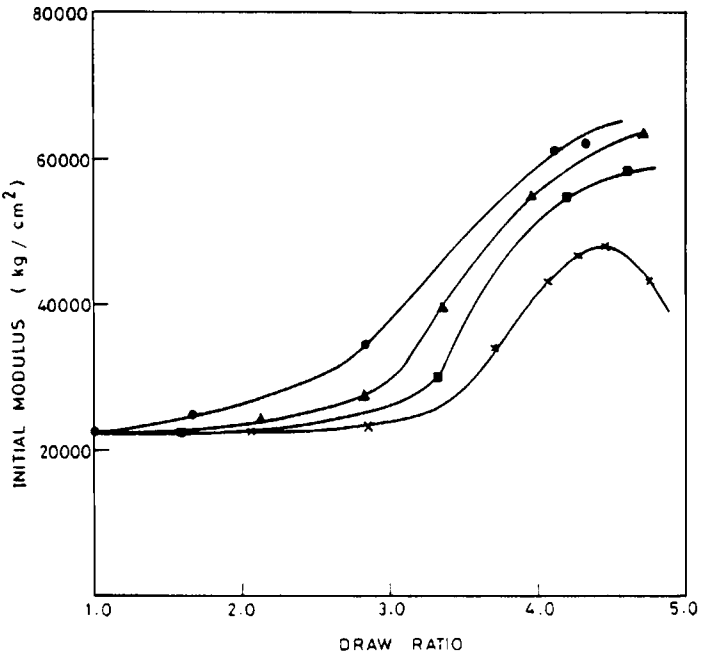

Fig. 8. Plots of initial modulus versus draw ratio for stretched PET films annealed under tension at 140°C. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

tension-annealed samples. These results support the trend of change in tenacity, yield stress, and initial modulus. In general the tensile properties improved with the increase in stretching rate and stretching ratio.

The percent crystallinity values as a function of draw ratio at all stretching rates for samples stretched and annealed under tension are shown in Figures 12 and 13, respectively. In case of stretched films the percent crystallinity measured by density method increases slowly with draw ratio up to 2 × and increases at a faster rate at higher draw ratios. On increasing stretching rate the crystallinity does not change much at low draw ratio while it increases more at higher draw ratio (Fig. 12). In the case of annealing under tension and relaxed conditions, crystallinity increases with the increase in stretching rate and the increase is greater at draw ratio around 3 × . Annealed samples show higher values of crystallinity compared to unannealed samples as would be expected. The maximum crystallinity of annealed undrawn sample is 38%, while that of completely drawn and annealed samples is 43%. This increase of 5% in crystallinity is attributed to orientation. These results support the improvement in tensile properties.

The % crystallinity values measured by the x-ray diffraction method are similar to % crystallinity values measured by density method (Table I).

The birefringence values as a function of draw ratio for all stretching rates are plotted in Figures 14, 15, and 16 for samples stretched, annealed under tension, and relaxed conditions, respectively. In case of stretched samples (Fig. 14), the birefringence increases with the increase in draw ratio. The birefrin-

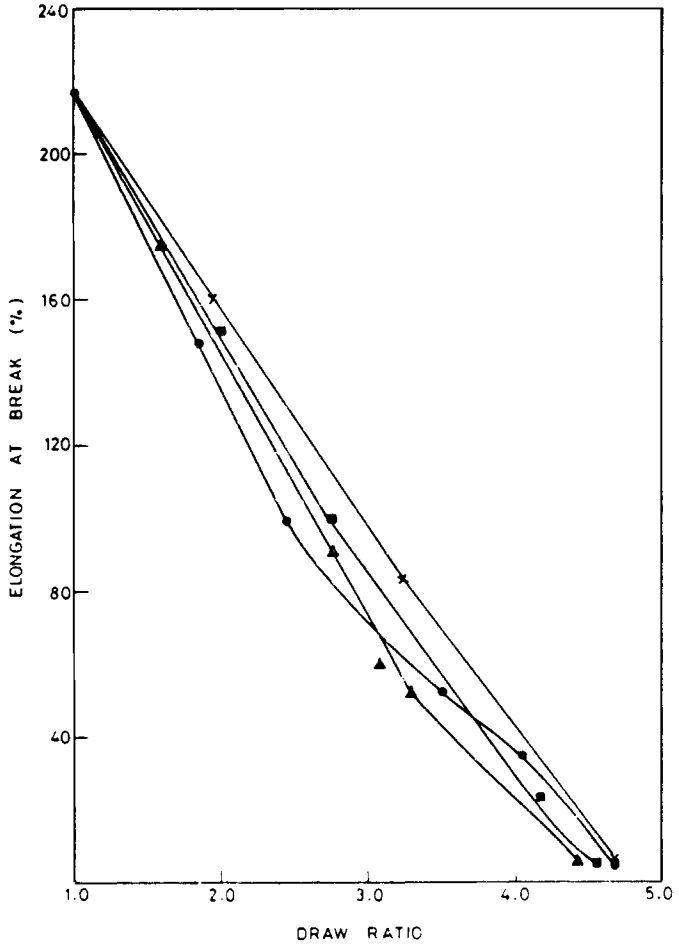

Fig. 9. Plots of % elongation at break versus draw ratio for amorphous PET films stretched at 85°C at different stretching rates. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

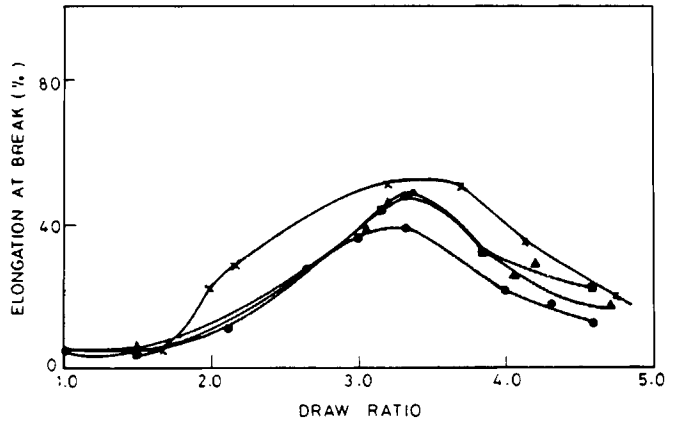

Fig. 10. Plots of % elongation at break versus draw ratio for stretched PET films annealed under tension at 140°C. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

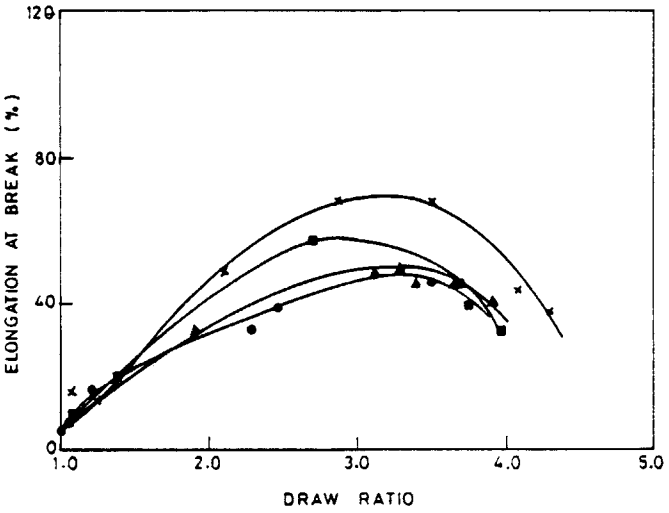

Fig. 11. Plots of % elongation at break versus draw ratio for stretched PET films annealed under relaxed condition at 140°C. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

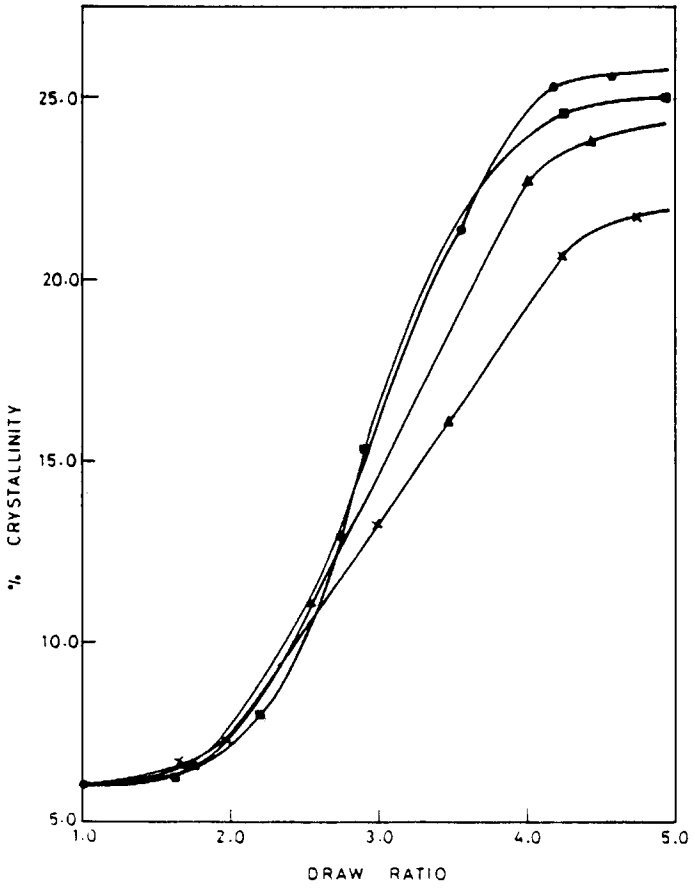

Fig. 12. Plots of crystallinity versus draw ratio for amorphous PET films stretched at 85°C at different stretching rates. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

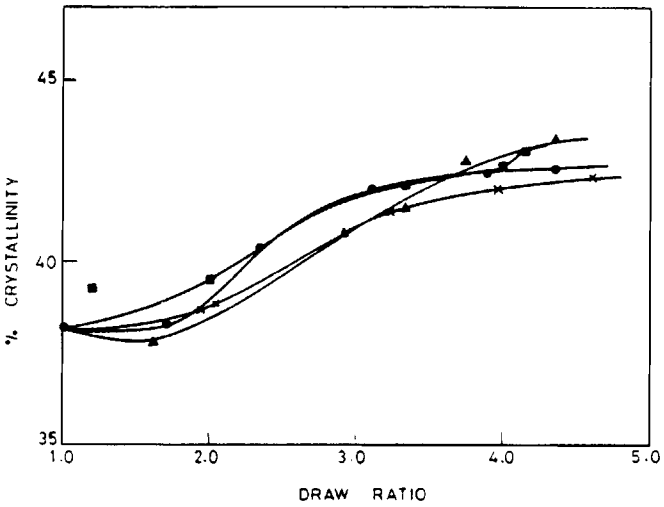

Fig. 13. Plots of crystallinity versus draw ratio for stretched PET films annealed under tension at 140°C. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

gence also increases with the increase in stretching rate. At low draw ratio the increase in birefringence value is less while at high draw ratio the increase in these values is more with the increase in stretching rate and stretching amount. Corresponding annealed samples show higher birefringence values. Samples annealed under tension show higher values compared to those annealed under relaxed condition.

TABLE I
Comparison of Structural Properties of PET Film Stretched and Annealed Under Tension and Relaxed Conditions at Stretching Ratio 5

Stretching rate (per min)	Actual draw ratio	Δn	% Crystallinity (by x-ray)	% Crystallinity (by density)	f_c	f_a
Stretched at 85°C						
100%	4.62	0.1115	22.5	21.7	0.9404	0.3312
200%	4.58	0.1407	23.8	23.0	0.9453	0.4084
400%	4.57	0.1432	24.2	23.8	0.9487	0.4370
600%	4.64	0.1611	26.1	25.5	0.9596	0.5059
Annealed under tension at 140°C						
100%	4.74	0.1526	42.6	42.3	0.9662	0.3561
200%	4.38	0.1659	43.6	43.0	0.9679	0.4581
400%	4.68	0.1727	44.2	43.0	0.9717	0.4752
600%	4.63	0.1733	45.1	42.5	0.9710	0.4825
Annealed under relax at 140°C						
100%	4.07	0.1548	—	42.1	0.9656	0.3724
200%	3.97	0.1550	—	41.8	0.9577	0.3809
400%	4.13	0.1606	—	42.6	0.9531	0.4129
600%	3.92	0.1663	—	42.3	0.9606	0.4463

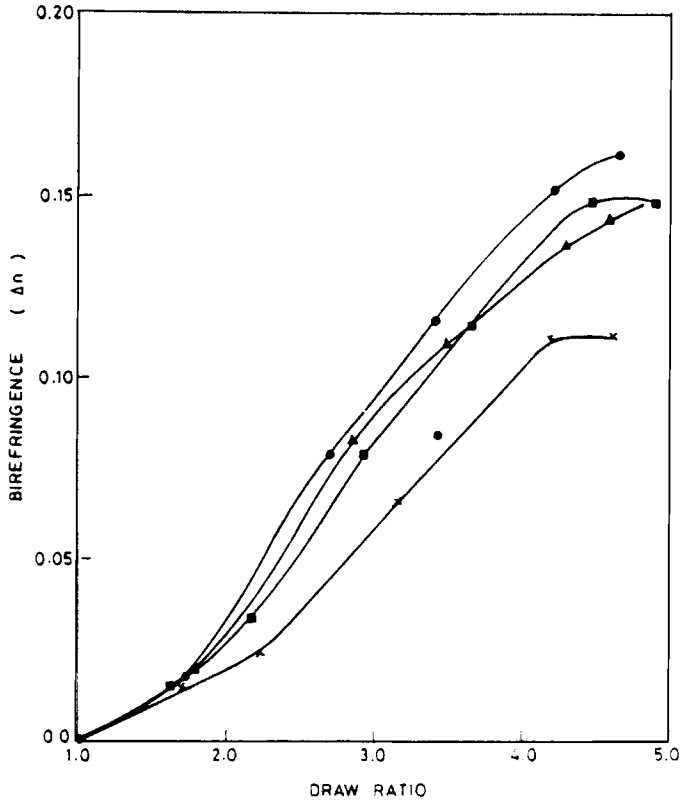

Fig. 14. Plots of birefringence versus draw ratio for amorphous PET films stretched at 85°C at different stretching rates. (x) Stretching rate 100%/min; (■) Stretching rate 200/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

Crystalline and amorphous orientation factors, birefringence, crystallinity by density method, and crystallinity by x-ray diffraction for all stretching rates and draw ratio 5 for samples stretched, annealed under tension, and relaxed conditions are compared in Table I. Herman's orientation factor (f_c) increases with the increase in stretching rate in case of stretched and tension-annealed samples. The amorphous orientation factor (f_a) increases greatly with the increase in stretching rate compared to f_c. These are compared with the corresponding birefringence and crystallinity values which support the trend of variation of mechanical properties.

The percent shrinkage as a function of draw ratio for all stretching rates are presented in Figure 17 during annealing under relaxed condition at 140°C for 15 minutes. At low draw ratio the shrinkage is high while at high draw ratio it is less. The % shrinkage decreases with the increase in stretching rate. At draw ratio 3 × the shrinkage is minimum for all the stretching rates.

DISCUSSION

During stretching of amorphous PET film above its T_g, the processes of molecular orientation and relaxation occur simultaneously. From the values of

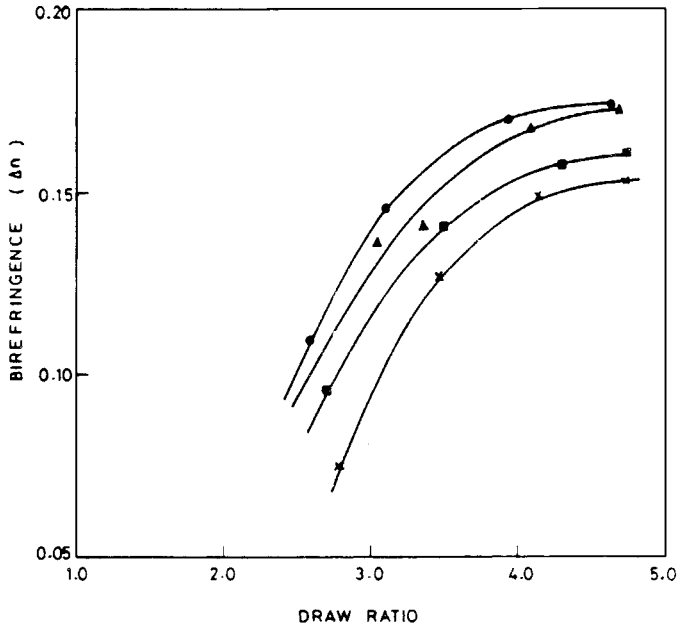

Fig. 15. Plots of birefringence versus draw ratio for stretched PET films annealed under tension at 140°C. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

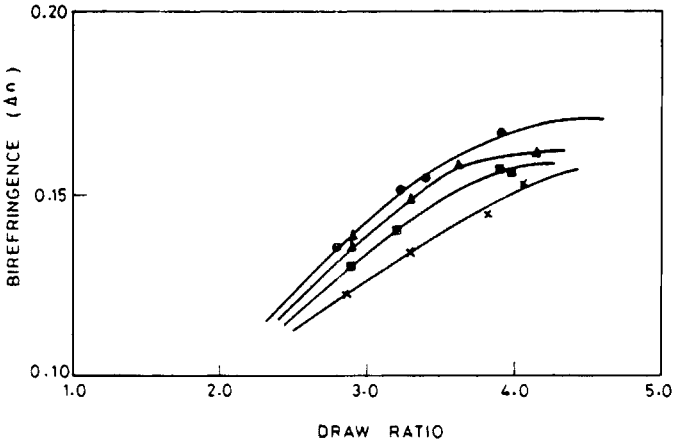

Fig. 16. Plots of birefringence versus draw ratio for stretched PET films annealed under relaxed condition at 140°C. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

Δn (Fig. 14), f_c, and f_a (Table I) it can be clearly seen that these parameters have higher values at higher stretching rates. This suggests that higher rate of stretching minimizes the relaxation process thus preserving higher molecular orientation. At low stretching rates significant relaxation takes place, thus resulting in less effective orientation. Furthermore, at high draw ratios, the

place in the samples which provide improved tensile properties. Furthermore, on annealing x-ray diffraction patterns become sharper showing that the crystals have become more perfect than in the unannealed samples which show diffused patterns.

During annealing under relaxed condition, stress relaxation takes place which results in significant amount of shrinkage. Lower values of shrinkage at high stretching rates are probably due to higher crystallinity and f_c values. At low draw ratios the polymer is amorphous but oriented and thus more prone to stress relaxation, whereas at high draw ratios, crystallinity sets in providing oriented crystalline regions which prevent the stress relaxation process, thus showing lower shrinkage. This is in support of high Δn values at high draw ratios in annealed samples.

CONCLUSION

1. The orientation of amorphous segments increases with the increase in stretching rate. Increase in birefringence values shows that overall orientation improves. Relaxation effects are lower at higher stretching rates.
2. Tensile properties (i.e., tenacity, yield stress, and initial modulus) improve with the increase in stretching rate. Increase in amorphous orientation and birefringence are probably responsible for this.
3. On annealing, the tensile properties improve considerably. Annealing under tension shows better results compared to annealing under relaxed condition.
4. This study provides a better understanding of stress-induced crystallization in oriented PET films and fibers.

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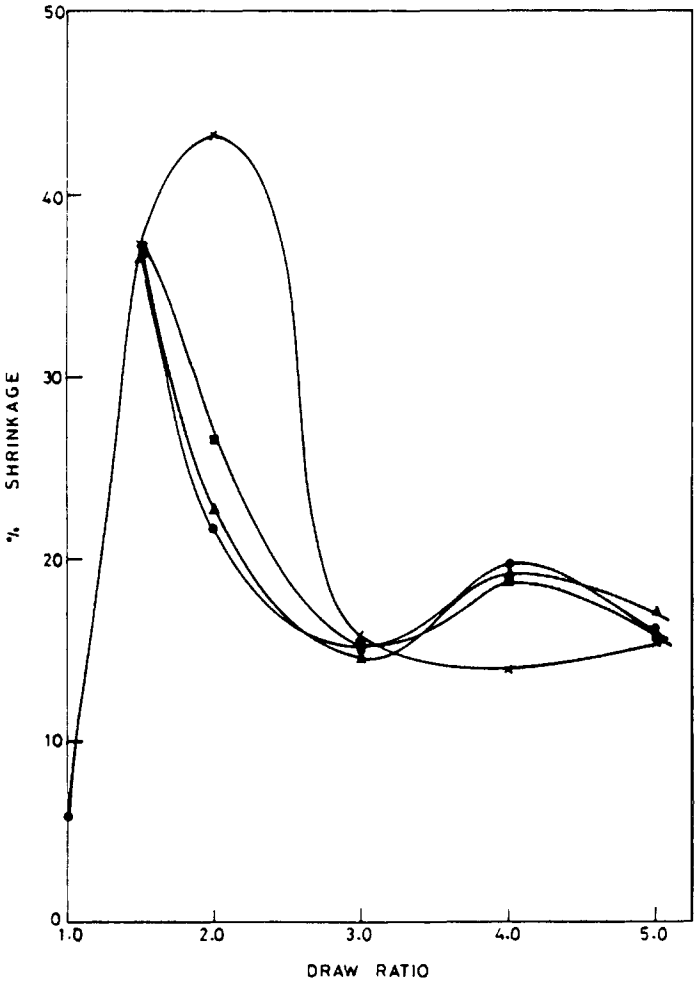

Fig. 17. Plots of % shrinkage versus draw ratio for stretched PET films during annealing under relaxed condition at 140°C. (x) Stretching rate 100%/min; (■) Stretching rate 200%/min; (▲) Stretching rate 400%/min; (●) Stretching rate 600%/min.

stresses in the stretched films are higher, thus providing an opportunity for greater relaxation. Thus if the stretching rate is higher followed by immediate quenching, higher orientations are likely to be preserved at high draw ratios. This explains the greater difference between Δn, tenacity, yield stress, initial modulus, and crystallinity values at high draw ratios than at low draw ratios when comparing samples at different stretching rates. The values of tenacity, yield stress, initial modulus, and elongation at break are in good agreement with the birefringence, amorphous and crystalline orientation factor, and crystallinity values. In general, higher molecular orientation results in higher mechanical properties.

On annealing, the tenacity, yield stress, initial modulus, and crystallinity increase considerably. This is because during annealing crystallization takes

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