Structural Changes in Draw-Textured Poly(ethylene terephthalate) Filaments during Heat-Setting

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SYNOPSIS

A sample of high-elastic-textured poly(ethylene terephthalate) (PET) yarns were subjected to different conditions of heat-setting, i.e., different temperatures and overfeeds. The structural changes were characterized by different physical methods. The orientation factors of crystalline and amorphous regions were calculated. The yarn tensions acting during the SET process were measured and corrected to the structural data. The results obtained show that two processes take place during the SET process: relaxation of the molecule segments in amorphous regions and change of crystallite orientation in microfibrils. A simple model for explanation of the structural changes in simultaneously draw-textured PET yarns is proposed.

INTRODUCTION

There are a number of studies related to changes in the structure of poly(ethylene terephthalate) (PET) fibers during heat-setting.[1-16] In most of these studies, PET fibers have been heat-set in free conditions.[1-10] There are several papers on the structural changes in PET fibers heat-set under tension or at constant length.[15,16]

The effect of the simultaneous drawing, heating, and twisting on the structural changes in PET yarns has not been studied systematically. Data concerning the influence of heat-setting on the mechanical and crimp properties of simultaneously draw-textured PET yarns were discussed in our earlier papers.[17,18] The present study is an attempt to reach a better understanding about structural changes in simultaneously draw-textured polyester yarns during heat-setting in the second heater of a draw-texturing machine.

EXPERIMENTAL

Sample Preparation

All work was done with middle-oriented polyester yarn 400 dtex 32 filaments spun at 2000 m/min.

The parameters of draw-texturing were kept constant as follows:

first heater temperature	195°C
draw ratio	2.45
spindle speed	500 000 rpm (2780 tpn
yarn speed	180 m/min
winding tension	0.5 cN/tex
yarn linear density	167 dtex 32 f

The high-elastic yarn produced at the above conditions without heat-setting was used as a control. In this case, the second heater was kept inoperative.

The parameters of heat-setting (second heater) were varied as follows:

- Second heater temperature—from 140 to 220°C with a step of 20°C.
- Overfeed—from 8 to 20% with a step of 4%.

The winding tension was kept constant by changing the winding speed in order to avoid the effect of package density on yarn properties.

Testing Methods

Linear Density

The linear density of heat-set draw-textured polyester yarn was measured by weighing the yarn length

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of 100 m winded under tension of 0.1 cN/tex. The linear density in dtex was calculated as the weight of 10 km yarn in grams. The winding tension of 0.1 cN/tex was enough to straighten the yarn crimp, thus avoiding the effect of yarn crimp on measured linear density.

Yarn Tension

Yarn tension during heat-setting was measured by a Rotshild tensometer type R-1092 with a measuring head of 10 g. Measurements were made before and after the second heater, and the mean value was taken as yarn tension during the heat-setting. The experimental results obtained are given in Figure 1.

Tensile Test

Textured yarns as well as single filaments were tested. Stress–strain curves of textured yarns were obtained on a Zwick 1501 unit. Single filaments were tested on a Fafegraph-T. Proper pretensioning was chosen in both tests to avoid the influence of crimping on stress–strain curves. A minimum of 50 measurements were made for each sample and average values were calculated.

Initial Modulus

The initial modulus was determined from the slopes of initial linear regions of the stress–strain curves (up to 3–4% elongation).

Density

A gradient column of our design with a mixture of n-heptane and carbon tetrachloride was used. A minimum of five measurements were made for each sample and average values were calculated.

Birefringence

The fringe shift inside the fibers was measured by a Pluta microscope[19] and birefringence was calculated using the equation[20]

$$\Delta n = \frac{dz \cdot \lambda}{z \cdot d} \qquad (1)$$

where dz is a fringe shift inside the fiber, z is an interfringe spacing, λ is the wavelength of the monochromatic light used (in our case, $\lambda = 550$ nm), and d is the fiber thickness.

Since textured filaments possess irregular cross sections, an average diameter ($\bar{d}$) was taken according to the expression

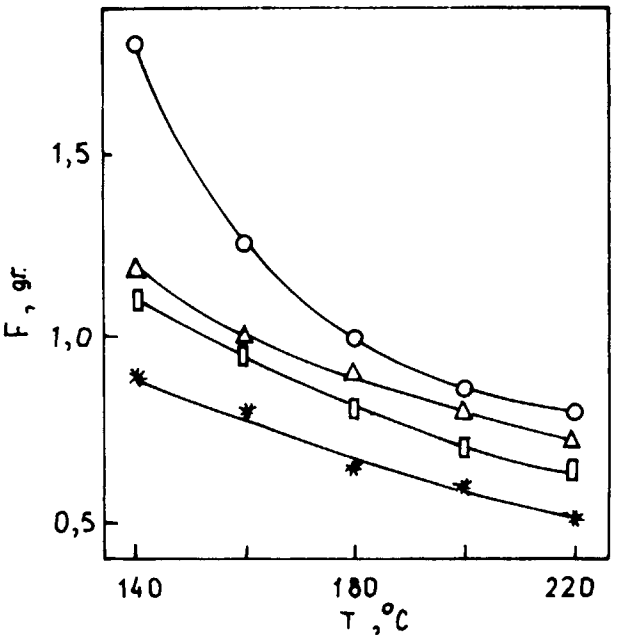

Figure 1 Yarn tension in second heater vs. heat-setting temperature. Overfeeds: (○) = 8%; (□) 16%; (*) 20%.

$$\bar{d} = (4 \cdot T \cdot 10^{-7}/\rho \cdot n \cdot \pi)^{1/2}$$

where T is the linear density of textured yarn, n is number of individual filaments, and ρ is density (measured by a gradient column).

An average of a minimum of 100 readings on different single filaments was taken to calculate the birefringence for a given sample of textured yarn. The accuracy in this case was 0.005. Hamza[21] proposed a method for determination of birefringence of fiber with a irregular cross section using a Pluta microscope. The results obtained by Hamza's method and the results obtained by the method described here have a good correlation.

Mass Fraction of Crystallinity

This parameter was determined from the experimental results of density. The density values of fully crystalline and amorphous PET were taken to be 1.457 and 1.136 g/cm^3, respectively.[22]

Crystallite Orientation Factor

This parameter was determined on the basis of the (1, 0, 5) plane. The method described in Refs. 23 and 24 was used for this purpose.

Amorphous Orientation Factor

This parameter was computed by the well-known expression originally given by Stein and Norris.[25]

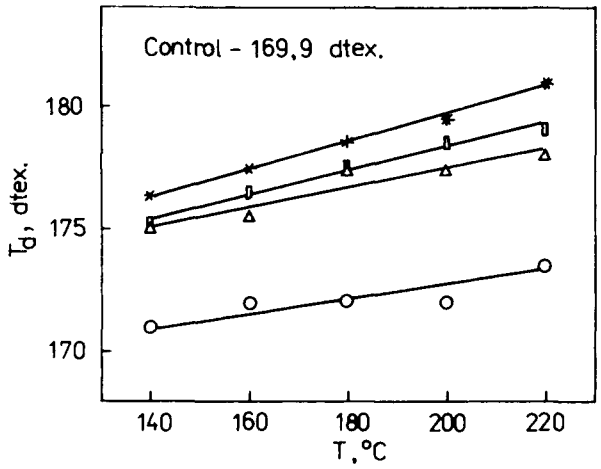

Figure 2 Linear density vs. heat-setting temperature. Overfeeds as indicated in Figure 1.

The values of intrinsic birefringence of crystalline and amorphous phases were taken to be 0.29 and 0.20, respectively.[26]

RESULTS AND DISCUSSION

The influence of temperature on the linear density of heat-set draw-textured yarn at different overfeeds is shown in Figure 2. Both increase of temperature and of overfeed lead to an increase of the yarn linear density. This effect can be explained by the influence of temperature and yarn tension on the relaxation taking place in the amorphous regions.[27] The same effect due to relaxation can be seen in the stress–strain curves presented in Figure 3. They show two regions: first, one up to deformation of 3–4% used for determination of initial modulus; and, second, one that includes a small region (up to deformation of 10%) showing a tendency to deformation without a change of the tensile stress. Obviously, after the heat-setting, the disorientation and relaxation in amorphous regions are enough to possibly give an orientational drawing. This effect is clearly shown on yarn samples obtained at a set temperature of 220°C and become visible when the temperature of the second heater surpassed the texturing temperature (195°C). A similar effect can be observed on the relationships of initial modulus vs. set-temperature (Fig. 4). The initial modulus in Figure 4(a) was calculated for single fibers, and in Figure 4(b) for yarns. It is evident that at overfeed of 8% the relation is almost linear, whereas at all other overfeeds, the initial modulus decreases at first and increases abruptly at temperatures over the texturing temperature (195°C). This result shows that there

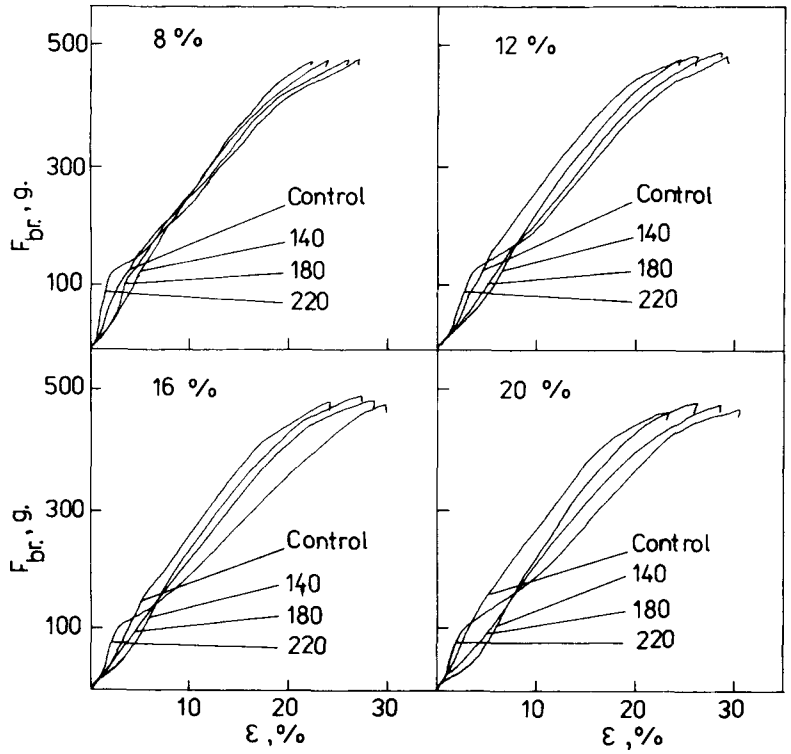

Figure 3 Stress–strain curves of heat-set yarns at different temperatures and overfeeds.

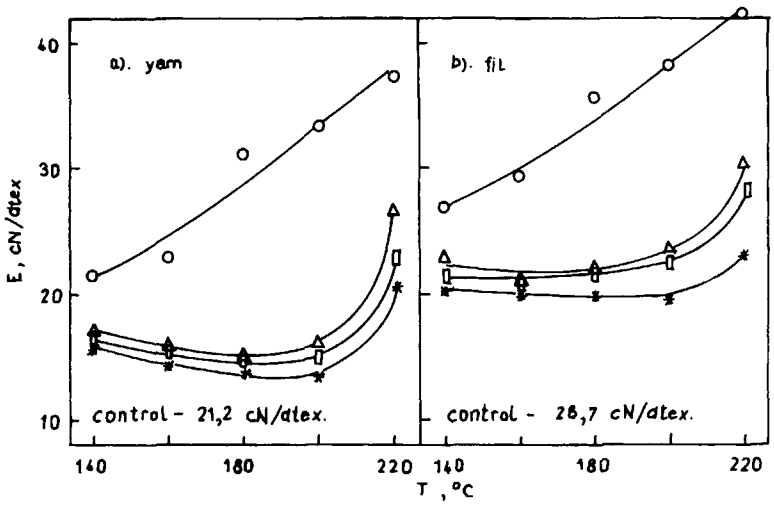

Figure 4 Initial modulus vs. heat-setting temperature. Overfeeds as indicated in Figure 1.

may be a specific stress at which the physical properties of SET yarns are changed considerably. This experimental fact was commented on in our previous paper.[17]

The results discussed above are in direct relation to changes that occurred in the structure of PET filaments during the SET process. The influence of setting temperature on the crystallinity is presented in Figure 5. One can see that the degree of crystallinity increases with the increase of heat-setting temperature. In regard to the overfeed, this parameter shows almost no effect on crystallinity. These results show that yarn tension in the second heater practically does not affect the secondary crystallization and improvement of the defects in crystalline regions. Both effects always occur with the thermal treatment of semicrystalline polymers.[28] These results are in good agreement with the results for crystallization of PET fibers in constant length.[16] On the other hand, an increase of crystallinity with setting temperature can be presented by two different relationships. The results for overfeed 20% are quite different from the others presented in Figure 5. The conclusion can be made that the structural changes have been affected eventually by mechanical tension during the setting process. This influence can be discussed on the basis of a two-phase model for macrofibril supermolecular structure in oriented polymers.

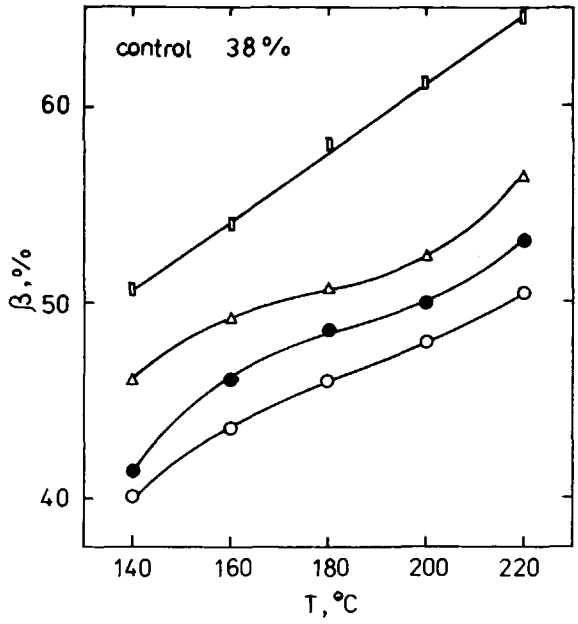

Figure 5 Crystallinity vs. heat-setting temperature. Overfeeds: (○) 8%; (●) 12%; (△) 16%; (□) 20%.

Curves of birefringence vs. setting temperature at different overfeeds are shown in Figure 6. It is obvious that the orientation decreases with the increase of setting temperature. A similar tendency exists in the relationships of orientation–overfeed. These relations could be expected. A possible explanation is that relaxation processes take place in the supermolecular structure of filaments during heat-setting. Once again, one can see that the curve at 20% overfeed has an essentially different character compared with the other curves presented in Figure 6. Probably there are many factors causing these differences. In any case, it is necessary to take into account the structural changes in amorphous as well as in crystalline regions of microfibrils and

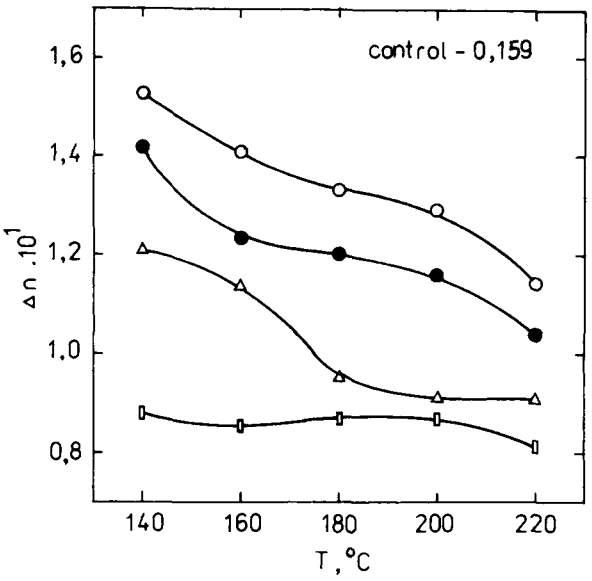

Figure 6 Birefringence vs. heat-setting temperature. Overfeeds as indicated in Figure 5.

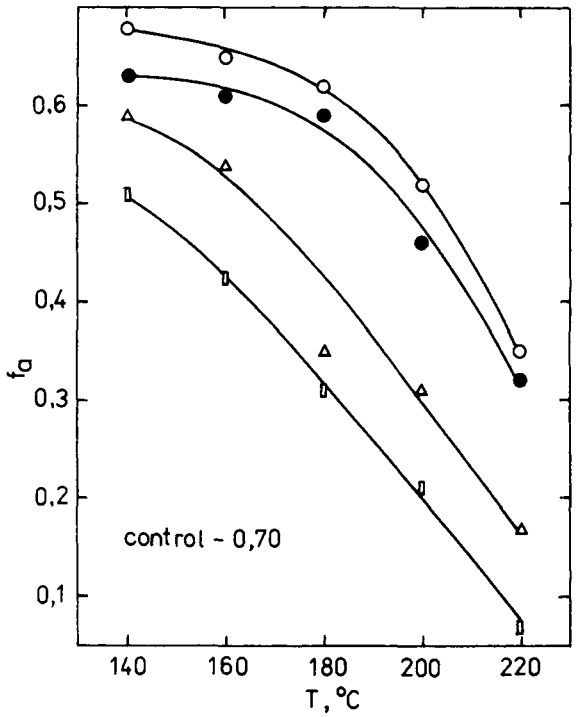

Figure 7 Amorphous orientation factor vs. heat-setting temperature. Overfeeds as indicated in Figure 5.

interfibrilous spaces. First of all, it should be expected that a disorientation will take place in the amorphous regions of microfibrils and interfibrilous spaces. On the other hand, the structural changes in crystalline regions will have as a result a change of the crystallite orientation. To consider in detail all the structural changes occurring in the textured SET yarns, it was necessary to determine the orientation factors of macromolecules in both regions: crystalline and amorphous ones. These dependencies are presented in Figures 7 and 8, respectively. It can be seen (Fig. 7) that the amorphous orientation factor decreases with the increase of heat-setting temperature and overfeed because of the relaxation processes in amorphous regions already discussed. In regard to the crystalline orientation factor, according to the dependencies presented in Figure 8, it can be concluded that this factor increases with an increase of the heat-setting temperature and overfeed. Obviously, this effect is a direct consequence of the simultaneous action of mechanical tension and heat during the SET process. A simple model for explanation of the structural changes in textured PET filaments during the SET process is presented in Figure 9. According to this model, the amorphous orientation factor decreases during the heat-setting because of the relaxation processes. On the other hand, the disorientation of the macromolecules in amorphous regions is kept by the action of the mechanical tension. The crystalline orientation factor increases during the heat-setting because of the movement of crystallites to the direction of the fiber axis. This movement is promoted by the action of the mechanical tension as well as by the action of heat. The reason is that the mobility of molecular segments in amorphous regions increases with an increase of the heat-setting temperature. Therefore,

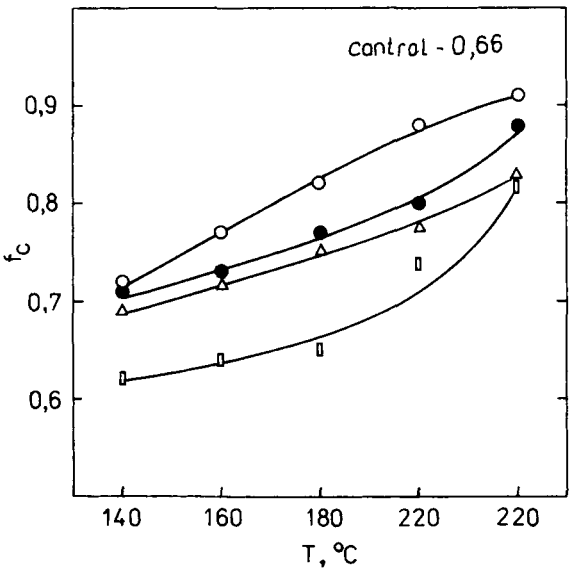

Figure 8 Crystalline orientation factor vs. heat-setting temperature. Overfeeds as indicated in Figure 5.

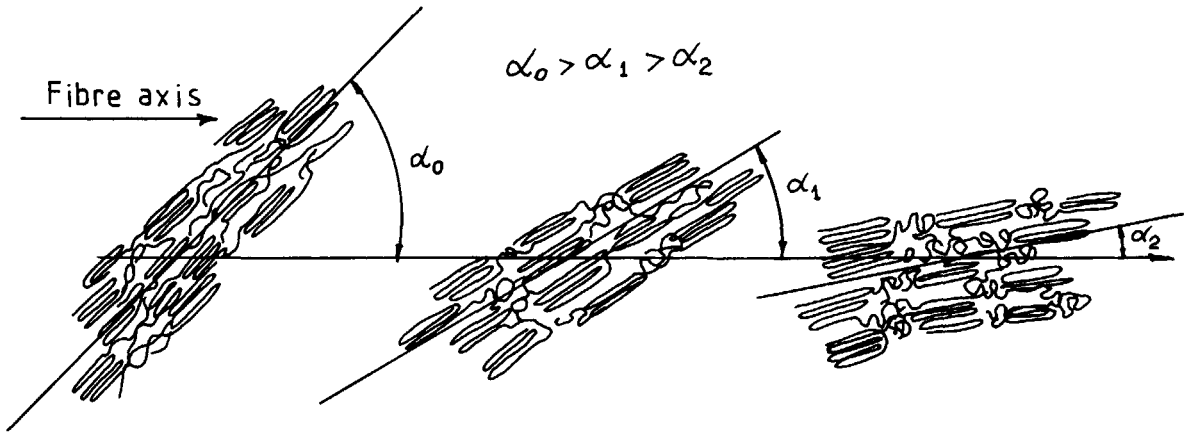

Figure 9 Schematic representation of the structural rearrangement in microfibrils of textured filaments during heat-setting.

it should be expected that the crystalline orientation factor will increase with an increase of the heat-setting temperature and decrease of the overfeed (increase of mechanical tension).

The relationships of amorphous and crystalline orientation factors vs. mechanical stress acting on the filaments during the SET process are presented in Figures 10 and 11, respectively. In this case, the calculation of the mechanical stress was made using results given in Figures 1 and 2. As seen in Figures 10 and 11, the mechanical tension stimulates the orientation of macromolecule segments in both regions: amorphous and crystalline. This was predicted by the structural model presented in Figure 9. On the other hand, the orientation factor of high-elastic-textured PET yarn taken as a control has a little bit higher value than the crystalline orientation factor of several SET yarns studied (Figs. 8 and 11). These experimental results cannot be explained by the model presented in Figure 9.

For explanation of the experimental results discussed above, it is necessary to suppose a more complicated structural organization of crystallites in the macrofibrils of textured PET filaments. The reason for this structural organization is the special condition of mechanical treatment during the draw-texturing. One can suppose the existence of helically

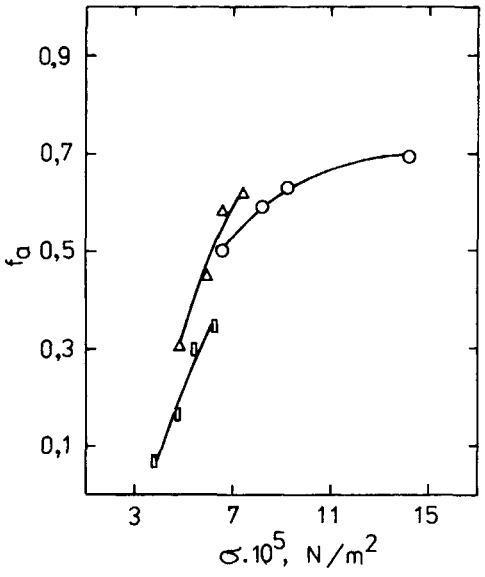

Figure 10 Amorphous orientation factor vs. yarn tension. Heat-setting temperatures: (○) 140°C; (△) 180°C; (□) 220°C.

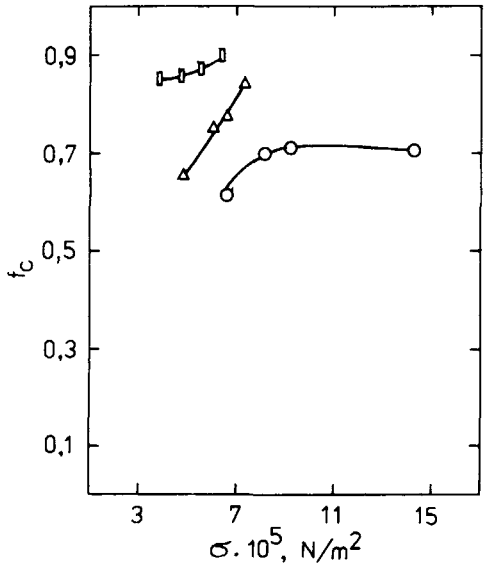

Figure 11 Crystalline orientation factor vs. yarn tension. Heat-setting temperatures as indicated in Figure 10.

oriented crystallites in microfibrils of the textured PET filaments. Such a structural organization was proposed in other work.[6] A direct analogy is not correct because samples investigated in that paper[6] have been essentially different. Nevertheless, the existence of a similar organization of oriented PET is possible in principle. Obviously, for a detailed explanation, it is necessary to carry out additional experiments and structural measurements. We emphasize only that a model assuming helically oriented crystallites in microfibrils of textured PET filaments offer a reasonable explanation for all the experimental results included in this paper.

CONCLUSION

The results of the present work show that two processes take place during heat-setting of textured PET filaments: relaxation of macromolecular segments in amorphous regions and movement of crystallites to the direction of mechanical stress, e.g., fiber axis. The existence of helically oriented crystallites in microfibrils of high-elastic-textured PET filaments is supposed. This hypothesis is used to explain the experimental results.

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