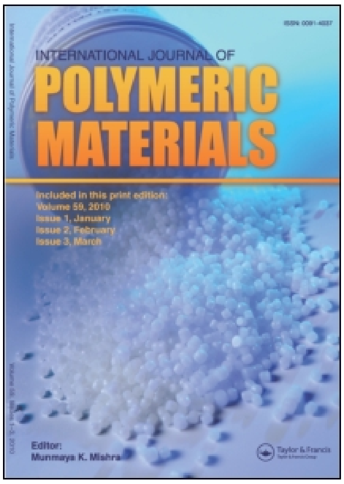

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Orientation and Shrinkability in Polymers

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Orientation and Shrinkability in Polymers

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This work deals with uniaxial orientation and shrinkage of two grades of well-characterized low-density polyethylene (LDPE), and a general-purpose polystyrene (PS). The LDPE grades differed in molecular-weight distribution and degree of long chain branching.

The polymer samples were stretched to different levels of deformation over a range of temperature, quenched, and subsequently annealed. The shrinkage and thermoelastic force during recovery were measured upon annealing. Molecular orientation resulting from the stretching process was characterized by birefringence measurements in the amorphous polymer and by X-ray diffraction in the semicrystalline polymer. Morphology changes in the latter were characterized by polarized optical and electron microscopy.

The relationship between the amount, rate and temperature of stretching, to the resulting orientation and morphology, and the shrinkage behavior were investigated.

INTRODUCTION

Orientation in amorphous polymers is obtained by applying on the polymer sample a deformation above the glass transition temperature, T_g. In the case of partially crystalline polymers, orientation can be obtained in two different methods: (a) by hot drawing above the melting point, T_m, followed by quenching and (b) by cold stretching ($T_g < T_{\text{def}} < T_m$) between the glass-transition temperature and the melting point. In the latter case one is dealing with deformation in the solid state, wherein changes in the shape and alignment of the crystallites lead to orientation. The effects of deformation on orientation and morphology of polymers is discussed in detail in the literature.[1,2]

Thermoelastic shrinkage is obtained by heating the oriented polymer. Above the highest transition temperature all orientation is lost.[3]

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The total linear deformation, ϵ_T, of the oriented sample may be described by three components[4]:

a) an instantaneous elastic component, ϵ_1
b) a viscoelastic component, ϵ_2
c) a plastic (viscous) component, ϵ_3.

The simplest mechanical model simulating this type of deformation consists of a combination in series of Maxwell and Voigt bodies. This combination is often called the Burger model.

The viscoelastic component, ϵ_2, can serve as a measure of the degree of recoverable orientation, that is, the thermoelastic shrinkage.

EXPERIMENTAL

The materials tested in this work were:

—a general-purpose type polystyrene (PS) characterized by:

MFI = 3.6 gr/10 min; density = 1.05 gr/cc
T_g = 98–100°C. $\overline{M}_w = 260{,}000$. $\overline{M}_n = 80{,}000$.

—two kinds of low-density polyethylenes (LDPE)

a) "Ipethene 110" with MFI = 0.68 gr/10 min; density = 0.923 gr/cc; T_m = 118–119°C; $\overline{M}_w = 320{,}000$; $\overline{M}_n = 24{,}000$.

b) "Ipethene 800" with MFI = 18.80 gr/10 min; density = 0.916 gr/cc; T_m = 117–118°C; $\overline{M}_w = 518{,}000$; $\overline{M}_n = 15{,}700$.

All three samples were products of the Israel Petrochemical Enterprises Ltd., Haifa. Uniaxial strands with different degrees of orientation were made with the hot drawing equipment shown in Figure 1, and on the cold stretching machine shown in Figure 2.

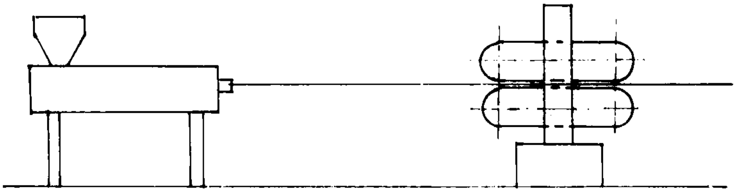


FIGURE 1 Drawing equipment.

The hot drawing system consists of a Boston take-off apparatus attached to a single-screw extruder (Thoret, 20 mm), (Figure 1). The cold stretching equipment essentially consists of two sets of rubber rolls, driven at differential speeds. The strands pass through the first series of rolls at low speed of 0–7.2 rpm, into a thermostatic controlled oven (Memmert) working at 20–300°C. From here the strands pass through an air cooler into the second series of rolls at higher speeds up to 14.4 rpm, in which the stretching is obtained (Figure 2).

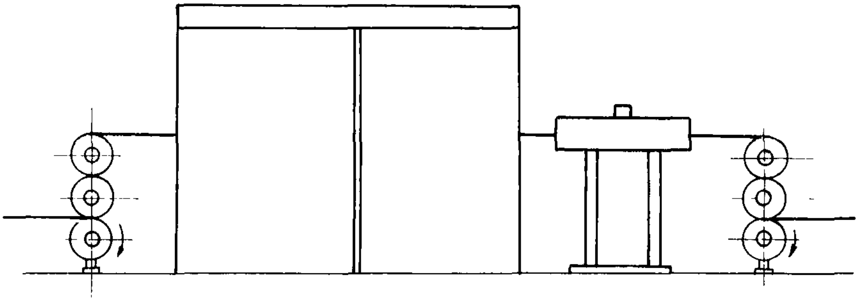


FIGURE 2 Stretching equipment.

The thermoelastic shrinkage experiments were performed either in a temperature controlled glycerine bath, or in the oven at various temperatures.

Birefringence measurements were performed with a polarizing microscope "Wild-Heerburgg" M-21, equipped with an "Ehringhaus" compensator.

The main experimental parameters were:

—l_0: the length of the sample before orientation.
—l_1: the maximum length of the sample during stretching.
—l: the length of the sample after orientation.
—l_f: the length of the sample after thermoelastic shrinkage

degree of orientation: $\frac{l - l_0}{l_0}$ (in drawing) $\frac{l_1 - l_0}{l_0}$ (in stretching)

degree of shrinkage: $\frac{l - l_f}{l_f}$

l_1 is determined while the sample is under tension at cold stretching. l is taken after one hour of relaxation at room temperature. For the case of hot drawing $l_1 = l$.

RESULTS AND DISCUSSION

A. Amorphous polymers

During the drawing the fiber is transparent and its diameter decreases steadily as indicated in Figure 3. A number of samples were drawn until fracture was obtained. The fractured region shows a fibrous structure, aligned parallel to the direction of draw as indicated in the scanning electron micro-

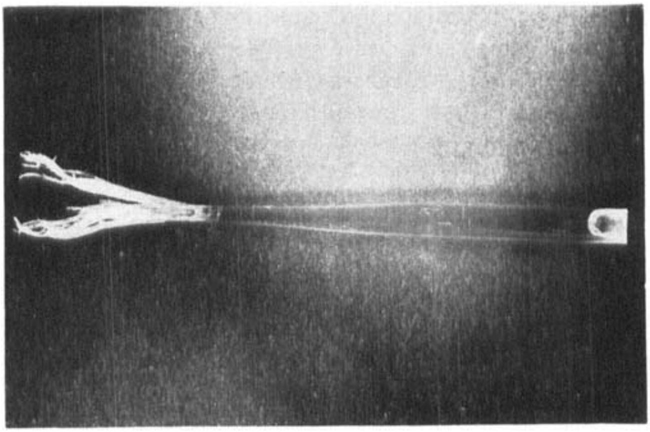


FIGURE 3 Photograph of the drawing region in polystyrene fiber (×3).

graph shown in Figure 4. The thermoelastic shrinkage of the oriented fibers begins when heated above T_g, resulting in a spiral-like form exactly at the transition point as shown in Figure 5. This curling phenomenon is believed to indicate non-homogeneous orientation within the strand. This can be attributed to the temperature profile set-up in the sample upon cooling resulting in

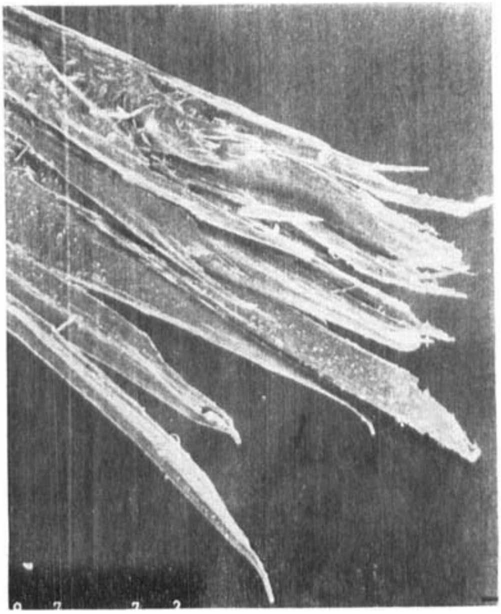


FIGURE 4 Scanning electron micrograph of fracture surfaces of oriented polystyrene fiber (×100).

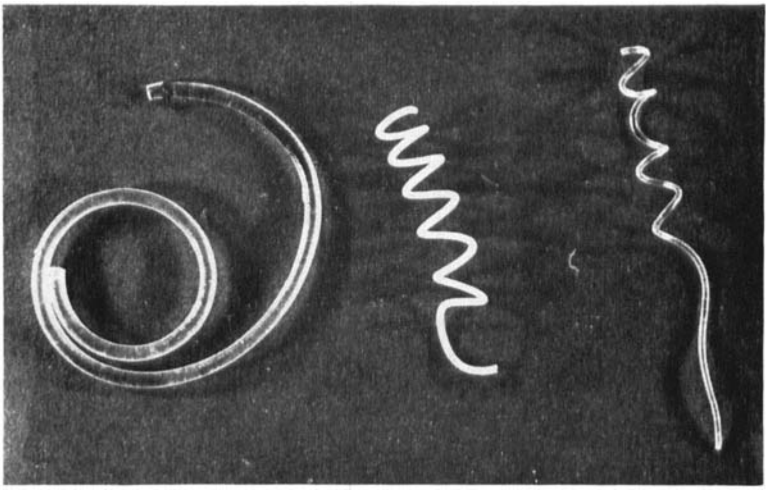


FIGURE 5 Spiral-like thermoplastic shrinkage of polystyrene fibres with uniaxial orientation.

different times for relaxation at different radial position, a phenomenon similar to that occurring in injection molding. It may serve as a simple although crude measure for T_g.

The thermoelastic response of PS after annealing for 5 minutes at 170°C (to nullify all orientation) is shown in Table I. The thermoelastic component,

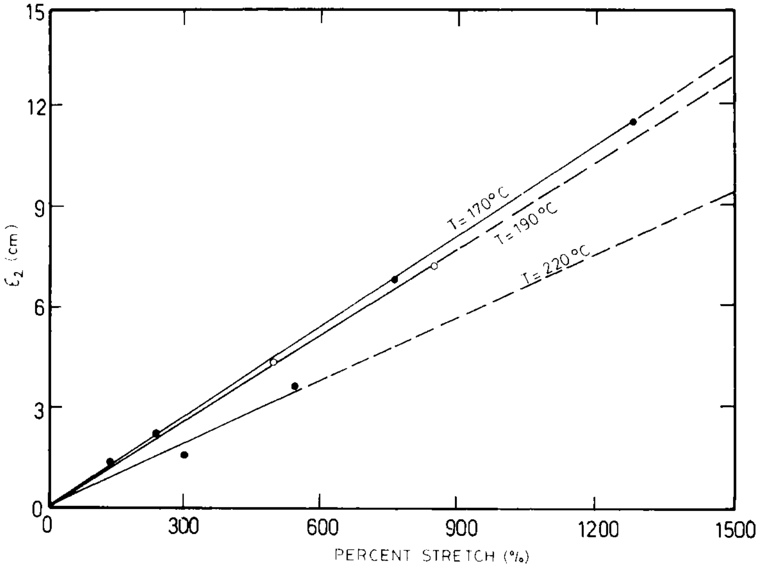


FIGURE 6 Effect of percent stretch on thermoelastic deformation.

ϵ_2 (of the total deformation ϵ_T) represents the degree of recoverable orientation. A linear correlation was found between ϵ_2 and either the degree of stretching (Figure 6) or the magnitude of birefringence (Figure 7). The time-temperature effects in shrinkability are shown in Figure 8. Clearly, increasing the temperature leads to an increase of the rate and extent of shrinkability.

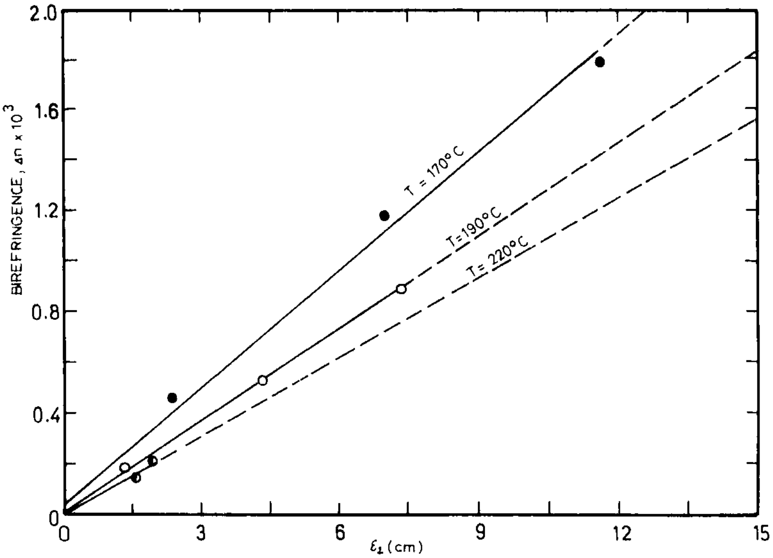


FIGURE 7 Effect of thermoelastic deformation on birefringence.

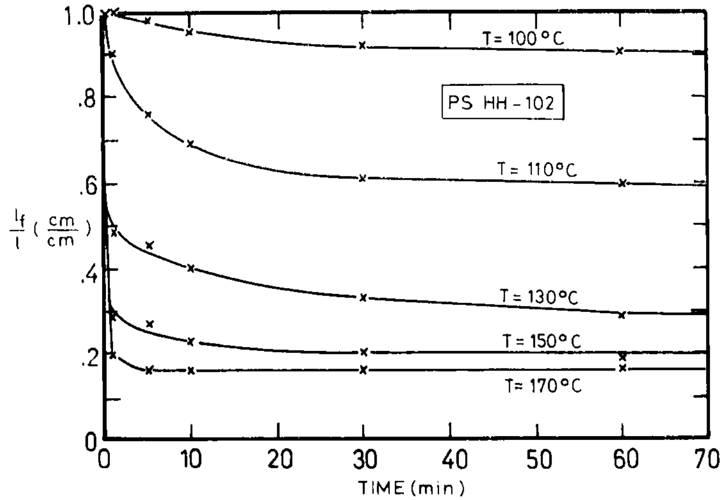


FIGURE 8 Thermoelastic shrinkage of PS HH-102 at various temperatures.

TABLE I

Thermoelastic deformation of polystyrene

T_{def} °C	Stretch %	Rate of stretch %/min	Shrinkage %	l_o cm	l cm	l_f cm	ϵ_T cm	ϵ_2 cm	ϵ_3 cm	ϵ_2/ϵ_T cm/cm
250	455	3640	39	1	5.6	4.0	4.6	1.6	3.0	0.35
220	305	1525	66	1	4.1	2.5	3.1	1.6	1.5	0.52
220	545	4360	127	1	6.5	2.9	5.5	3.6	1.9	0.65
190	140	280	113	1	2.4	1.1	1.4	1.3	0.1	0.93
190	495	2475	257	1	6.0	1.7	5.0	4.3	0.7	0.86
190	850	6800	335	1	9.5	2.2	8.5	7.3	1.2	0.86
170	245	490	186	1	3.5	1.2	2.5	2.3	0.2	0.92
170	760	3800	400	1	8.6	1.7	7.6	6.9	0.7	0.91
170	1280	10,240	525	1	13.8	2.2	12.8	11.6	1.2	0.91
160	200		115	1	3	1.3	2	1.7	0.3	0.85
150	200		150	1	3	1.2	2	1.8	0.2	0.90
140	200		173	1	3	1.1	2	1.9	0.1	0.95
130	200		200	1	3	1.0	2	2	0	1.0
120	200		200	1	3	1.0	2	2	0	1.0

The data presented in Table I point out that the relative thermoelasticity ϵ_2/ϵ_T increases when the drawing temperature decreases (due to the diminishing of the flow-component ϵ_3). On approaching T_g (at 120–130°C) the ratio ϵ_2/ϵ_T reached the limiting value 1, exhibiting a complete reversibility in deformation.

B. Partially crystalline polymers

If orientation is obtained by hot drawing ($T_{\text{def}} > T_m$), a certain similarity exists to the case of the amorphous polymers. On freezing, the polymer crystallizes. During the drawing the fiber is transparent and its diameter decreases steadily.

The results of the thermoelastic measurement obtained after 5 minutes at $T_{\text{shrink}} = 125°\text{C}$ (above melting point) are shown in Table II for PE 110, and in Table III for PE 800.

The thermoelastic component, ϵ_2, represents the degree of orientation. Figure 9 shows a linear correlation between this parameter and the stretch percentage. It should be noted that both PE grades are indistinguishable

When orientation is obtained by cold stretching (at $T_g < T_{\text{def}} < T_m$), necking shows up. The unoriented material before the necking point

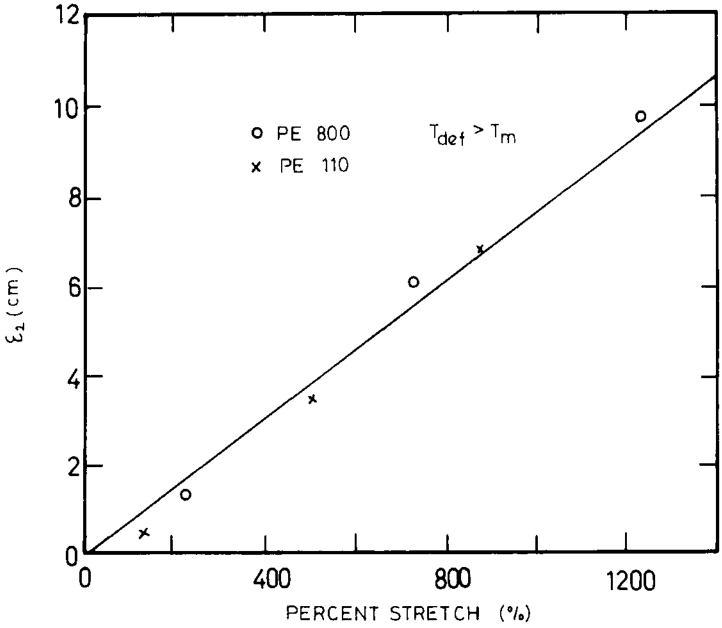


FIGURE 9 Effect of percent stretch on thermoelastic deformation: polyethylene.

TABLE II

Thermoelastic deformation of PE 110 after hot drawing

Stretch %	Rate of stretch %/min	Shrinkage %	l_o cm	l cm	l_f cm	ϵ_T cm	ϵ_2 cm	ϵ_3 cm	ϵ_2/ϵ_T cm/cm
876	7008	226	1	9.8	3.0	8.8	6.8	2.0	0.77
510	2550	138	1	6.1	2.6	5.1	3.5	1.6	0.69
144	288	47	1	2.4	1.7	1.4	0.7	0.7	0.50

TABLE III

Thermoelastic deformation of PE 800 after hot drawing

Stretch %	Rate of stretch %/min	Shrinkage %	l_o cm	cm	l_f cm	ϵ_T cm	ϵ_2 cm	ϵ_3 cm	ϵ_2/ϵ_T cm/cm
1233	9867	335	1	13.3	3.1	12.3	10.2	2.1	0.83
733	3666	257	1	8.3	2.3	7.3	6.0	1.3	0.82
233	466	69	1	3.3	1.9	2.3	1.4	0.9	0.61

(Figure 10) shows a spherulitic morphology and is opaque. After the necking the point, oriented regions show no spherulitic structure and are transparent.

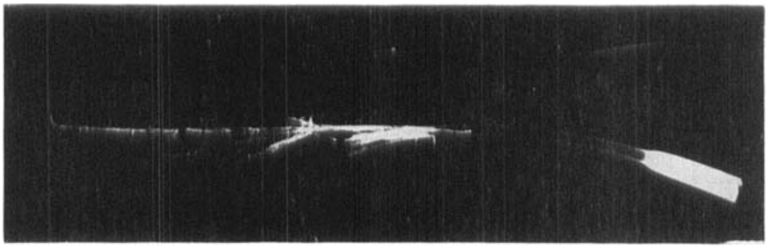


FIGURE 10 Photograph of necking point of a stretched polyethylene fiber and fracture of the unoriented and oriented regions (× 3).

The fracture below T_g of the oriented regions presents a fibrous structure with an alignment parallel to the direction of stretch as shown by scanning electron micrograph in Figure 11. The results of the thermoelastic measurements obtained after 5 minutes at $T_{\text{shrink}} = 125°\text{C}$ are shown in Table IV.

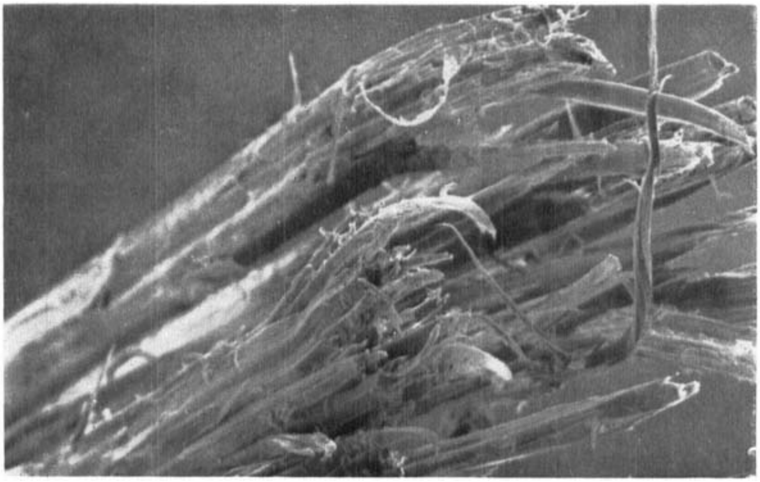


FIGURE 11 Scanning electron micrograph of fracture of oriented polyethylene fiber (× 160).

In this case too, a linear correlation exists between the thermoelastic component (ϵ_2) and the degree of stretching (Figure 12). However, ϵ_2 increases with increasing temperature of stretching, in contrast to the behavior of hot drawing. In this case the instantaneous elastic component ϵ_1 interferes at lower temperatures (see also Table IV).

TABLE IV

Thermoelastic deformation of PE 110, after cold stretching

T_{def} °C	Stretch %	Rate of stretch %/min	Shrinkage %	l_o cm	l_1 cm	l cm	l_f cm	ϵ_T cm	ϵ_1 cm	ϵ_2 cm	ϵ_3 cm	ϵ_2/ϵ_T cm/cm
20	100	91	—	1	2	1.1	1.1	1	0.9	—	0.1	—
20	300	546	123	1	4	2.9	1.3	3	1.1	1.6	0.3	0.67
20	700	1274	400	1	8	7.0	1.4	7	1.0	5.6	0.4	0.80
60	100	91	17	1	2	1.4	1.2	1	0.6	0.2	0.2	0.20
60	300	546	169	1	4	3.5	1.3	3	0.5	2.2	0.3	0.73
60	700	1274	454	1	8	7.2	1.3	7	0.8	5.9	0.3	0.84
100	100	91	28	1	2	1.8	1.4	1	0.2	0.4	0.4	0.40
100	300	546	177	1	4	3.6	1.3	3	0.4	2.3	0.3	0.77

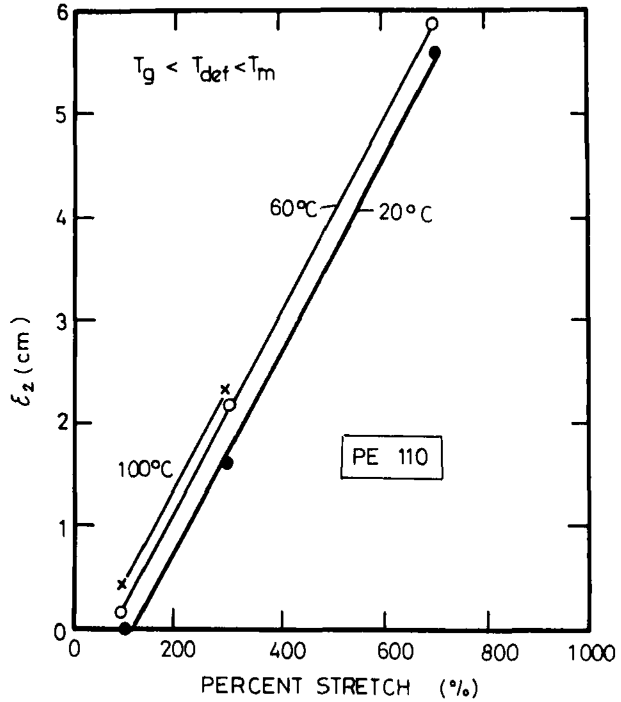


FIGURE 12 Effect of percent stretch on thermoelastic deformation after stretching.

Shrinkability may also be followed by direct measurements of the internal stress (force of shrinking) at various temperatures. This is clearly shown in Figure 13, for cold-stretched PE fibers. The force rises to a maximum after which it drops towards T_m. The forces depend on degree of stretching and its temperature. Simultaneous measurements of rate of shrinkage as a function of temperature on oriented PVC samples were demonstrated by Tobias and Taylor.[5] In our work the degree of shrinking (Figure 14) verifies an increasing correlation with temperature and degree of stretch. It is interesting to note, that in the case of cold-stretching a slight difference is found between the shrinkability performance of PE 110 and 800. The latter demonstrates some higher shrinking tendency, which may be attributed to its broader MWD and in particular to its higher degree of long-chain branching. Indeed it was previously claimed that an increase in long-chain branching results in higher elasticity.[6]

A different tool for orientation analysis was also utilized, namely, X-ray diffraction. Typical results for cold-stretched PE fibers at various degrees of orientation are shown in Figure 15. The progressive changes are self-explanatory.

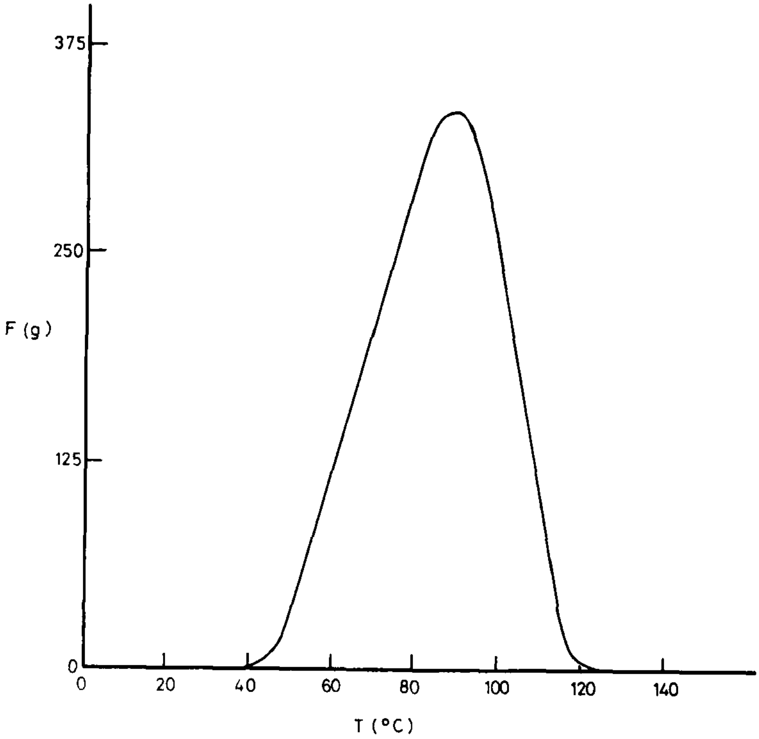


FIGURE 13 Effect of temperature on shrinkage force.

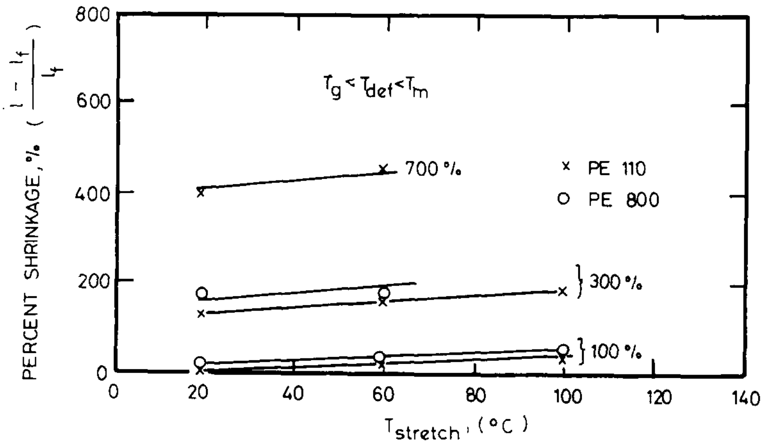
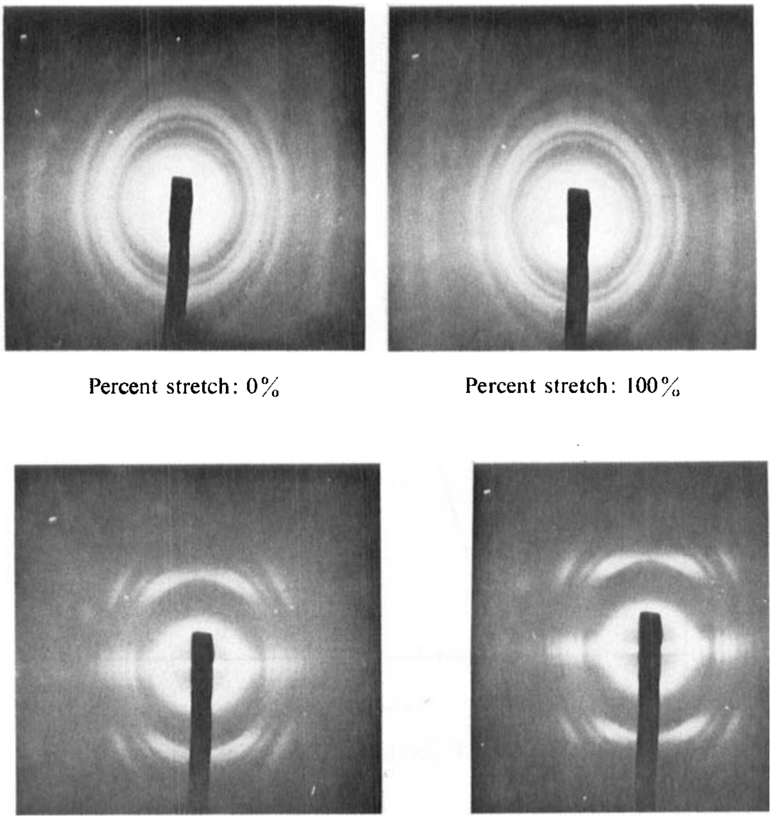


FIGURE 14 Effect of stretching temperature on percent shrinkage.



Percent stretch: 0% Percent stretch: 100%

Percent stretch: 300% Percent stretch: 700%

FIGURE 15 X-ray diffraction patterns for PE-110 after stretching at different extents.

CONCLUSION

Shrinkability of oriented fibers is a paramount thermoelastic phenomenon. It is strongly affected by time and temperature at both stages of stretching and annealing.

Various techniques may be used in order to measure and describe the degree of frozen orientation. There is a principal difference between the behavior after cold-stretching of semi-crystalline polymers as related to hot-drawing of amorphous or semi-crystalline polymers. The molecular structure has a slight effect on the shrinkability process.

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