New routes to polyethylene terephthalate with improved mechanical properties

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Two-stage cold drawing with each stage followed by high temperature annealing was used to prepare high performance polyethylene terephthalate (PET). By this means a very high draw ratio ($\lambda = 20$) is achieved at room temperature. The different supermolecular structures in the materials with $\lambda = 5$ and $\lambda = 20$ are measured by means of SAXS and WAXS. Mechanical and thermal treatments give rise to an alternating structure in PET with $\lambda = 5$ and to an almost parallel extension of the macrochains in the absence of alternation in PET with $\lambda = 20$. This difference in the supermolecular structure affects the mechanical behaviour of the two materials: the samples with $\lambda = 20$ have double the tensile strength (0.60 against 0.26 GPa) and elasticity modulus (18.6 against 11.5 GPa) of those with $\lambda = 5$.

(Keywords: polyethylene terephthalate; mechanical properties; SAXS; WAXS)

INTRODUCTION

The development of high performance polymer materials is one of the most important tasks of contemporary material science. Such polymers require the creation of a proper supermolecular structure usually comprising maximal orientation of the macromolecules, perfect crystallites built up by extended chains, and a relatively high molecular weight of the polymer.

There are two principal and basically different approaches to the realization of high modulus and high strength polymer materials: synthesis of new polymers with 'tailored' properties; and structural modification of known and widely applied polymers.

Liquid crystalline (lyotropic and thermotropic) polymers represent a good illustration of the successful synthesis of new types of materials[1–4]. In spite of their excellent mechanical properties, this new class of polymers still has a limited practical application, mainly due to high production costs.

The methods based on structural modification of commercial polymers are much more accessible. They can be classified as cold or hot drawing[1,5], solid state extrusion[1,5,6], zone drawing[7,8] and rapid drawing from melts or solutions[1,9,10]. These mechanical and/or thermal treatments result in transformation of the isotropic structure into a fibrillar one[1,5]. The models of microfibrillar morphology proposed by Peterlin (for polyolefins)[5] and Prevorsek (for polyesters)[11] provide a very good explanation of some properties, particularly the mechanical properties. The concept that the mechanical properties of the fibrillar material are determined to a greatest extent by the number of molecules under stress is generally accepted. Because tie molecules represent from 1–3% (ref. 5) or from 10–20% (ref. 12) of the total number of chains in the crystallites, it is quite natural that the achieved maximal values of the tensile strength (σ_b) and the elasticity modulus (E) are considerably lower (by orders of magnitude) than those calculated theoretically or observed with liquid crystalline polymers. The high mechanical parameters in the latter case result from the supermolecular organization of liquid crystalline polymers: maximal alignment of parallel chains in the absence of chain folding. Unfortunately, such a fibrillar morphology has not been obtained in polyolefins and polycondensates.

The purpose of the present study is to consider the possibilities of obtaining high modulus and high strength polyethylene terephthalate (PET) by means of two-stage drawing. Each stage is followed by annealing to achieve the optimal structure.

EXPERIMENTAL

Commercial PET monofilaments, 1 mm thick, with a relative viscosity $\eta_{rel} = 1.36$ (1% solution in a phenol–tetrachloroethane mixture (1:1) at 25°C) were used in the present study. The material was drawn at room temperature on a Zwick 1464 machine at a draw rate of 5 mm/min. Mechanical test samples were 50 mm long and tested under the same conditions by means of an incremental extensiometer with a sensitivity of 0.002 mm. The samples were annealed under constant strain for 2–6 h at temperatures in the range of 200–270°C in a vacuum oven at 30 m bar.

Small and wide angle X-ray scattering measurements (SAXS and WAXS) were carried out on a Siemens Kristalloflex apparatus with CuKα radiation.

RESULTS AND DISCUSSION

A model is proposed in *Figure 1*, outlining the structural and chemical changes in oriented polycondensates taking place during the thermal and mechanical treatments.

Together with the structural changes, linear polycondensates could undergo chemical interactions caused by the thermal treatment, e.g. additional condensation, destruction, exchange reactions, due to the presence of reactive groups in these polymers (–CONH–, –COOH, $-NH_2$, –OH, –COO–) in contrast to polyolefins where only destruction could take place[13].

The chemical nature of the polycondensates enables their structure to be altered at will. Thus, for example,

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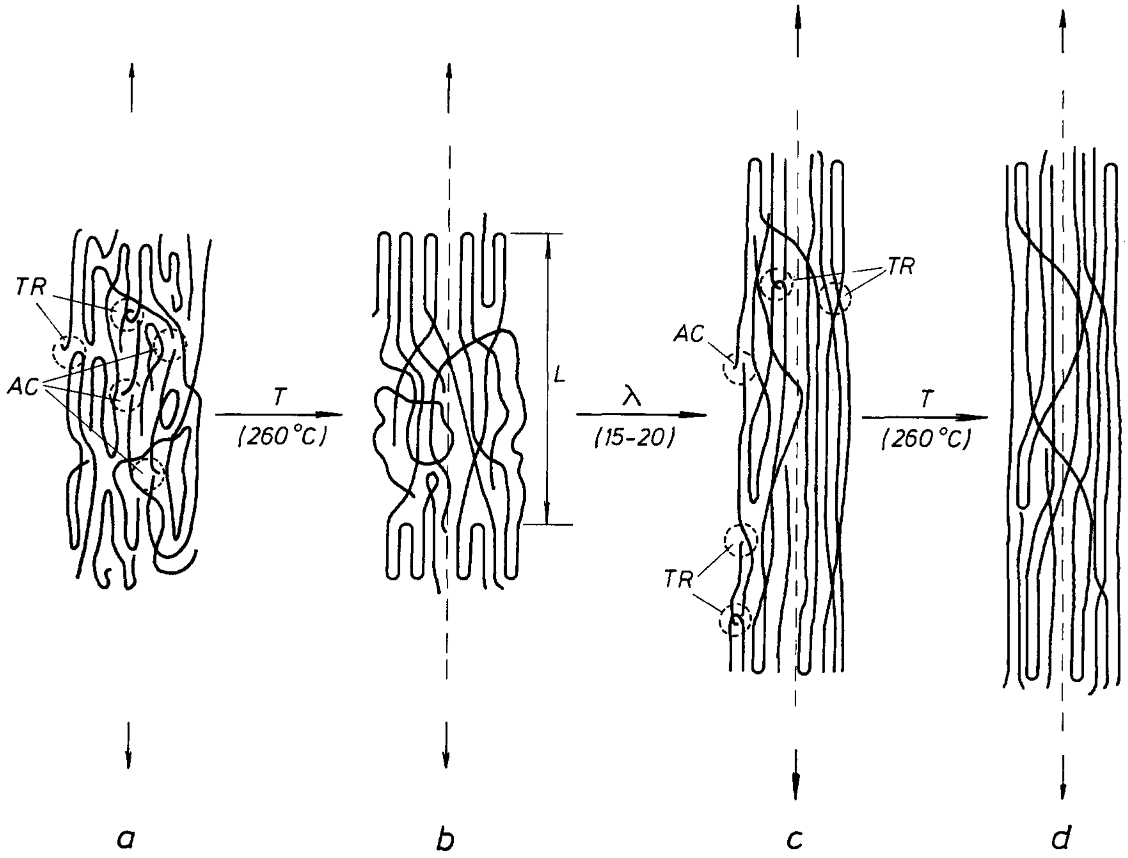

Figure 1 Models illustrating the physical and chemical changes in oriented partially crystalline PET subjected to additional drawing and annealing with fixed ends: (a) structure of the sample after cold drawing ($\lambda=4$–5); (b) structure of the same sample after annealing ($T_a=260°C$); (c) structure of the same sample after a second cold drawing ($\lambda=15-20$); (d) structure of the same sample after a second annealing ($T_a=250$–$270°C$). AC, additional condensation; TR, trans (exchange) reactions; the dashed line denotes two separate microfibrils

additional condensation and trans (exchange) reactions (*Figure 1a,b*) can be used to eliminate defects due to such things as chain ends in the fibrils, entanglements and chain-folds, as shown schematically in *Figure 1*. Furthermore, due to the increased molecular weight as a result of additional condensation, an improvement of the deformation ability is observed[13].

When an oriented and annealed partially crystalline high molecular weight material (*Figure 1b*) is subjected to a second drawing, conformational changes related to the complete extension (at moderate stresses) of the macrochains in the amorphous regions is effected along the direction of the external strain. Further drawing could result in the destruction of the crystallites by chain defolding and alignment in the draw direction. Such a conformational transition has already been proved for PET[14], PA-6[15], and PBT[16]. The structure created as a result of such mechanical treatment is shown schematically in *Figure 1c*.

All these changes in highly oriented linear polycondensates lead to further perfection of the crystallites of extended macrochains and correspondingly to a small increase in the density of the crystalline regions (ρ_c) and the density difference ($\Delta\rho$) between the crystalline and amorphous regions. For this reason a slight rise of the overall scattering power of SAXS is quite probable in comparison to that of unannealed highly oriented ($\lambda=15$–20) samples.

The final morphological structure of highly oriented polycondensates illustrated in *Figure 1d* is similar to that of polymers obtained from liquid crystalline mesophases (parallel alignment of the macrochains along the fibril axis). It is quite natural to expect that a polymer with such supermolecular structure should be characterized by very good mechanical properties due to the great number of chains bearing the external mechanical strain and to the presence of strong molecular interactions.

In view of the practical applications of polycondensates with improved mechanical properties, evidence should be provided about the extent to which the above discussed processes actually occur.

SAXS curves of samples with different draw ratios ($\lambda=5$ and $\lambda=20$) are shown in *Figure 2*. It is seen that five-fold drawing (*Figure 2a*) does not lead to the appearance of a SAXS maximum. This is an experimental indication of the absence of alternating regions with a substantial density difference in the structure of these samples. It can be concluded from this observation that the material consists of more or less extended chains, building up a predominantly amorphous phase embedding a large number (but small in size) of defective crystallites (*Figure 1a*)[17]. WAXS studies of these samples confirm this conclusion (*Figure 3a*).

Thermal treatment of this material ($T_a=260°C$) leads to considerable structural changes, as indicated by the change in the trend of the curve shown in *Figure 2b*. This experimental evidence of the structural changes is presented in *Figure 1b*. The simultaneous occurrence of crystallization and relaxation processes during thermal treatment leads to formation of alternating crystalline

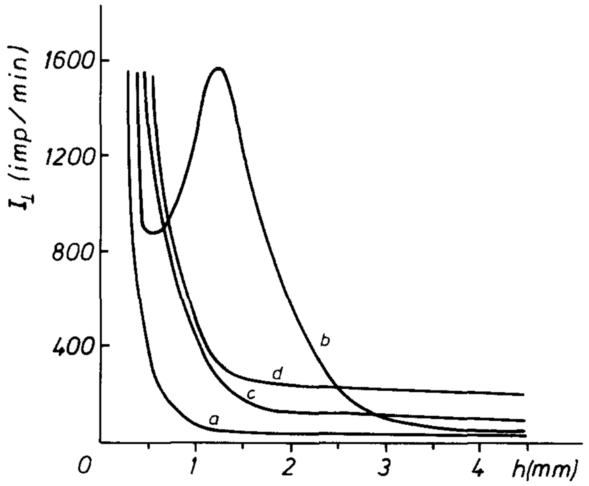

Figure 2 SAXS curves of a drawn PET bristle. (a) $\lambda=5$, unannealed; (b) $\lambda=5$, annealed at 260°C for 6 h; (c) $\lambda=20$, unannealed; (d) $\lambda=20$, annealed at 260°C for 2 h

and amorphous regions; perfection of the crystallites resulting in a significant rise of ρ_c and subsequently of $\Delta\rho$; and appearance of a long spacing, L. The much more perfect crystalline structure of these samples is confirmed by their WAXS patterns presented in *Figure 3b*.

The absence of a SAXS maximum in the samples with $\lambda=20$ (*Figure 2c*) is an indication that the second drawing at room temperature causes the disappearance of the alternating structure as well as a partial destruction of the crystallites through defolding and extension of the chains in the draw direction, as shown in *Figure 1c*. The slight shift of the SAXS curve to higher intensities suggests a more perfect structure of the crystallites built up mainly by extended chains in comparison with the small and more defective ones built up by folded chains in the case of samples with $\lambda=5$ (*Figure 1a*). The WAXS patterns of the samples with $\lambda=20$ (*Figure 3c*) are another confirmation of the more perfect crystalline structure of this material (compare *Figures 3a* and *3b*).

It is seen in *Figure 2d*, which shows the SAXS curve

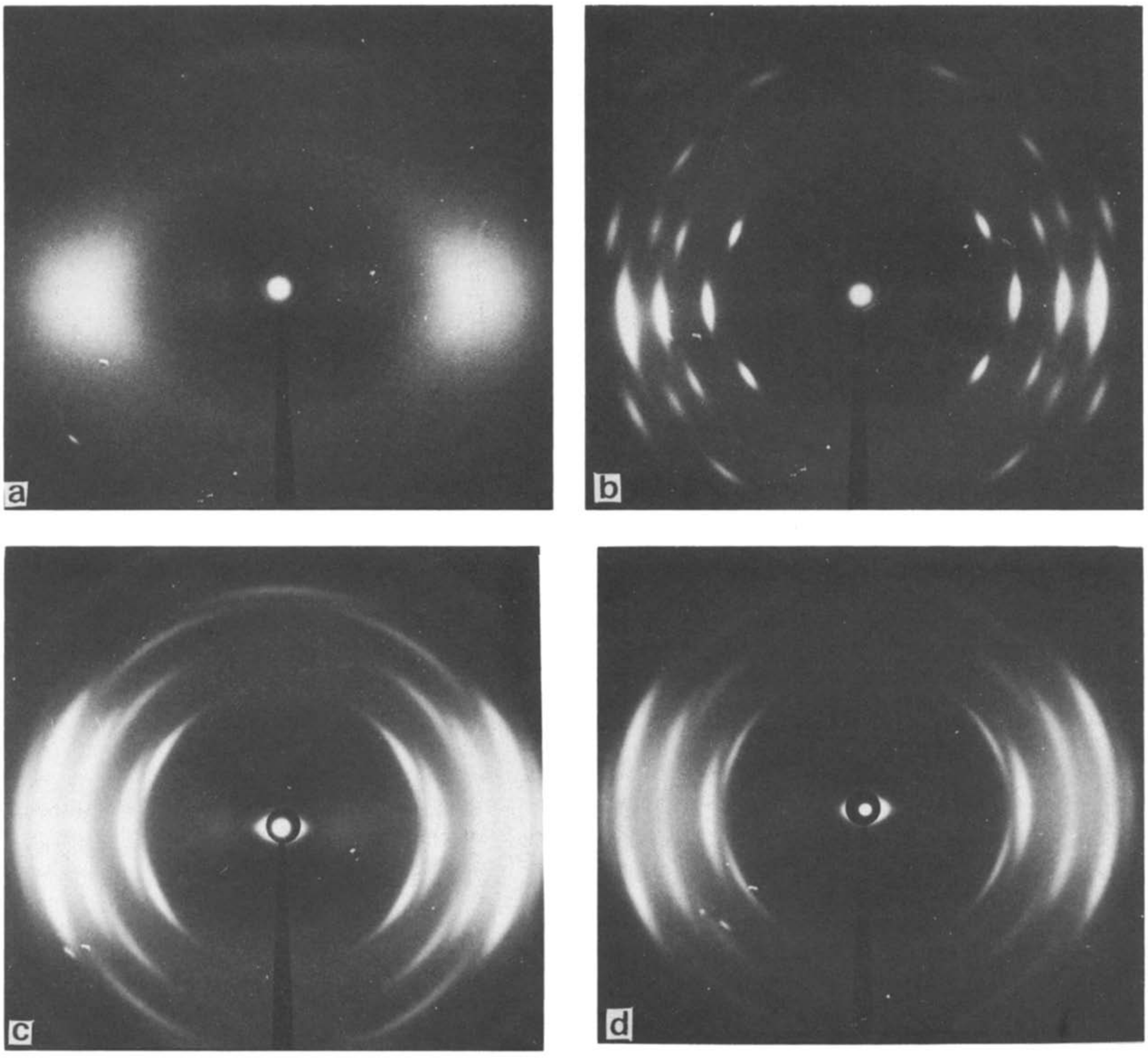

Figure 3 WAXS patterns of a drawn PET bristle: (a) $\lambda=5$, unannealed; (b) $\lambda=5$, annealed at 260°C; (c) $\lambda=20$, unannealed after the second drawing; (d) $\lambda=20$, annealed at 260°C. (Samples a and b are about 0.5 mm thick, exposed for 6 h; samples c and d are about 0.3 mm thick, exposed for 14 h)

Table 1 Mechanical tests of drawn PET bristles annealed under constant strain

		$\lambda=5$, annealed for 6 h			$\lambda=20$, annealed for 2 h		
Sample no.	T_a (°C)	σ_b (GPa)	E (GPa)	ε_b (%)	σ_b (GPa)	E (GPa)	ε_b (%)
1	unannealed	0.22	9.3	61	0.51	13.8	17
2	200	0.26	11.5	38	0.60	18.6	16
3	260	0.14	6.5	320	0.57	16.7	18

of a sample with $\lambda=20$ annealed at 260°C, that in this case, too, a SAXS maximum is not registered. This fact is an experimental confirmation of the assumption that due to the extremely low molecular mobility in a highly oriented polymer system with very strong intermolecular bonds and high energy of the molecular interactions, the occurrence of physical (crystallization and mostly relaxation) processes is strongly hampered. The insolubility of this material (in a phenol–tetrachloroethane mixture, 1:1 by weight, at 140°C (ref. 18)) is an indirect proof of the creation of dense packing with strong molecular interactions.

The slight shift toward higher intensities of the SAXS curve (without the appearance of a maximum) of the twenty-fold drawn samples annealed at 260°C (*Figure 2d*) is an indication of the increase of the sample density as a result of perfection of the structures, mostly of the crystallites. This conclusion is also supported by the WAXS patterns of the material (*Figure 3d*).

The results of the mechanical tests of samples with different draw ratios ($\lambda=5$ or 20) are presented in *Table 1*. They are further experimental proof of the difference in the morphological structures of both materials. It is seen that the samples with $\lambda=5$ annealed at 260°C for 6 h show an extremely high deformation ability ($\varepsilon_b=320\%$, *Table 1*, sample 3). The latter is an indication that, under these conditions, the chemical reactions presented in *Figure 1b* have taken place with a subsequent rise in the molecular weight. Taking into account that the five-fold drawn samples are subjected to a second drawing at room temperature (after annealing at 240°C), the total draw ratio amounts to $\lambda=20$. It is seen in *Table 1* that the tensile strength and elasticity modulus of the samples with $\lambda=20$ are almost twice as high as those of the samples wth $\lambda=5$ ($\sigma_b=0.51$ GPa and $E=13.8$ GPa against $\sigma_b=0.22$ GPa and $E=9.2$ *GPa, Table 1*, samples 1). After annealing at $T_a=200$°C the samples with $\lambda=20$ have $E=18.6$ GPa and $\sigma_b=0.6$ GPa. These parameters become slightly lower than annealing at 260°C, but their values are three times (E) and four times (σ_b) higher than those of the samples with $\lambda=5$ annealed at the same temperature (*Table 1*, samples 3).

These substantial differences in the mechanical properties of both materials are mainly due to the relatively greater number of chains under stress bearing the external strain, as well as to the strong molecular interactions in the highly oriented material. This statement is also supported by the fact that the samples with $\lambda=20$ show a rather low and constant elongation at break (16–18%), regardless of the annealing temperature in contrast to the case of $\lambda=5$ ($\varepsilon_b=61$–320%).

The experimental data discussed above represent a serious proof of the conformational transitions and chemical changes illustrated in *Figure 1* for polycondensates subjected to mechanical (orientational) and thermal treatment. All these processes contribute to the formation as well as to the perfection of the structure of highly oriented polycondensation materials. Such a structure results in improved mechanical properties as compared with those of commercial polymers with the same chemical composition.

Taking into account the similarity in the specificity of condensation polymers, it should be expected that the approaches leading to high performance PET described in the present study should apply also to other polymers of this class. Studies aiming to check this assumption on polyamides are in progress.

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