Influence of thermal history on the mechanical properties of thermotropic poly(triethylene glycol p,p'-bibenzoate)

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Summary

The influence of thermal history on the mechanical properties of thermotropic poly(triethylene glycol p,p'-bibenzoate) has been studied. The mechanical parameters of three samples of this polyester with different thermal histories have been determined at two deformation rates (1 and 10 cm/min) and two drawing temperatures (23 and 50°C), showing the influence of the thermal and mechanical histories on the stress-strain plots. The phase state and the degree of crystallinity of the samples also affect the mechanical parameters (Young modulus, yield stress and deformation at break).

Introduction

Thermotropic behaviour has been observed in many polymers that contain rigid-rod units alternating regularly with relatively flexible spacer units. Several papers have been published by us concerning liquid crystalline polymers, LCP´s, derived from bibenzoic acid and oxyethylene diols (1-6). In this work, attention is focused on the mechanical properties of poly(triethylene glycol p,p´-bibenzoate) (PTEB), with the structural formula

$$\left[OC-\langle\!\langle\bigcirc\rangle\!\rangle\!-\!\langle\!\langle\bigcirc\rangle\!\rangle-CO-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O \right]_n$$
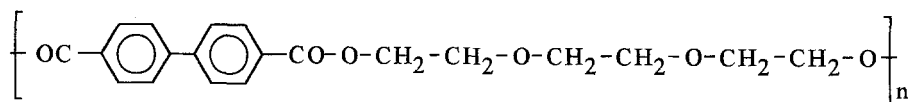
The study of macroscopic properties in flexible mesomorphic polymers is of great importance for potential technological applications of these polymers. The best known commercially are lyotropic polymers. Typical values of the tensile parameters of these materials are given in several works (7). However, mechanical properties of thermotropic polymers are less explored.

The effects on the modulus, E, on going through the glass transition region have already been discussed (8). The yield stress, σ_Y, decreases as temperature increases and the deformation at yield, ϵ_Y, generally decreases with an increase in temperature for amorphous materials. The opposite effect has been observed in some semicrystalline polymers (9). In

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addition to this, the elongation at break, λ_B, generally decreases for rigid polymers as the rate of testing increases.

The aim of this paper is to present and discuss relevant results on stress-strain behaviour referred to samples of PTEB with different thermal histories, and analyze the effect of the strain rate and the drawing temperature.

Experimental

The polyester investigated has been synthesized by melt transesterification of the diethyl ester of *p,p´*-bibenzoic acid and triethylene glycol, using isopropyl titanate as catalyst. The polymer was purified by precipitating into methanol the solution in chloroform. The value of the intrinsic viscosity, measured at 25°C in chloroform, is 1.15 dL/g. The thermal characterization was made with a Perkin Elmer DSC7 calorimeter, and X-ray diffraction patterns were taken with a Philips X-ray diffractometer in the 2θ range between 3° and 36°, using Ni-filtered CuKα radiation.

In order to prepare specimens for stress-strain tests, the polymer was placed in a Collin press fitted with smooth polished plates and hot pressed at 1 MPa and 150°C for 1 min. The cooling process was carried out by quenching the molten polymer with water to room temperature under the same pressure (sample PTEB-Q). Part of this film was annealed at 55°C in a thermostatic bath for five days (PTEB-55) and another one was left at room temperature, RT, for about 4 months (PTEB-RT).

Dumbbell specimens for the drawing process were cut with a standardized die and ink marked at 2 mm intervals. The actual draw ratio, λ, was determined from the displacement of the parallel marks in the homogeneously stretched portion of the drawn specimen.

An Instron box furnace was used to provide an isothermal test environment accurate to ± 1°C. Tests were performed at two drawing temperatures, T_d: ambient conditions (around 23°C) and 50°C. Two deformation rates, v_d, (crosshead speeds) were used in this study: 1 and 10 cm/min. For each temperature and deformation rate, three tests were performed and mean values for the mechanical parameters obtained. The stress and modulus were calculated dividing the force by the initial section. The breaking stress was calculated with the final section.

An Ehringhaus compensator attached to a polarizing microscope (Amplival Pol) was used to measure the optical retardation of the stretched specimens. The birefringence, Δn, was obtained dividing the optical retardation by the thickness.

Results and discussion

The morphology and properties of a semicrystalline polymer are largely determined by the initial rate of cooling or by posterior annealing treatment. Ageing or slow annealing processes may also occur below or above the glass transition temperature, T_g, over long periods of time. When dealing with liquid crystal polymers, control of thermal history is very important since this can affect the degree of order and/or the phase state, and hence the

mechanical properties of the material.

In the case of the PTEB-Q film, obtained after melting at 150°C and quenching to room temperature, the DSC traces show only the glass transition ($\sim$ 20°C) and an endotherm at 114°C, corresponding to the isotropization, T_i, of the mesophase (2). This mesophase is stable at room temperature for several days, and thus PTEB-Q exhibits a liquid crystalline state. The α relaxation associated with the T_g has also been reported by dynamic mechanical analysis (4). X-ray photographs revealed diffractions corresponding to the length of the smectic layer (2). The diffraction pattern at wide angles (figure 1) of this quenched sample shows only a very broad peak, similar to that of amorphous polymers.

Stress-strain curves corresponding to room temperature drawing of PTEB-Q show homogeneous deformation, similarly to amorphous polymers (8), and the stress values are low (figure 2). The yield stress defines the elastic-plastic transition. When a clear load maximum is not observed the yield stress is obtained by intersecting two tangent lines, below and above the yield point in the stress-strain plot. Otherwise, the yield stress is defined as the first maximum on the stress curve. Clearly, different experimental conditions, such as temperature and strain rate, may lead to curves requiring a different definition of yield in the same material (8,9).

Table 1. Average values[a] of the modulus, yield stress, yield deformation, deformation at break and birefringence (draw ratios are indicated in parentheses) for the three samples of PTEB at different temperatures and deformation rates.

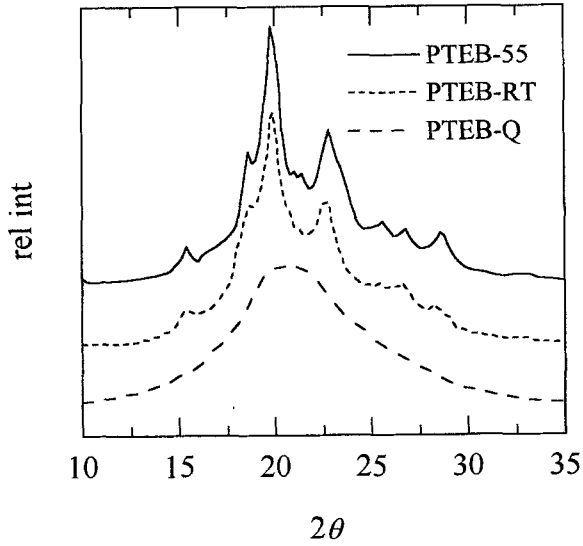| Sample	T_d (°C)	v_d (cm/min)	E (MPa)	σ_Y (MPa)	ϵ_Y (%)	ϵ_B (%)	Δn (λ)
PTEB-Q	23	1	9	2.8	31	1200	0.328 (7)
		10	9	3.2	36	1150	0.332 (7)
	50	1	2	--	--	1100	0.304 (8)
		10	4	--	--	1350	0.306 (10)
PTEB-RT	23	1	45	9	21	1050	0.344 (7.5)
		10	60	11	45	950	0.307 (7.5)
PTEB-55	23	1	470	28	12	30	--
		10	430	25	9	20	--
	50	1	250	14	9	450	0.222 (5.5)
		10	150	12	12	450	0.282 (5.5)

[a]Average of three tests

Fig. 1. X-ray diffractograms of the three samples of PTEB with different thermal treatment.
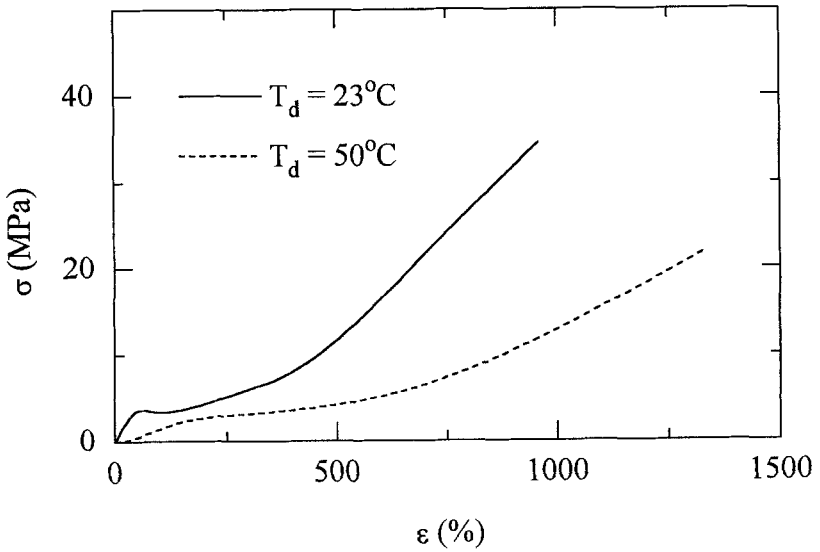

Fig. 2. Stress-deformation curves corresponding to sample PTEB-Q stretched at 10 cm/min at the indicated deformation temperatures.

A considerable change in the properties is observed (figure 3) when the sample is left at room temperature for a long time (PTEB-RT sample). At temperatures between T_g and T_i, the mesophase of PTEB exhibits a transformation to a crystalline state. This transformation is very slow at any temperature and particularly at ambient conditions, as the temperature is then only a few degrees above T_g. After stretching this annealed sample at room temperature, both the yield stress and the Young modulus increase relative to sample PTEB-Q, and the drawing process takes place through necking even though T_d is higher than T_g. In general, a slight increase in the values of different parameters (yield stress, modulus, strain hardening) with the drawing rate is observed. This is due to the existence of some crystallinity in these specimens, as revealed by the X-ray diffraction pattern shown in figure 1. A crystallinity of 0.38 ± 0.05 is estimated from the diffractogram corresponding to this sample.

The influence of the annealing process at higher temperatures was also studied. A sample was annealed at 55°C for 5 days (PTEB-55 sample) and significant changes in the properties were observed. The specimens were also stretched at 1 and 10 cm/min, but the behaviour was similar in both cases. Typical stress-strain plots are shown in figure 4 for samples stretched at 23°C and 50°C. The X-ray results (figure 1) indicate the presence of a slightly higher degree of crystallinity in this sample (0.42 ± 0.05), and a clear effect on the mechanical properties is observed: the Young modulus increases considerably (Table 1) and the elongations at break are very small ($\lambda_B = 1.20$) at room temperature, as observed for semicrystalline polymers. By increasing the temperature of the drawing process, it is possible to increase the elongation at break up to $\lambda_B = 6$ but the values of modulus decrease, although they remain higher than those of Q and RT samples.

From these results, it can be deduced that the mechanical parameters of PTEB-RT are closer to those of the quenched sample, despite the fact that the former sample displays a degree of crystallinity very close to that for sample PTEB-55. Linear relations between yield stress and crystallinity level or crystallite thickness have been proposed for polyethylene (12). It is evident from Table 1 that such a direct relation with crystallinity does not hold for PTEB. No data is available concerning crystallite thickness for these samples, but a previous study on similar samples (5) has shown that isothermal crystallization of PTEB at high temperatures produces considerably thicker crystals than those obtained at room temperature. This may be the reason for the low values obtained for the yield stress (and modulus) in sample PTEB-RT compared with those of the sample crystallized at 55°C.

Regarding the birefringence (last column of Table 1), relatively high values in relation to other polymers (13) were obtained for all the PTEB samples. As usual, lower values are observed for higher deformation temperatures. Moreover, it is found that the maximum of the birefringence is attained at draw ratios as low as 2. It is assumed that deformation of the polymer involves the motion of the chain or part of the chain over potential energy barriers. This motion produces alignment in the amorphous and crystalline structures leading to a highly oriented polymeric material. This orientation is accompanied by the development of
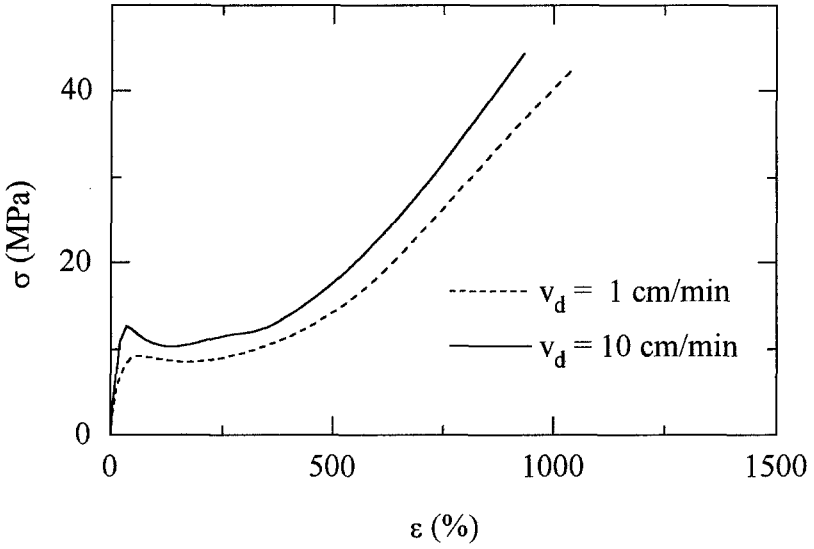
Fig. 3. Stress-deformation curves corresponding to sample PTEB-RT stretched at 23°C at the indicated deformation rates.
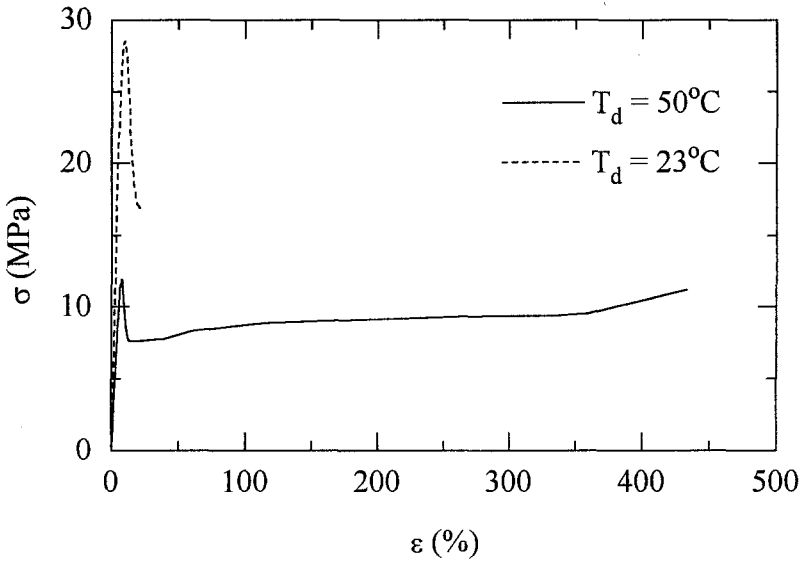

Fig. 4. Stress-deformation curves corresponding to sample PTEB-55 stretched at 1 cm/min at the indicated deformation temperatures.

birefringence and of enhanced strength properties in the direction of the applied stress. The high values obtained in this work are indicative of a great facility to produce ordered structures (and large draw ratios) in PTEB.

In conclusion, a common feature of the three PTEB samples is that the Young modulus and the yield stress decrease as the drawing temperature increases, whereas they do not change significantly with the strain rate. The deformation at break increases with the drawing temperature, while the final birefringence decreases. Regarding the influence of the thermal history, the main conclusion is that the behaviour of PTEB-RT is intermediate between the other two samples, showing the advantage of a considerable increase in the modulus, without much decrease in the elongation at break, in relation to sample PTEB-Q.

Acknowledgment

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