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A comparison of the effect of annealing on two liquid crystalline polymers

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The mechanical properties of aligned tapes and monofilaments of a random copolyester, containing 17.5% of biphenol (COTBP), were investigated using macroscopic and X-ray techniques on both unannealed and annealed samples. The results were compared with similar studies of a random copolyester of hydroxybenzoic acid and hydroxynaphthoic acid (BNA/HNA). Whereas in the HBA/HNA copolymer on the scale observed by X-ray diffraction, the chain is sinuous, with an increasing sinuosity upon annealing, the COTBP is straight and no effect is seen upon annealing. The macroscopic moduli of both polymers increases with annealing. This is attributed to an increase in the shear modulus caused by an increase in the packing density of the chains. © 1997 Elsevier Science Ltd.

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INTRODUCTION

In previous articles[1,2] we reported the effects of annealing on random co-polyesters of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) (composition ratio 0.73:0.27). Highly oriented fibres of this polymer can be produced, but since perfect alignment cannot be obtained the tensile modulus is greatly affected by the shear modulus. Annealing improves the packing between chains, leading to an increase in crystallinity[3], and hence to an increase in both tensile and shear moduli. However on a small scale (that probed by X-ray diffraction) the sinuosity of the chains increases and leads to a reduction in both the orientation and modulus of an X-ray unit.

This article describes measurements of both the macroscopic tensile and shear modulus and the X-ray modulus of a similar copolyester COTBP. This is a four component system made up of 60% HBA, 5% HNA, 17.5% terephthalic acid (TA) and 17.5% biphenyldiol (BP). It differs from HBA/HNA in that there is a much lower quantity of naphthalene residues, the ester groups are not all in the same orientation (as they are in HBA/HNA) and the inclusion of the straight biphenyl residues.

EXPERIMENTAL

Materials

Samples of COTBP were supplied by Hoechst Celanese. They were supplied both as tapes of thickness about 40 μm and width 5 mm, and as monofilaments of diameter 1 mm. The tapes were used for the X-ray measurements and (cut to 2 mm width) for the tensile measurements, while the monofilaments were used for the shear measurements. Annealed samples were prepared by holding under zero tension in nitrogen for 5 h at a temperature of 292°C, this being 3°C below the initial melting temperature as measured by DSC.

Macroscopic measurements

Dynamic tensile and shear measurements were made in similar fashion to those reported on HBA/HBA[2].

Tensile measurements were made on 2 mm tapes using a non-resonance dynamic mechanical modulus apparatus constructed in our laboratory and described previously[1]. The dynamic strain was fixed at 0.05% and the frequency at 1 Hz. A constant deadload of 130 MPa was applied and data collected over the temperature range -100 to 100°C. As before, the data were corrected to zero deadload by measuring the deadload dependence of the tensile modulus at certain temperatures.

Shear measurements were made on a 1 mm monofilament using an inverted torsion pendulum apparatus as described previously[4]. The data were corrected to zero static stress to take into account the axial tensile stress exerted on the monofilaments by the deadload, and the data adjusted to 1 Hz (the same frequency as used in the tensile measurements) using the expression[5]:

$$\frac{\Delta G(\omega)}{\Delta \ln\omega} = \frac{2}{\pi} G''(\omega)$$

X-ray measurements

Measurements of the chain modulus of the polymer were obtained by measuring the shift in diffraction angle of the strong meridional reflection at $2\theta_b = 43°$ (with Cu Kα radiation) when a stress was applied to the sample (a 5 mm tape, 40 mm in length). A detailed description of the apparatus and method are given elsewhere[6].

The position of this meridional reflection was also measured.

A measure of the orientation within the tape was made by measuring the profile of the equatorial reflection at $2\theta_b = 20°$ using a Huber diffractometer. Assuming that the intensity of diffraction at a particular angle is proportional to the number of chains at that inclination to the tape axis, an estimate of the orientation as $<\sin^2\theta>$ was obtained.

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RESULTS AND DISCUSSION

Macroscopic mechanical properties

The tensile modulus as a function of temperature of the unannealed and annealed COTBP samples are shown in *Figure 1*. As with previous results, the modulus shows a steady decrease with increasing temperature. Annealing leads to an increase in the modulus at all temperatures, to a greater degree than was found with HBA/HNA. A similar trend is seen in the shear moduli data shown in *Figure 2*. HBA/HBA[2] showed similar trends in tensile and shear moduli.

X-ray data

The chain modulus as a function of temperature as measured by X-ray techniques is shown in *Figure 3*. The accuracy of these results is estimated to be ±15 Gpa which arises from the irregularity of the tape thickness and slight misalignment of the tape in the clamps giving rise to an inhomogeneity of the stress along the tape. There is little difference between the unannealed and annealed samples, in contrast to HBA/HNA where a decrease in X-ray modulus upon annealing was seen. This reduction in modulus was explained by an increase in the sinuosity of the chain upon annealing. The absence of any effect of annealing seen in COTBP suggests that there is little reorganisation of the structure at a scale seen by the X-ray diffraction (about 10 units[6]).

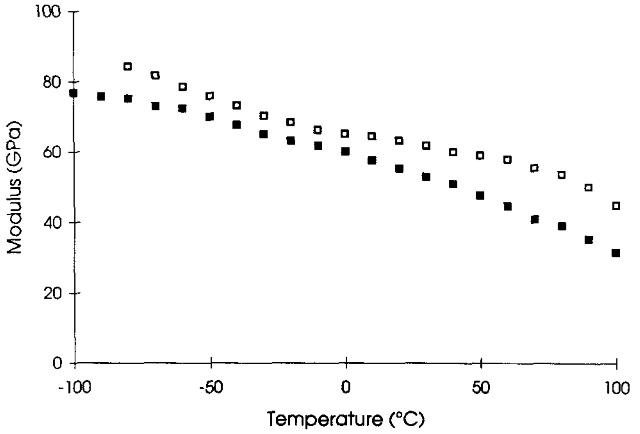

Figure 1 Tensile modulus, corrected to zero shear stress, as a function of temperature for COTBP; filled symbols unannealed, open symbols annealed

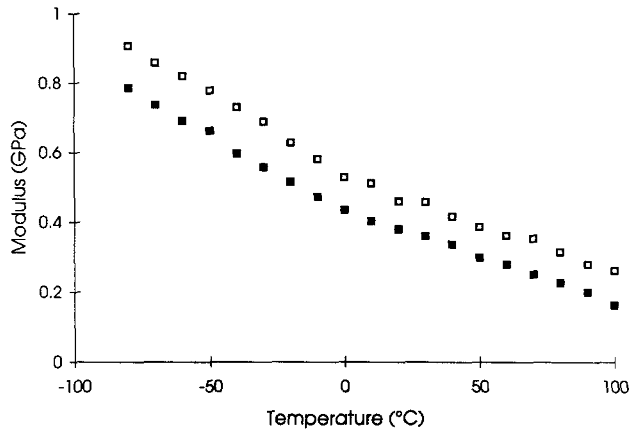

Figure 2 Shear modulus as a function of temperature. Symbols as for *Figure 1*

The peak positions are shown in *Table 1*, where they are compared to similar data for HBA/HNA[2]. Whereas for HBA/HNA annealing leads to an increase in the peak position, which corresponds to a decrease in the repeat spacing giving rise to the reflection, no such change is observed in COTBP.

Measurements of equatorial orientation are given in *Table 2*, where they are compared to similar data for HBA/HNA[2]. The orientation of the COTBP is similar to that of HBA/HNA, however annealing does not affect the orientation for COTBP while in HBA/HNA it is improved.

Aggregate modelling

As was successful in the past, the data were analysed in terms of the aggregate model[7]. The sample is considered to be composed of an aggregate of anisotropic units, with the properties of the whole sample being obtained from a summation of contributions from the constituent units. For highly oriented systems the model can be expressed as a relationship between the tensile (E) and shear (G) moduli of the aggregate:

$$\frac{1}{E}=\frac{1}{E_u}+\frac{1}{G}<\sin^2\theta>$$

where E_u is the tensile modulus of the units making up the aggregate and θ the angle a unit makes with the symmetry axis. Angle brackets indicate an average taken over all units in the aggregate.

This model can be applied to the data in two ways. *Figure 4* is the result of plotting $1/E$ against $1/G$ using the mechanical data of *Figure 1* and *Figure 2*. Both sets of data fall on the same line which suggests that there is little change in either the modulus (E_u) or the orientation ($\langle\sin^2\theta\rangle$) of the fundamental units making up the aggregate. Although the points lie on the same line, at any value of $1/G$ the results for the unannealed and annealed samples correspond to different temperatures. We therefore conclude that the increase in shear modulus reported in *Figure 2* occurs at a constant value of the unit tensile modulus. A similar result

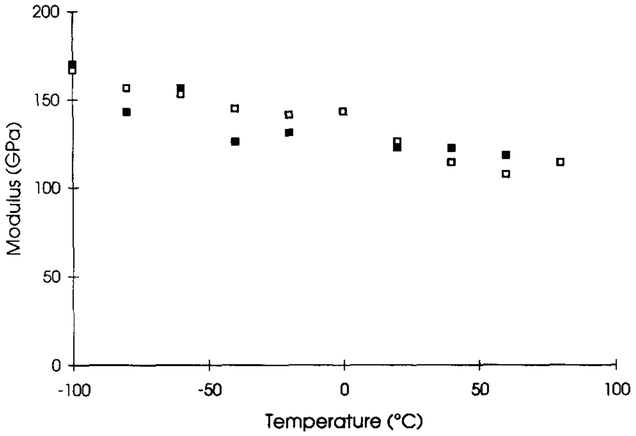

Figure 3 X-ray modulus as a function of temperature. Symbols as for *Figure 1*

Table 1 Position of the major meridional X-ray diffraction peak (°$2\theta_b$) for COTBP (this work) and HBA/HNA[2]

	COTBP	HBA/HNA
Unannealed	43.1	43.4
Annealed	43.0	43.8

Table 2 Orientation parameters expressed as $\langle \sin^2\theta \rangle$ measured from the equatorial X-ray reflection and calculated using the aggregate model. The 'constituent units' correspond to the plot in *Figure 4* and the 'X-ray units' to the plot in *Figure 5*. Data for HBA/HNA is from ref. [2]

	COTBP		HBA/HNA	
	Unannealed	Annealed	Unannealed	Annealed
X-ray equatorial	0.0047	0.0046	0.0056	0.0049
Aggregate: constituent units	0.0042		0.0100	
Aggregate: X-ray units	0.0045		0.0064	0.0044

was obtained for the HBA/HNA copolymer. The extrapolated line to the $1/E$ axis predicts a tensile modulus for the aggregate units of 180 GPa, which is similar to the 200 GPa reported for HBA/HNA.

It is also possible to associate the aggregate 'units' not with the fundamental aggregate units but with those units of a size probed by X-ray methods, thus using $E_{\text{x-ray}}$ as E_u in the above equation and plotting $1/E - 1/E_{\text{X-ray}}$ against $1/G$. *Figure 5* is the result of this. The line drawn goes through the origin, thus confirming that the aggregate model is appropriate, but in contrast to the HBA/HNA results there is no difference with annealing. This implies again that there are little structural changes on annealing on a scale observed in the X-ray modulus measurements.

Table 2 includes the orientation parameters obtained from the slopes of aggregate plots such as *Figures 4 and 5*, together with the X-ray orientation results. In HBA/HNA the orientation calculated for the fundamental units is much lower than that for the X-ray units, and there is a decrease in slope for the X-ray units upon annealing. This was explained[2] in terms of the sinuosity of chains within the X-ray units which allows the latter to be better oriented. Annealing increases the sinuosity, leading to an improvement in the orientation of the X-ray units.

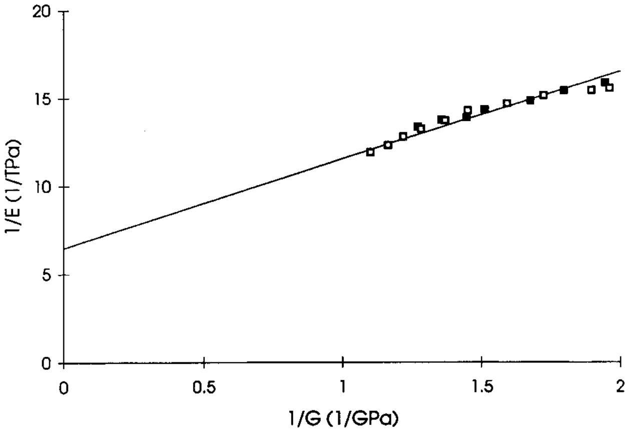

Figure 4 Aggregate model plot using the tensile data of *Figure 1* and the shear data of *Figure 2*. Symbols as for *Figure 1*

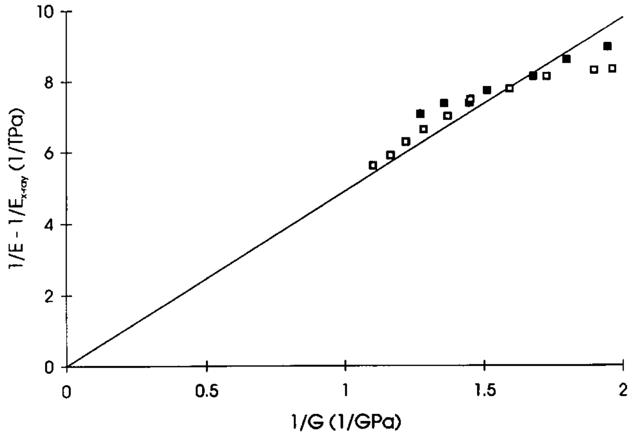

Figure 5 Aggregate model plot associating the X-ray modulus with the tensile modulus of the aggregate units. Symbols as for *Figure 1*

For COTBP the slopes of the two aggregate plots are almost identical. This implies that the degree of orientation of both the fundamental aggregate units and the X-ray units are similar. Thus the orientation within a X-ray unit must be high and the chains parallel; there is no sinuosity on a X-ray scale in COTBP. The orientation results for both polymers are in broad agreement with the experimental X-ray orientation measurements.

X-ray diffraction measurements of crystal size by Hoechst Celanese[8] confirm that the structural changes under annealing are different in these two polymers. Harget and Saw suggested that in HBA/HNA annealing attempts to create a three-dimensional order with the formation of 'organised kinks' which hinder the improvement of both lateral chain order and chain orientation. In COTBP no three-dimensional order is produced nor do any 'organised kinks' form, resulting in straighter chains, which is in agreement with our findings. The straighter chains would be more able to pack laterally which would lead to an increase in the lateral stiffness of the units upon annealing and hence to the more marked increase in the macroscopic mechanical properties observed.

CONCLUSIONS

In the case of HBA/HNA annealing leads to an increase in the sinuosity of the chain on a small scale (that probed by X-ray diffraction). This was observed by a reduction in the X-ray modulus and a decrease in the meridional repeat period. In COTBP however no such change in sinuosity is observed and the X-ray modulus remains unchanged upon annealing.

On a macroscopic scale the effect of annealing is to increase the tensile and shear moduli in both cases. Since the tensile modulus of the fundamental aggregate units remains constant the increase in tensile modulus can therfore be attributed solely to an increase in the shear modulus of the units caused by the improved packing between chains. This effect is greater in COTBP where the chains are straighter.

REFERENCES

1. Troughton, M. J., Davies, G. R. and Ward, I. M., *Polymer*, 1989, **30**, 58.
2. Zhang, W., Nicholson, T. M., Davies, G. R. and Ward, I. M., *Polymer*, 1996, **37**, 2653.
3. Klein, P.G., Nicholson, T. M. and Ward, I. M. to be published.
4. Zhang, H., Davies, G. R. and Ward, I. M., *Polymer*, 1992, **33**, 2651.
5. Alfrey, T., *Mechanical behaviour of High Polymers*. Interscience Publishers, New York, 1948.
6. Troughton, M. J., Unwin, A. P., Davies, G. R. and Ward, I. M., *Polymer*, 1988, **29**, 1389.
7. Ward, I. M., *Mechanical Properties of Solid Polymers*. Wiley, 1983.
8. Harget, P. and Saw, C., Hoechst Celanese, Private communication.