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The effect of branching on the mechanical properties of HBA/HNA copolymer

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The mechanical properties of aligned fibres and monofilaments of random copolyesters of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) with and without the inclusion of a trifunctional branching monomer have been investigated using both macroscopic and X-ray techniques. Results for unbranched samples are in line with previous work while including the branching monomer reduces both the shear and tensile moduli as measured macroscopically. Annealing the samples increases the moduli. On the scale observed by X-ray diffraction the inclusion of branching has little effect whereas annealing increases the sinuosity of the chains and hence reduces the apparent chain modulus determined by X-ray measurements on samples under stress. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Random copolyesters of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) form thermotropic liquid crystalline melts. By melt-spinning at high wind-up speeds highly oriented fibres may be produced[1]. The tensile modulus of such fibres is greatly affected by the shear modulus since the fibres are not perfectly aligned[2]. This paper investigates the effect of adding branching to the polymer by the inclusion of a small amount of a trifunctional group 1,1,1-tris-(4-hydroxyphenyl) ethane (THPE). The effect of annealing the unbranched and branched polymers is also investigated.

EXPERIMENTAL

Materials

Samples of HBA/HNA copolymers were supplied by Hoechst Celanese. The composition details of the two samples studied are given in *Table 1*. Samples were supplied both as oriented fibres $\sim 45\,\mu$m diameter and as granules which were spun at a temperature of 315°C into a water bath to produce oriented monofilaments of 0.9 mm diameter. The fibres were used for the tensile and X-ray measurements and the monofilaments for the shear measurements.

Samples of both fibre and monofilament were also annealed by holding under zero tension in nitrogen for 5 h, the unbranched sample at 265°C, and the branched sample at 262°C. These temperatures were chosen to be 3°C below the initial melting temperatures of the fibres as measured by differential scanning calorimetry. The cross-sections of the samples (required for data analysis) were determined by measuring their density, weight and length.

Dynamic tensile measurements

Tensile measurements were made on single fibre samples using a non-resonance dynamic mechanical modulus apparatus constructed in our laboratory and described previously[2]. The dynamic strain was fixed at 0.05% and the frequency at 1 Hz. A constant deadload of 123 MPa for the unbranched and 130 MPa for the branched sample was applied and data collected over the temperature range −100 to 100°C.

At certain temperatures the deadload was varied to enable the static stress dependence of the compliance to be calculated. As in previous work[3] the compliance as a function of deadload was modelled by an exponential relationship

$$J = A + B\exp(-C\sigma) \tag{1}$$

where J is the compliance and σ the stress. A, B and C were fitted using a least-squares method. The zero static stress compliance was then $J_0 = A + B$. At each temperature this enabled a static stress correction factor to be calculated. Correction factors at other temperatures were obtained by interpolation and these were then used to correct the tensile data to zero deadload.

Dynamic shear measurements

Shear measurements were made on an inverted torsion pendulum apparatus as used in previous work[4]. The data were corrected to zero static stress by subtracting the axial tensile stress exerted on the monofilaments. Varying periods of around 3 s were obtained and so the data were adjusted to the same frequency as the tensile measurements using the expression[5]:

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

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Table 1 Composition of studied polymers

	%HBA	%HNA	%THPE
Unbranched	73.0	27.0	0.0
Branched	72.8	26.8	0.4

X-ray modulus 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 detailed description of the apparatus and method are given elsewhere[6]. Bundles of about 30 fibres, 40 mm in length, were clamped in an extensometer and mounted in the X-ray beam at the correct angle to observe this reflection. They were subjected to a series of loads, applied in an alternating high–low sequence, with each load being applied for 30 s while a peak profile was collected, and the sample allowed to relax for 6 min between application of loads. For each load the shift in peak position from that at zero load was calculated, and thus an X-ray modulus calculated. The cross-sectional area of the sample required for this calculation was obtained by weighing the sample; however, it is likely that this will be an overestimate since it is not certain that all the fibres were experiencing the applied stress. This will lead to an underestimate of the calculated modulus.

X-ray orientation measurements

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

The position of the meridional reflection used for the modulus measurements was also measured.

RESULTS AND DISCUSSION

Macroscopic mechanical properties

The tensile moduli of the four samples, corrected to zero shear stress as discussed above, are shown in *Figure 1*. The results for the unbranched samples are similar to those reported earlier[2] with a steady decrease in modulus with increasing temperature. Annealing the sample increases the modulus at all temperatures, with the effect being greater at higher temperatures. The branched sample has a significantly decreased tensile modulus at all temperatures, this effect being more marked at the lower temperatures. Plots of tan δ *versus* temperature were similar for all samples.

A similar series of results can be seen in the shear moduli data shown in *Figure 2*, and again the unbranched results are comparable with previous work. The effects of branching and annealing are the same as those observed in the tensile data.

X-ray data

The X-ray moduli calculated are shown in *Figure 3*. Here the differences between the unbranched and the branched samples are much smaller than the differences between the unannealed and annealed samples. This is to be expected because the X-ray data result from measurements of scattering from chain segments of about 10 units[6]. The properties of such units would be expected to be little affected by the inclusion of a low percentage of branched monomers. In contrast to the mechanical data, annealing reduces the moduli, this effect being much more marked than that due to differences in branching.

Meridional peak positions and orientation parameters measured by X-ray diffraction are shown in *Table 2*. Annealing leads to an increase in the peak position and

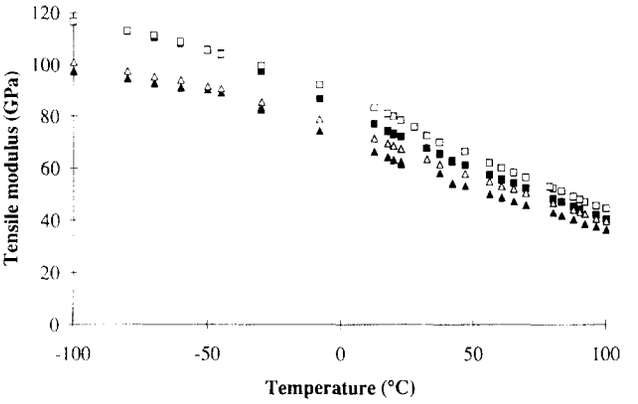

Figure 1 Tensile modulus, corrected to zero shear stress, as a function of temperature. □, Unbranched; △, branched. Filled symbols, unannealed; open symbols, annealed

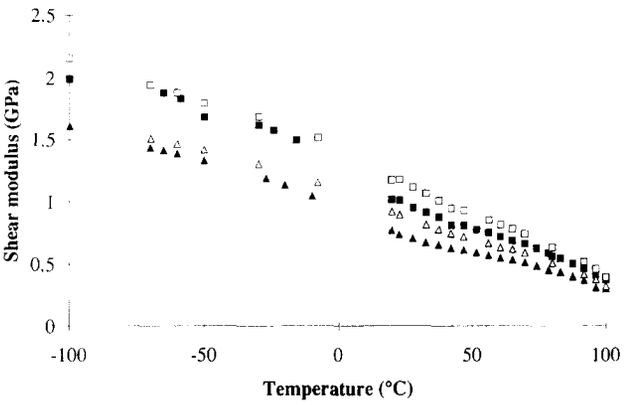

Figure 2 Shear modulus as a function of temperature. Symbols as for *Figure 1*

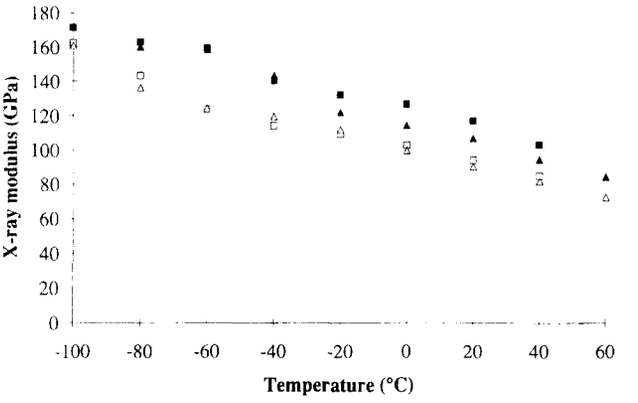

Figure 3 X-ray modulus as a function of temperature. Symbols as for *Figure 1*

Table 2 X-ray meridional peak positions and equatorial orientation parameters

	Peak position ($°2\theta_b$)		Orientation ($\langle\sin^2\theta\rangle$)	
	Unannealed	Annealed	Unannealed	Annealed
Unbranched	43.40	43.77	0.0056	0.0049
Branched	43.65	43.85	0.0072	0.0057

hence a decrease in the repeat spacing giving rise to the reflection. The orientation of the equatorial reflection is improved upon annealing and worsened by the addition of branching.

Aggregate modelling

As has been 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, the properties of the whole sample being obtained from a summation of contributions from the constituent units. For highly oriented systems the model simplifies to give a relationship between the tensile (E_a) and shear (G_a) moduli of the aggregate:

$$\frac{1}{E_a} = \frac{1}{E_u} + \frac{1}{G_a}\langle\sin^2\theta\rangle \qquad (3)$$

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

Figure 4 shows the mechanical data of *Figure 1* and *Figure 2* replotted in terms of the above equation. All four sets of data fall on the same line which suggests that there is little difference in either the properties (E_u) or the orientation ($\langle\sin^2\theta\rangle$) of the units making up the aggregate. The extrapolated line to the $1/G = 0$ axis predicts a modulus for the aggregate units of about 200 GPa which is not unreasonable.

It is also possible to model the sample as being composed of units of the size measured by X-rays. *Figure 5* is the result of associating the X-ray modulus with E_u in equation (3) and plotting $1/E - 1/E_{x\text{-ray}}$ *versus* $1/G$; E and G are the mechanical tensile and shear moduli. Here a difference between the unannealed and annealed samples is apparent. Both give straight lines passing through the origin (which confirms that the aggregate model is appropriate in this situation) but the annealed data show a lower slope and hence a greater degree of orientation. There is little difference between the unbranched and branched results.

This can be modelled by considering the orientations of the aggregate units relative to the sample[8]. This is illustrated in *Figure 6* where the aggregate units make an angle θ_U to the sample axis and θ_S to the X-ray unit. The X-ray unit makes an angle θ_X to the sample axis. In terms of the aggregate model plots presented, the slope of *Figure 4* is $\langle\sin^2\theta_U\rangle$ and that of *Figure 5* $\langle\sin^2\theta_X\rangle$. These slopes, calculated from the aggregate model graphs, are given in *Table 3*. The orientations calculated from *Figure 5* which correspond to the orientation of X-ray units follow the same trend as the experimental data of *Table 2*; however, since they are calculated in different ways a quantitative comparison is not possible.

The relationship between these orientation functions may be obtained from the Legendre addition theorem

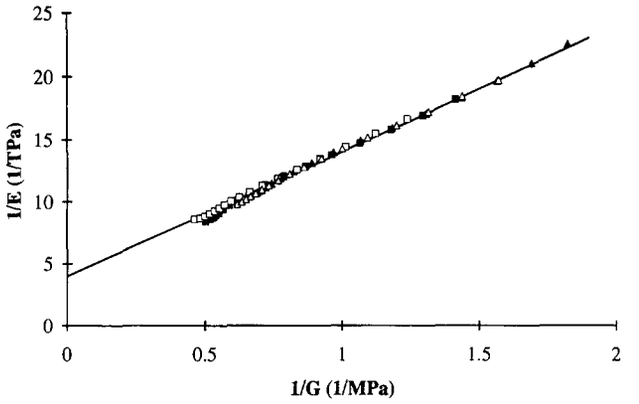

Figure 4 Aggregate model plot using the tensile data of *Figure 1* and the shear data of *Figure 2*. Symbols as for *Figure 1*

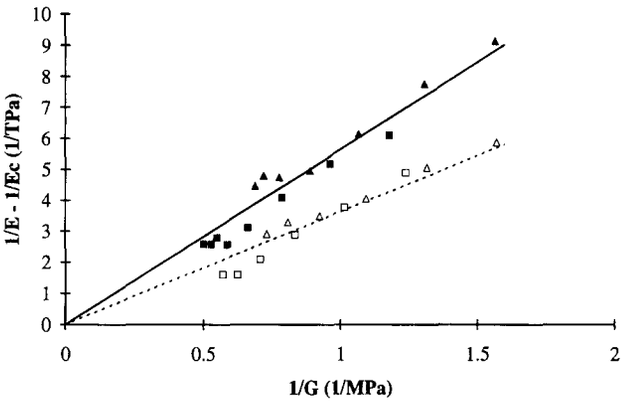

Figure 5 Aggregate model plot using equation (3) in the text, associating the X-ray modulus with the modulus of the aggregate units. Symbols as for *Figure 1*

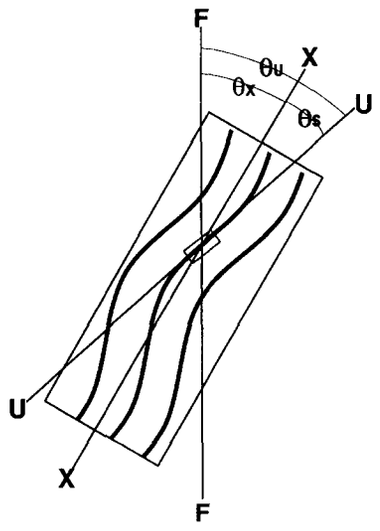

Figure 6 Schematic representation of the orientation of aggregate units relative to X-ray domains and the fibre (from ref. 8). F–F is the sample fibre axis, X–X the axis of an X-ray domain and U–U the orientation of an individual unit

which (for small θ) reduces to:

$$\langle\sin^2\theta_U\rangle = \langle\sin^2\theta_X\rangle\langle\sin^2\theta_S\rangle \qquad (4)$$

Since $\langle\sin^2\theta_U\rangle$ stays constant upon annealing but $\langle\sin^2\theta_X\rangle$ decreases it follows that $\langle\sin^2\theta_S\rangle$ must increase

Table 3 Orientations calculated from the aggregate model graphs (*Figure 4* and *Figure 5*)

	Unannealed	Annealed
Figure 4	0.0100	
Figure 5	0.0064	0.0044

with annealing. This corresponds to an increase in the sinuosity of the chain on a local level (within the X-ray domains). The increase in sinuosity leads to a decrease in the period, which is consistent with the X-ray peak position measurements. It would also be expected that a more sinuous chain would have a lower modulus, as was observed.

CONCLUSIONS

On a small scale (that probed by X-ray diffraction), the introduction of branched monomers has little effect on the properties of the polymer since only a small proportion of polymer units is affected. By contrast, annealing has a greater effect, leading to increased sinuosity of the chains and hence a reduction in orientation and modulus.

On a macroscopic scale, the inclusion of a small amount of branched material leads to a large reduction of the shear modulus and hence of the tensile modulus. This reduction in shear modulus could arise from the branched material preventing the polymer chains from packing as closely. Annealing the samples increases the shear and tensile moduli, again probably because of a change in the packing of the chains.

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