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Elastic modulus of the crystalline regions of *p*-hydroxybenzoic acid/poly(ethylene terephthalate) copolymers

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The elastic modulus (E_l) of the crystalline regions in the direction parallel to the chain axis was measured for *p*-hydroxybenzoic acid (HBA)/poly(ethylene terephthalate) (PET) copolymers by X-ray diffraction. The E_l values are 59 and 105 GPa for HBA/PET 60/40 and 80/20 copolymers, respectively, which are considered to reflect the linearity of the skeletal structure of the chain molecule. The elastic modulus (E_t) of the crystalline regions in the direction perpendicular to the chain axis was 2.1 GPa for both copolymers, which was much smaller than that of polyethylene (~ 4 GPa, where only van der Waals forces act). Though π-electron interaction could be expected, loose and/or disordered lateral packing of the chains leads to the small E_t values of these copolymers.

(Keywords: elastic modulus; crystal structure; liquid crystalline polyesters)

INTRODUCTION

The elastic moduli of polymer crystals provide important information on the molecular conformation and intermolecular forces in the crystal lattice, and of the relation of these to the mechanical properties of polymers. We have been measuring the elastic modulus of the crystalline regions in the direction parallel (E_l) and perpendicular (E_t) to the chain axis for a large number of polymers by X-ray diffraction[1–7]. Examination of the data accumulated so far has led us to be successful in relating the E_l values, i.e. the extensivity of a polymer molecule, to the molecular conformation and the deformation mechanism of a polymer molecule in the crystal lattice[1–6]. The values of E_l for polymers composed of a fully extended planar zigzag conformation, e.g. polyethylene (PE) and poly(vinyl alcohol) (PVA), were found to be 235 and 250 GPa, respectively. Knowing E_l of the crystalline regions of polymers is also of importance in connection with the mechanical properties of polymers, because E_l gives the maximum value for the specimen modulus of a polymer. On the other hand, E_t provides information on the intermolecular force and its anisotropy[7].

Recently, many kinds of wholly aromatic polyesters have been reported to show liquid crystalline state. Thermotropic liquid crystalline polymer chains are easy to orient by stress during an injection/ extrusion process, which leads to the excellent mechanical, thermal, chemical and dimensional stabilities of the materials. The copolyester consisting of *p*-hydroxybenzoic acid (HBA)/poly(ethylene terephthalate) (PET) was the first thermotropic liquid crystalline polymer[8], to be industrialized, and its excellent properties have been recognized.

In this paper, we measured the E_l and E_t values of HBA/PET copolymers by X-ray diffraction, and then investigated the relationships between the mechanical properties, the conformation and the intermolecular interactions. Comparisons were made among HBA/PET copolymer, PET and HBA homopolymers.

EXPERIMENTAL

Liquid crystalline polyesters (LCPs) of HBA/PET copolymer, Rodrun LC-3000 and LC-5000 extruded sheets (thickness = 50 μm) supplied from Unitika Ltd[9], were studied. The copolymer compositions were HBA/PET 60/40 and 80/20, respectively. These LCPs are said to have a less blocky monomer alignment than the conventional LCPs by improving the reaction process[10]. These sheets were annealed at 200°C for 30 min at constant length.

The density of the specimen was measured by a flotation method (carbon tetrachloride–bromoform system) at 30°C.

The degree of crystallite orientation was determined from the equation:

$$\pi = (180 - H^\circ)/180 \qquad (1)$$

where H° is the half-width of the intensity distribution curve for the reflection ($2\theta \doteqdot 20.3^\circ$ for CuKα radiation) along the Debye–Scherrer ring.

Crystallite size along the chain direction was determined by measuring the profile of the meridional reflection ($2\theta \doteqdot 43.3^\circ$) followed by correcting both for

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the instrumental broadening and the broadening by CuKα doublet, and then applying Scherrer's equation.

The lattice extension under a constant load was measured by means of an X-ray diffractometer (Rigaku Denki RAD-B system) equipped with a stretching device and a load cell. The strain ϵ in the crystalline regions was estimated by use of the relation:

$$\epsilon = \Delta d / d_o \qquad (2)$$

where d_o denotes the initial lattice spacing for the meridional reflection, and Δd is the change in lattice spacing induced by the applied constant stress. The experimental error in determing the peak shift was evaluated ordinarily to be $< \pm 1/100°$ in 2θ angle.

The stress σ in the crystalline regions was assumed to be equal to the stress applied to the sample. This assumption of homogeneous stress distribution has been already proven experimentally to be reasonable for many polymers including polyethylene (PE)[11], poly(p-phenylene terephthalamide)[12] and PET[6].

The elastic modulus E_l was calculated by using the equation:

$$E_l = \sigma / \epsilon \qquad (3)$$

The elastic modulus E_t was also investigated by employing the equatorial reflection.

More detailed descriptions of the measurement have been given in earlier papers[1-7,11,12]

Elongation ξ of the whole sample was measured with a laser transducer (Keyence Co. Ltd) at the same time as the E_l measurements. Specimen modulus Y_L was also evaluated from the initial slope of the σ *versus* ξ curve.

RESULTS AND DISCUSSION

Characteristics of samples

Table 1 shows some characteristics of annealed LCPs, i.e. HBA/PET 60/40 and 80/20 copolymers. All the characteristics were higher for the HBA/PET 80/20 copolymer.

Table 1 Characteristics of HBA/PET copolymers

HBA/PET	60/40	80/20
Density (g cm^{-3})	1.392	1.401
Orientation	0.872	0.924
Crystallite size (Å)	63	75

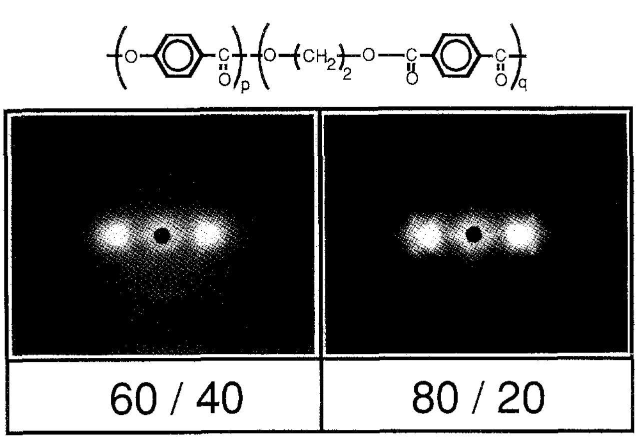

Figure 1 X-ray photographs of HBA/PET copolymers annealed at 200°C for 30 min

Figure 1 shows the X-ray photographs of the annealed LCPs. The degrees of crystallite orientation were not so high, especially for HBA/PET 60/40 copolymer, compared with the conventional crystalline polymers. Low degree of crystallite orientation indicates that the crystalline regions are not fully oriented in spite of high modulus, which implies that chain molecules in the amorphous region were well oriented. The diffraction patterns of LCPs resemble neither those of poly(HBA) nor PET. Further, reflections are not so sharp, particularly on the equator, and only a few reflections could be observed. This means that the lateral molecular packing is poor for LCPs and is apparently pseudo-hexagonal. However, a full analysis of the crystal structure has not been done yet. On the other hand, they have two sharp meridional reflections corresponding to the periodicity parallel to the chain axis as shown in *Figure 2* for HBA/PET 80/20. The peak position of higher angle reflection is $2\theta = 43.23°$ and that of the lower angle reflection is 27.24° for CuKα radiation. These correspond to d-spacings of 2.056 and 3.274 Å, respectively. Here, higher angle reflection was employed for the evaluation of E_l, since the peak shift was accurately measured because of high diffraction intensity and high sensitivity to determining the lattice strain.

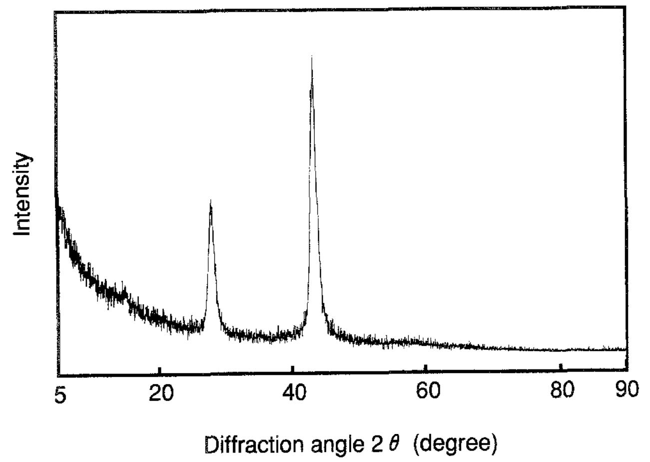

Figure 2 Meridional X-ray diffraction profile of HBA/PET 80/20 copolymer annealed at 200°C for 30 min

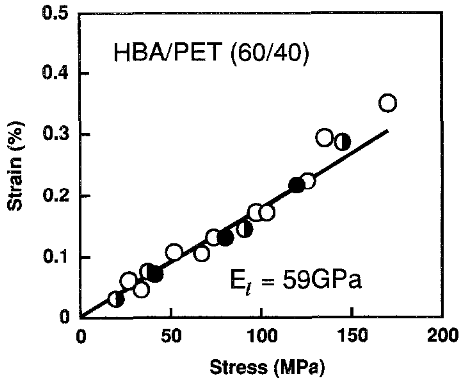

Figure 3 Stress–strain curves for the meridional reflections of HBA/PET 60/40 copolymer annealed under different conditions: (○) 200°C, 2 h; (●) 220°C, 30 min; (◑) 200°C, 30 min

Elastic modulus E_l *of the crystalline regions*

Figure 3 shows the stress σ–strain ϵ curves for the meridional reflection of HBA/PET 60/40 copolymer annealed under different conditions. Strains were always reversible. All the plots coincided with each other, and could be expressed by a straight line through the origin. This indicates that the annealing condition studied did not influence the chain extension behaviour. From the initial slope, the E_l value of 59 GPa was obtained for HBA/PET 60/40 copolymer at 25°C.

Figure 4 shows the stress σ–strain ϵ curve for the meridional reflection of HBA/PET 80/20 copolymer. Again all the plots were expressed by a straight line through the origin, and strains were reversible. The E_l value of 105 GPa was obtained for HBA/PET 80/20 copolymer at 25°C, which is ~ 1.8 times larger than that of HBA/PET 60/40 copolymer. The observed E_l value of PET is 108 GPa[6]. An E_l value of 105 GPa was obtained for HBA and a value of 99 GPa was tentatively measured from the shoulder peak located at $2\theta = 26.9°$ for Vectran (HBA/hydroxynaphthoic acid 73/27 copolymer)[13]. This shoulder is considered to be originated from HBA residue[13]. The calculated E_l value of HBA homopolymer was from 137 to 204 GPa depending on the assumed skeletal conformation[14]. Here by assuming the mechanical series linkage between PET and HBA residues, the E_l value of the copolymer can be estimated as follows:

$$1/E_l = (p/E_{l(\mathrm{HBA})}) + (q/E_{l(\mathrm{PET})}) \qquad (4)$$

where p and q are the contents of HBA and PET, respectively ($p + q = 1$). The estimated E_l values ($101 \sim 102$ GPa) are almost independent of the copolymer composition. The calculated values coincided with the observed E_l values for HBA/PET 80/20 copolymer. This suggests that the LCP of HBA/PET 80/20 copolymer is composed of monomer residues connected in series mechanically. In contrast, the observed E_l value for HBA/PET 60/40 copolymer is much lower than expected, which suggests a more contracted skeletal conformation.

Figure 5 shows the possible skeletal model of the LCP of HBA/PET 80/20 copolymer. Here, the structural models proposed by Yamashita *et al.*[15] and Daubeny *et al.*[16] are employed for the HBA and PET residues, respectively. Internal rotation around the ester bond between the HBA and PET residues gives the winding skeleton for the copolymer. This winding will lead to a reduction of linearity of the main chain and result in the inclination of both the residues from the direction of the applied stress. This tendency is enhanced by increasing the content of PET residue because the arms, where the moment of force acts during the deformation, are longer for PET. This is considered to be the reason why the E_l value of HBA/PET 60/40 is lower than that of the HBA/PET 80/20 copolymer. A more detailed discussion will be needed after the full structural analysis of these copolymers.

Table 2 summarizes the observed E_l values and the specimen modulus Y_l of LCPs of HBA/PET copolymers. The E_t and Y_t values are also shown. Both copolymers showed high Y_l values despite the fact that they were not drawn after being extruded. The ratio Y_l/E_l is higher than that of conventional crystalline polymers. This indicates that processing from the liquid crystalline state is very effective for high mechanical performance.

Elastic modulus E_t *of the crystalline regions*

Figure 6 shows the stress σ–strain ϵ curves for the equatorial reflection of HBA/PET copolymers. The stress that could be applied to the sample is smaller for

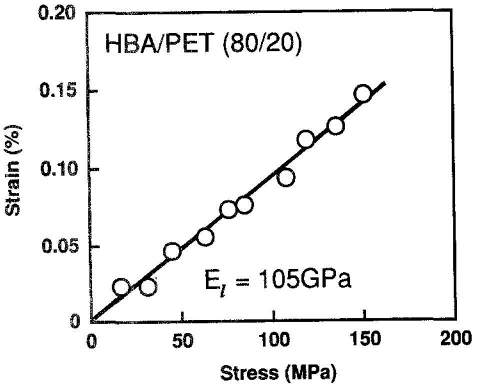

Figure 4 Stress–strain curves for the meridional reflection of HBA/PET 80/20 copolymer annealed at 200°C for 30 min

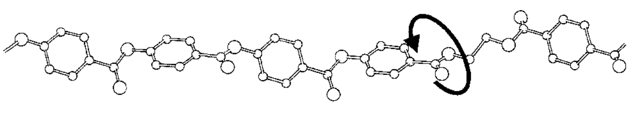

Figure 5 Possible skeletal structure of HBA/PET 80/20 copolymer

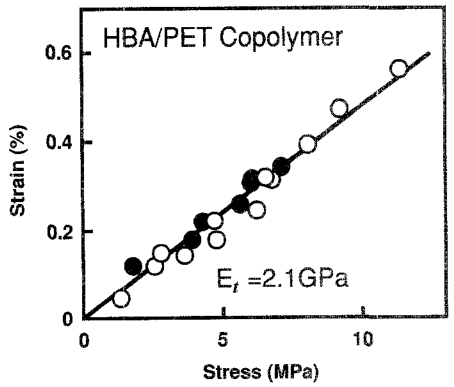

Figure 6 Stress–strain curves for the equatorial reflection of HBA/PET copolymers: (○) 60/40; (●) 80/20

Table 2 Elastic moduli of the crystalline regions and of the macroscopic specimen of HBA/PET copolymers

HBA/PET	60/40	80/20
Y_l	22	65
E_l	59	105
Y_l/E_l	0.37	0.62
Y_t	0.95	0·58
E_t	2.1	2.1
Y_t/E_t	0.45	0.28

HBA/PET 80/20 copolymer than for HNA/PET 60/40, because the fibrillar structure is more fully developed for the former copolymer. This is reflected in the lower Y_t value for HBA/PET 80/20 shown in *Table 2*. All the plots in *Figure 6* could be expressed by a straight line through the origin, and strains were reversible. The E_t values for both copolymers are 2.1 GPa. These values are much smaller than that of PE (~ 4 GPa, where only van der Waals forces act)[7]. Loose packing of LCP chains in the liquid crystalline state leads to the good processability of LCPs through slippage of chains. This loose packing is frozen at room temprature. Although π-electron interaction could be expected, loose and/or disordered lateral packing of the chains leads to the small E_t values of these copolymers.

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