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# Effects of molecular weight and monomer composition on tensile properties of thermotropic liquid crystalline poly(*p*-oxybenzoate-co-ethylene terephthalate)s

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## Summary

Relations between molecular structure and mechanical properties of as-spun filaments of thermotropic liquid crystalline poly(p-oxybenzoate-co-ethylene terephthalate)s have been investigated. The tensile modulus is independent of molecular weight, which suggests that the flow-induced orientation is not affected by molecular weight. On the other hand, the tensile breaking strength is inversely proportional to the reciprocal of molecular weight with the critical molecular weight of approximately 6000. The modulus and a balance between tensile strength and processability are enhanced with increasing the content of a rigid p-oxybenzoate unit in the copolyester.

## Introduction

It has been revealed by the present authors (1) that the dominant processing factors for the flow-induced molecular orientation of thermotropic liquid crystalline 60/40 poly(p-oxybenzoate-co-ethylene terephthalate) are spin-draw ratio and initial size of the sample. The flow-induced molecular orientation and resultant mechanical properties may be also affected by the molecular structure, such as molecular weight and monomer composition. Few reports have been published on the relation between the flow-induced orientation and the molecular structure so far. In the present research, the effects of molecular weight and monomer composition on the flow-induced orientation and tensile properties of the copolyesters have been investigated.

## Experimental part

The well-known thermotropic liquid crystalline poly(p-oxybenzoate-co-ethylene terephthalate)s, which had been synthesized by Jackson et al. (2) from p-hydroxybenzoic acid (PHB) and poly(ethylene terephthalate) with the PHB content of 50, 60, and 70 mol%, were used. These copolyesters are referred to as PHB50, PHB60, and PHB70, respectively. The weight-average molecular weight of PHB60 was 7490, 10400, 12700, 16700 (3). The inherent viscosity was 0.43, 0.57, 0.68, and 0.80 dL/g for PHB60, 0.54 dL/g for PHB50, and 0.78 dL/g for PHB70 in a mixture of phenol/p-chlorophenol/1,1,2,2-tetrachloroethane (25/40/35 by weight) at a concentration of 0.1 g/dL and 25 C.

Filaments were obtained by means of piston-driven extrusion and spinning at various spin-draw ratios using capillaries of 0.44 and 2.0 mm in diameter with a length/diameter ratio of 20. The average values of initial modulus and breaking strength were determined from five separate measurements of tensile stress-

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strain curves. Results are mainly reported on the filament spun at a spin-draw ratio of 100 by interpolation of the plot of tensile properties against spin-draw ratios. The absolute values of the complex viscosity for those samples (4,5) were used as an index of processability.

## Results and discussion

### Effect of Molecular Weight

Figure 1 shows the plot of tensile modulus (E) against weight-average molecular weight for the filaments of PHB60 spun at a spin-draw ratio of 100. The tensile modulus is independent of molecular weight, if the experimental error in the measurement is taken into account. This result suggests that the flow-induced orientation is not affected by molecular weight, since the tensile compliance defined as reciprocal value of tensile modulus can be linearly related to orientation function (1).

Figure 2 shows the plot of tensile strength $\sigma_b$ against molecular weight for the same samples as Fig. 1. The tensile strength increases with increasing molecular weight in the both cases of capillary diameter of 0.44 and 2.0 mm. It has been shown (6) that there is a linear relation between the tensile strength and the reciprocal of molecular weight for polymer materials as follows:

$$\sigma_b = \sigma_{b0} - K/M \qquad (1)$$

where $\sigma_b$ represents the tesile breaking strength, $\sigma_{b0}$ the limiting value of $\sigma_b$ at large molecular weight, K the constant, and M the molecular weight. Figure 3 shows the plot of tensile strength against the reciprocal of weight-average molecular weight.

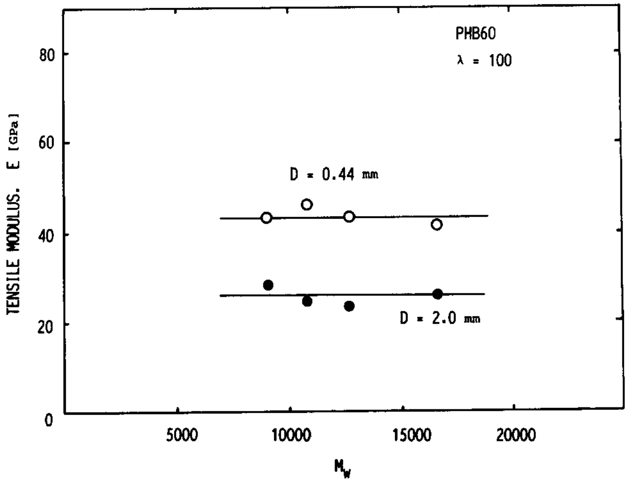

Fig. 1 Molecular weight dependence of the tensile modulus of the PHB60 filaments which was spun at a spin-draw ratio of 100 from capillaries of 0.44 and 2.0 mm in diameter.

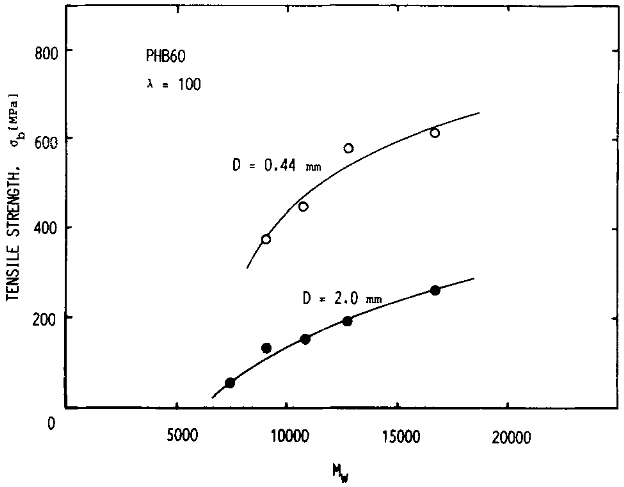

Fig. 2 Molecular weight dependence of tensile strength of the PHB60 filament which was spun at a spin-draw ratio of 100 from capillaries of 0.44 and 2.0 mm in diameter.

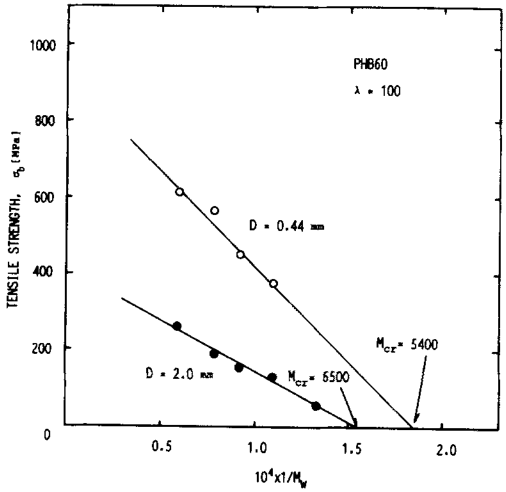

Fig. 3 Plots of tensile strength against the reciprocal of molecular weight for the PHB60 filaments which was spun at a spin-draw ratio of 100 from capillaries of 0.44 and 2.0 mm in diameter.

The critical molecular weight ($M_c$), which is defined as the lowest molecular weight indicating the strength no less than zero, was determined by extrapolation using Eq.(1). In the initial diameter of 0.44 mm and 2.0 mm, the critical molecular weight was obtained to be 5400 and 6500, respectively.

## Effect of Monomer Composition

The change of chemical structure would generally result in the change of all the physical properties of polymers. Then, the balance between processability and mechanical properties would be especially important, if the polymer is practicaly expected as a processing material. From such a point of view, the relation between complex viscosity at 10 $s^{-1}$ and tensile properties is described for PHB50, and PHB70 as compared with PHB60. Figure 4 shows the plot of tensile modulus vs. the complex viscosity for those copolyesters. It is natural that the viscosity of PHB60 does not affect the tensile modulus, because the modulus is independent of molecular weight as shown in Fig. 1. If the absence of molecular weight dependence of modulus holds for PHB50 and PHB70, the tensile modulus increases with increasing the content of a rigid p-oxybenzoate unit.

Figure 5 shows the plot of the tensile strength vs. the complex viscosity. The tensile strength of PHB60 increases with increasing complex viscosity caused by the increase of molecular weight. Assuming that the tensile strength of PHB50 and PHB70 increases with increasing complex viscosity parallel with that of PHB60, the tensile strength increases as the content of a rigid p-oxybenzoate unit increases.

## Conclusions

The tensile modulus is independent of molecular weight, suggesting that the flow-induced orientation is not affected by

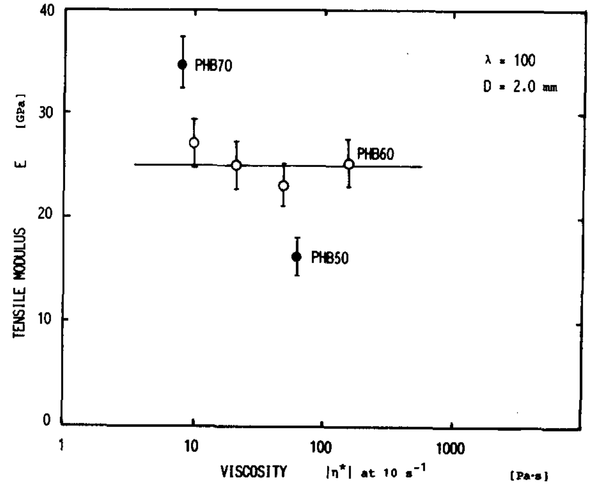

Fig. 4 Plots of tensile modulus against the complex viscosity at 10$s^{-1}$ for PHB50, PHB70 and a series of PHB60 samples having various molecular weight.

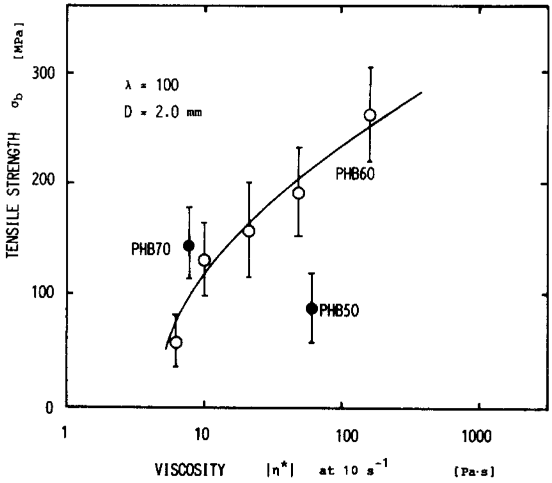

Fig. 5 Plots of tensile strength against the complex viscosity at 10 $s^{-1}$ for PHB50, PHB70 and a series of PHB60 samples having various molecular weight.

molecular weight. The tensile strength is inversely proportional to the reciprocal of molecular weight with the critical molecular weight of approximately 6000. The higher content of a rigid p-oxybenzoate unit resulted in the higher tensile modulus and the better balance between tensile strength and processability.

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