

NOTES

Effects of Monomer Sequence Alignment on Properties of *p*-Hydroxybenzoic Acid/Poly(ethylene terephthalate) Copolyester

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P-hydroxybenzoic acid (PHB)/poly(ethylene terephthalate) (PET) copolyester¹ is a representative thermotropic liquid crystal polyester (LCP) which is classified into a semi-aromatic LCP.² This PHB/PET copolyester (original LCP) has typical properties of LCPs, but, is not competitive with all-aromatic LCPs³ in mechanical and thermal properties. Original LCP has been proved to have blocky monomer sequence alignment.⁴⁻⁶ On the other hand, all-aromatic LCP has random monomer sequence alignment.⁷⁻⁹

We reported that the LCP synthesized by a new process (NP LCP) consisting of divided additions of *p*-acetoxybenzoic acid (APHB) to PET improves the properties of original LCP, and that the insoluble fraction of original LCP damages its properties qualitatively.¹⁰ The present research was carried out to inspect the relationship between insoluble fraction and properties quantitatively by analyzing the average sequence length of homopolymerized PHB in LCPs.

EXPERIMENTAL

Synthesis of PHB/PET Copolyester

a) Original LCP was synthesized by a two-step reaction reported by Jackson.¹ In the first step, an acidolysis step, all of the PET

and APHB monomer were heated up to 275°C quickly for an acidolysis reaction under nitrogen flow in a reactor. In this step, PET was cleaved to create copolyester fragments. In the second step, a condensation step, the pressure in the reactor was gradually decreased to 0.3 Torr to form the high molecular weight copolyester (original LCP).

b) NP LCP was synthesized by a new process consisting of divided additions of APHB to PET. At first, PET and half of the APHB were reacted by same procedure as a) to obtain a intermediate LCP which has PHB/PET molar ratio of 60/40. This intermediate LCP and shorted APHB were reacted by a repeated same procedure as a) to yield NP LCP.

c) LCP with intermediate amount of insoluble fraction between original LCP and NP LCP was synthesized by the same procedure as b) except for reducing the stirring speed.

Measurement of Insoluble Fraction

Glinded LCP powder with a size of 100 mesh pass was dissolved in 1/1 mixed solvent of phenol and tetrachloroethane at 150°C. Insoluble fraction was separated by a centrifugal separator.

Table I. LCPs synthesized under different conditions

LCP	LCP-1 ^b	LCP-2	LCP-3	LCP-4	LCP-5 ^c
Amount of the insoluble fraction ^a (%)	0	3	9	15	30

^a Insoluble fraction in phenol-tetrachloroethane (1:1) mixed solvent.

^b LCP-1, NP LCP synthesized by a new process.

^c LCP-5, original LCP synthesized according to Jackson.

¹³C NMR

¹³C NMR spectra was measured by Varian Model VXR-300 operating at 75 MHz. Solution for ¹³C NMR analysis was prepared by dissolving powdered LCP in hot pentafluorophenol.

Properties

Representative properties of LCPs were measured under the ASTM standard (D-790 for flexural modulus and flexural strength, D-256 for Izod impact strength, D-648 for heat deflection temperature). LCPs melted at 290°C were injection-molded into a mold of 90°C to prepare the test pieces.

Melt viscosity was measured by a plunger-type viscometer (Flow Tester CFT-500, Simazu Seisakusho) at 290°C, 1000 s⁻¹ of shear rate.

RESULTS AND DISCUSSION

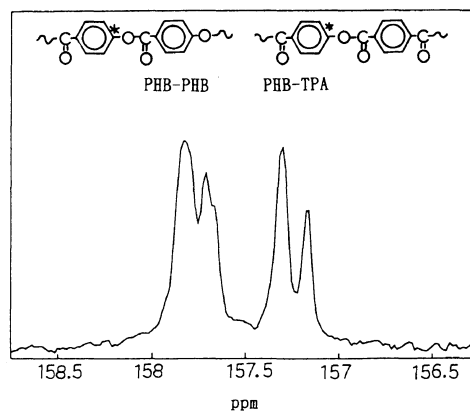
Table I shows five LCPs with various amount of insoluble fractions. LCP-5 with 30% of insoluble fraction is the original LCP, and LCP-1 without insoluble fraction is the NP LCP. LCP-2 to LCP-4 have the intermediate amount of insoluble fractions between original LCP and NP LCP.

Table II shows elemental analysis of LCP-5, LCP-1 and the insoluble fraction of LCP-5. These results show that there are no differences in compositions among them.

Carbon on PHB aromatic ring next to oxygen give informations of the monomer sequence alignment in ¹³C NMR spectrum.¹¹ As shown in Figure 1, peaks of 157—

Table II. Elemental analysis of LCP-1, LCP-5, and insoluble fraction of LCP-5

	C	H
LCP-1	67.81	3.56
LCP-5	67.68	3.56
Insoluble fraction of LCP 5	67.92	3.49
Calculated for PHB/PET = 80/20	67.86	3.60

**Figure 1.** ¹³C NMR spectrum of PHB/PET copolyester.

157.5 ppm were assigned to the carbon related to PHB-TPA bond, and peaks of 157.5—158 ppm is assigned to the carbon related to PHB-PHB bond. Average sequence length of homopolymerized PHB (*ASL*) can be presented by

$$ASL = \frac{\text{PHB-PHB bond}}{\text{TPA-PHB bond}} + 1$$

Table III shows *ASL* evaluated for LCP-5, LCP-1, and the insoluble fraction of LCP-5. LCP-1 is found to have much less blocky

Table III. Average sequence length of homopolymerized PHB

	LCP-1	LCP-5	Insoluble fraction of LCP-5
Average sequence length of homopolymerized PHB	2.3	3.1	4.5

Table IV. Representative properties of LCPs having various amounts of insoluble fractions

LCP	Unit	LCP-1	LCP-2	LCP-3	LCP-4	LCP-5
Flexural strength	kgf cm ⁻²	1500	1420	1300	1230	1150
Flexural modulus	kgf cm ⁻²	110000	102000	88000	76000	60000
Izod impact strength	kgf cm cm ⁻¹	31	30	18	14	11
Heat deflection temp	°C	168	158	154	141	135
Viscosity at 290°C	Poise	1200	1300	1500	1600	1800

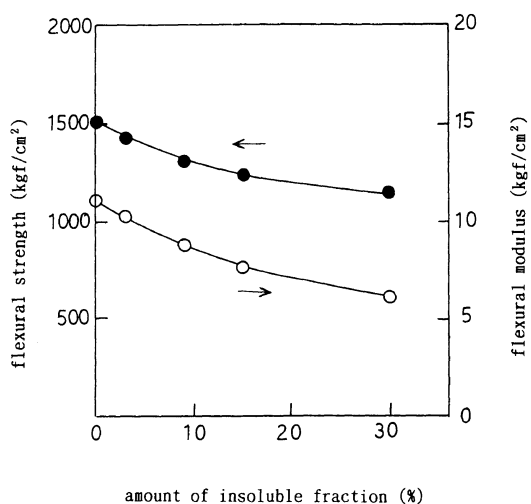


Figure 2. Effects of the insoluble fraction on flexural strength (—●—) and flexural modulus (—○—).

monomer sequence alignment than LCP-5. Since *ASL* of 2 means an ideally alternative copolymer, LCP-1 with *ASL* of 2.3 has almost random monomer sequence alignment. The insoluble fraction was found to have large *ASL* of 4.5.

Table IV shows representative properties of LCPs that have various amount of insoluble fractions. Figures 2 and 3 show that flexural properties and heat deflection temperature

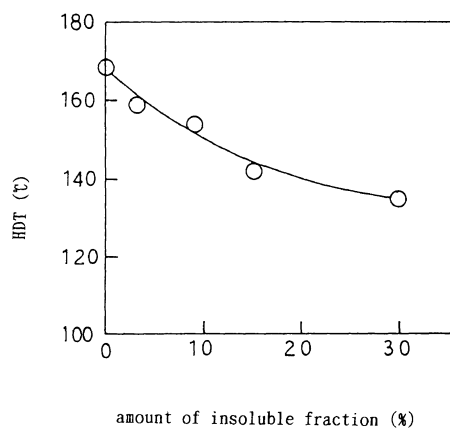


Figure 3. Effects of the insoluble fraction on heat deflection temperature.

(HDT) decrease along with the amount of insoluble fraction increasing, respectively. The insoluble fraction apparently damages mechanical and thermal properties of LCPs. PHB homopolymer blocks with *ASL* larger than 4 is infusible and insoluble.^{1,2)} Insoluble fraction with *ASL* of 4.5 should contain infusible homopolymer blocks. Since infusible PHB homopolymer blocks in LCPs disturb molecular orientation, mechanical properties are damaged by the insoluble fraction.

If cleaved PET remains as ethylene terephthalate unit in the LCP, *ASL* would be 4

because it has a composition of 80/20 for PHB/PET. In LCP-5 with large *ASL*, the ethylene terephthalate unit must remain, at least in the insoluble fraction. Deformation of LCP-5 at lower temperature will be caused by this ethylene terephthalate unit.

CONCLUSION

The effects of insoluble fraction on properties of semi-aromatic LCP were investigated. Both the mechanical and thermal properties of semi-aromatic LCP decrease with the amount of insoluble fraction increase. Original LCP (LCP-5) with 30% of insoluble fraction, synthesized by Jackson's process,¹ was found to have blocky monomer sequence alignment by ¹³C NMR spectrum. On the other hand, NP LCP (LCP-1) without the insoluble fraction, synthesized by a new process, was found to have random monomer sequence alignment.

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