Effect of the Phase Structure on Biodegradability of Polypropylene/Poly(ε-caprolactone) Blends

INTRODUCTION

Poly(ε-caprolactone) (PCL) is a scarce biodegradable plastic that has been proved to be biodegradable by microorganisms[1] and enzyme[2] and is commercially produced.

Biodegradable plastics including PCL have gained attention for treating plastic wastes because the environmental pollution caused by the plastic wastes has been increasingly serious.

The biodegradable plastics include the completely biodegradable plastics and the disintegrable plastics resulting in the shape disintegration and volume reduction by the partial biodegradation. Since even the disintegrable plastics can reduce the environmental effect more than the nonbiodegradable ones, it is expected that PCL will be applicable to the disintegrable plastics.

Although Brode et al.,[3] Kalfogu,[4] Cruz et al.,[5] Chiu et al.,[6] and Koleske[7] reported the blends of PCL and other plastics aimed at the improvement of their physical properties, their biodegradabilities were not studied. Clendining et al.[8] reported the disintegrabilities of low-density polyethylene (LDPE)/PCL blend and polypropylene (PP)/PCL blend in the natural world, but the morphological control and the biodegradation of PCL on these blends were not investigated.

The authors previously found that the enzymatic degradability of the blend of PCL and LDPE depends on the melt viscosities and quantities compounded in the mixing of these plastics and inferred from the phase structure of the blend that it is the continuous phase of PCL that gives it degradability.[9]

This study describes that the same phenomenon as in the blend of PCL and LDPE takes place also in the blends of PCL and plastics other than LDPE. It also investigates the relationship in the blend of PCL and PP between the enzymatic degradability and the phase structure to confirm whether the phenomenon is caused by the phase structure or not.

EXPERIMENTAL

Samples and Reagents

Tone 767 and Tone 787 manufactured by Union Carbide were used as PCL in the experiment. FY-6 manufactured by Mitsubishi Petrochemical Co. and MJ-170 manufactured by Tokuyama Soda Co. were used as PP.

Purified *R. arrhizus* lipase manufactured by Sigma Chemical Co. was used as the enzyme for the evaluation of biodegradability and Plysurf A210G manufactured by Daiichi Kogyo Seiyaku Co. was used as the surface active agent.

Measurement of Melt Viscosity

The melt viscosities of PCL and PP at each shear rate were measured with the CFT-500 Type Flow Tester of Shimadzu Corp. at 230°C under loads of 20, 40, 60, 80, and 100 kg. The melt viscosities at 230°C, at shear rate of 60 s^{-1} were determined by extrapolation of linear melt viscosity versus shear rate, as show Figure 1.

Preparation of PP/PCL Blend

PP/PCL blends were prepared according to the combinations shown in Table I. Actually the blends containing 26, 35, 44, 55, and 66 vol % of PCL were prepared at four melt viscosity ratios of 0.20, 0.67, 1.0, and 3.3 at 230°C, at shear rate of 60 s^{-1} using the CS-194 Type Extruder of Custom Scientific Instrument Co.

Evaluation of Biodegradability of Blend

The biodegradabilities of blends were determined in such a way that the blends with the compositions shown in Table II were reacted with enzyme, and the concentration of water-soluble total organic carbon (TOC) produced by the enzymatic degradation of PCL was measured with the TOC-500 Type TOC Analyzer of Shimadzu Corp. The same procedure was conducted for a control sample without undergoing the reaction with enzyme to correct those measurements.

Observation of Phase Structure of Blend

After etching a section of the blend sample with chloroform to remove PCL, its phase structure was observed using the JSM-T220 Type scanning electron microscope (SEM) of JEOL Co.
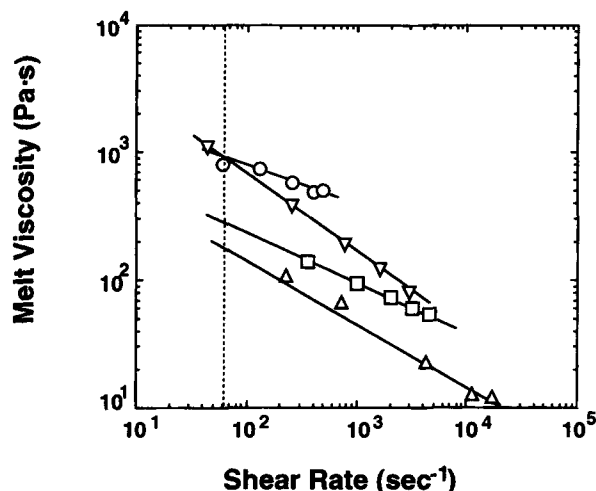
Figure 1 Relationship between shear rate and melt viscosity of PP and PCL. The melt viscosities of PCL and PP were measured with the Flow Tester at 230°C under loads of 20, 40, 60, 80, and 100 kg. PP; (△), MJ-170; (▽), FY-6, PCL; (○) Tone 787; (□) Tone 767.

RESULTS

Enzymatic Degradability of Blend

Figure 2 illustrates the relationships in the PP/PCL blends between the enzymatic degradability and PCL content. No TOC is produced at any PCL content in the blend with the melt viscosity ratio of 0.20. No TOC is produced at any PCL content except 65 vol % in the blend with the melt viscosity ratio of 0.67. Although little TOC is produced at a PCL content of 44 vol % or under in the blend with the melt viscosity ratio of 1.0, the TOC content in the reaction mixture is high at a PCL content of 55 vol % or over. TOC is produced even at the PCL content as low as 26 vol % in the blend with the melt viscosity ratio of 3.3, increasing with the increase of the PCL content. As mentioned above, the PCL content required for producing TOC by the enzymatic degradation in the PP/PCL blends reduces in inverse proportion to the increase of the melt viscosity ratio, η_{PP}/η_{PCL}, in the same manner as in the PCL/LDPE blend.

Observation of Phase Structure

Figure 3 shows SEM photographs of PP/PCL blends containing 55 vol % of PCL with various values of η_{PP}/η_{PCL} taken after removing PCL by etching. The melt viscosity ratios of the photographs of Figure 3(a)-(d) are 0.20, 0.67, 1.0, and 3.3, respectively. The phase structures of Figure 3(a)-(d) are PCL-in-PP, PCL-in-PP, PP-in-PCL, and PP-in-PCL, respectively. The PCL-in-PP structure of (b) has finer phases than that of (a). The

Table I   Combination of PCL and PP for Blending

| Combination | Melt Viscosity at 230°C (Pa s) | | Value of |
	η_{PP}[a]	η_{PCL}[b]	η_{PP}/η_{PCL}
a	180	900	0.20
b	180	270	0.67
c	900	900	1.0
d	900	270	3.3

[a] η_{PP}: melt visocity of PP.
[b] η_{PCL}: melt viscosity of PCL.

PP-in-PCL structure of (c) has finer phases than that of (d).

DISCUSSION

The factors participating in the phase structure of a blend prepared by melt extrusion of polymers A and B with different compatibilities include composition and melt viscosity of the blend. Jordhamo et al.[10] investigated the phase structures of blends of polybutadiene and polystyrene prepared by melt extrusion and derived the following formula concerning the composition and melt viscosity of the blend:

$$\alpha = \frac{\eta_A}{\phi_A} \times \frac{\phi_B}{\eta_B} \qquad (1)$$

where η_A is melt viscosity of polymer A at blending temperature, η_B is melt viscosity of polymer B at blending temperature, ϕ_A is volume fraction of polymer A at blending temperature, and ϕ_B is volume fraction of polymer B at blending temperature.

In Eq. (1), if α (phase structure index) > 1, then polymer B is a continuous phase, while if α < 1, then polymer A is a continuous phase, and $\alpha \fallingdotseq 1$. Both polymers are continuous phases. It is known that if the volume fraction

Table II   Composition of Reaction Mixture[a]

0.2M phosphate buffer (pH 7.0)	2.0 mL
0.1% Plysurf A210G	1.0 mL
Blend sample	100 mg as PCL
$R.\ arrhizus$ lipase	60 units
Total volume	20.0 mL

[a] Reaction time, 16 h; reaction temperature, 30°C; 1 unit, 1 μmol fatty acids from olive oil at 35°C per minute.
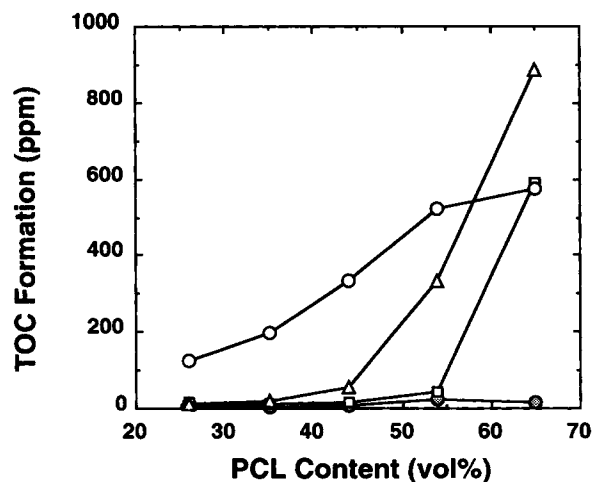
Figure 2 Relationship between PCL content and TOC formation by lipase from PCL/PP blend yarns. The value of η_{PP}/η_{PCL}: (●) 0.20; (□) 0.67; (△) 1.0; (○) 3.3. η_{PP}: Melt viscosity of PP, η_{PCL}: Melt viscosity of PCL.
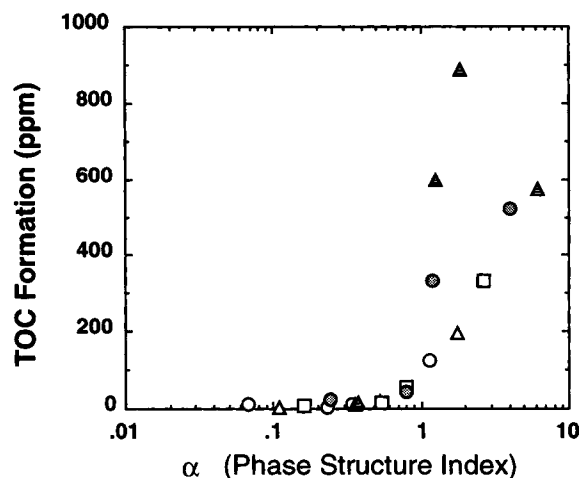
Figure 4 Relationship between α (Phase Structure Index) and TOC formation by lipase from PCL/PP blend yarns. PCL Content: (○) 26 vol %; (△) 35 vol %; (□) 45 vol %; (●) 55 vol %; (▲) 65 vol %.
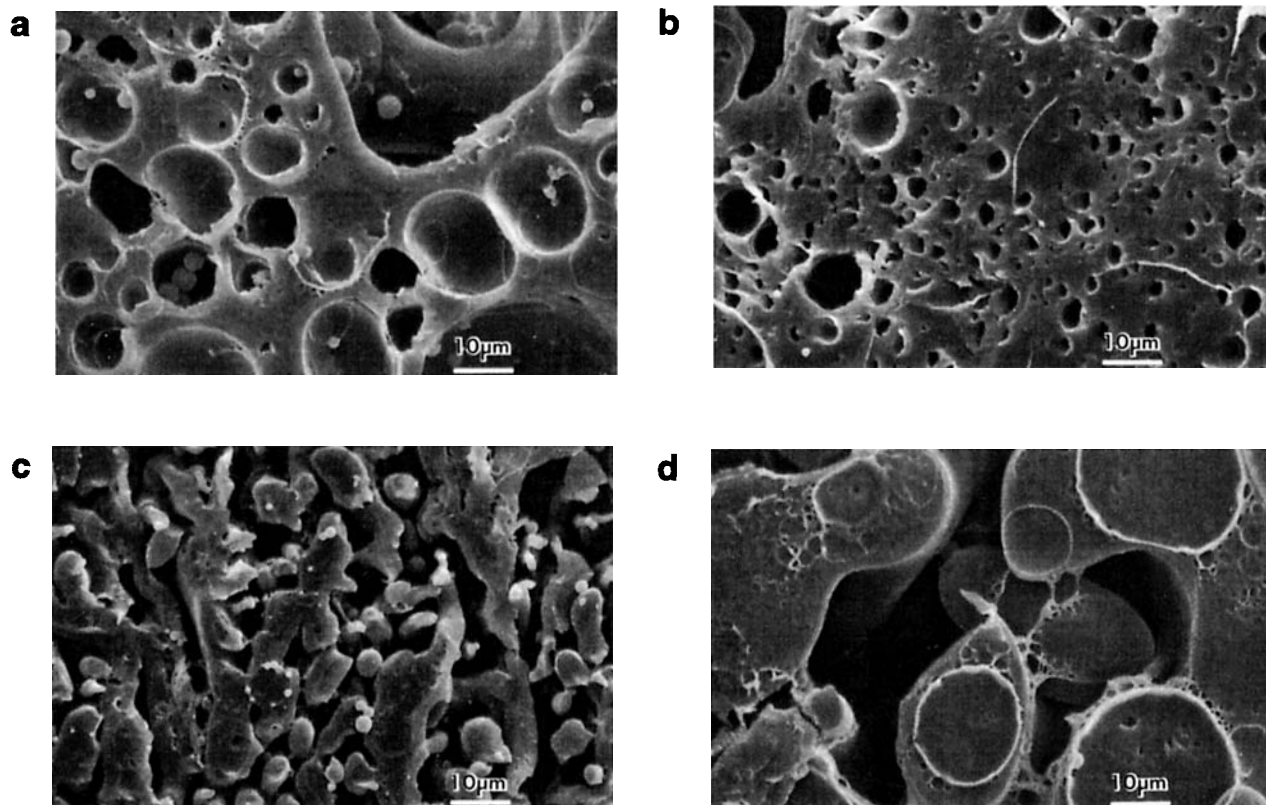

Figure 3 SEM photographs of PP/PCL blend yarns containing 55 vol % of PCL taken after removing PCL by chloroform etching. The melt viscosity ratios (η_{PP}/η_{PCL}) of the photographs of (a), (b), (c), and (d) are 0.20, 0.67, 1.0, and 3.3, respectively.

of either of those polymers is 75% or over, the polymer is a continuous phase irrespective of the value of α.[11] Since polymer A is PP and polymer B is PCL in this study, PCL is a dispersed phase irrespective of the melt viscosity ratio if the PCL content is lower than 25 vol %, while it is a continuous phase if the PCL content is higher than 25 vol % and $\alpha > 1$. The values of α of the blends shown in Figure 3(a)–(d) are 0.24, 0.80, 1.20, and 3.3, respectively. In the blends of (c) and (d) exhibiting the PP-in-PCL (PCL: a continuous phase) phase structure, $\alpha > 1$, while in those of (a) and (b) exhibiting the PCL-in-PP (PCL: a dispersed phase) phase structure, $\alpha < 1$. The relationship between the value of α and the phase structure agrees with the result of Jordhamo et al.[10] Therefore, Eq. (1) may be applicable to the identification of the phase structure. Figure 4 illustrates the relationship in the blends used for this study between the value of α and the TOC formation due to enzymatic degradation.

TOC is produced in all the blends meeting the condition of $\alpha > 1$ in the same manner as in LDPE/PCL blends presented in a previous study. Since TOC is hardly produced in the blends of $\alpha < 1$, these blends are not enzymatically degraded. It is inferred that the former blends are enzymatically degraded because PCL is a continuous phase, while the latter ones are not enzymatically degraded because PCL is a dispersed phase. It is, however, estimated that the blends of $\alpha \fallingdotseq 1$ are enzymatically degraded because both polymers are continuous phases.

As a result, it is concluded that the enzymatic degradability can be effectively provided to a blend by conducting the design of mix combining the composition and melt viscosity ratio of the blend so as to form the continuous phase of the biodegradable plastic based on the phase structure index, α, because the biodegradability of the blend depends on the phase structure.

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