ORIGINAL ARTICLE

The toughening effect of a small amount of poly(ε-caprolactone) on the mechanical properties of the poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)/PCL blend

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To improve the mechanical properties of bacterial poly(3-hydroxybutyrate) [P(3HB)] and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HH)], the materials were blended with poly(ε-caprolactone) (PCL). The P(3HB-co-7 mol% 3HH) cast film and the P(3HB-co-11 mol% 3HH) melt-pressed film show brittleness after aging, although unaged samples show ductile behavior. However, the addition of a small amount of PCL was found to greatly improve the toughness of the P(3HB-co-7 mol% 3HH) cast film and the P(3HB-co-11 mol% 3HH) melt-pressed film. Reduction in the whitening of the elongated P(3HB-co-7 mol% 3HH) film by blending with PCL indicates that a transition in the deformation mechanism of the film was induced. In P(3HB-co-11 mol% 3HH)/PCL melt-pressed films, a cloud of craze initiation created by the dispersed PCL was observed. Differential scanning calorimetry thermograms and scanning electron microscopy images of the blended films indicated that finely dispersed PCL, the crystallization of which was restricted, and/or voids formed during preparation contribute to the delocalization of the applied stress and ductile deformation of P(3HB-co-3HH) films. In conclusion, the transition in the deformation mechanisms and the delocalization of the applied stress are expected to be important for enhancing the toughness of aged P(3HB-co-3HH)s, and blending with a small amount of PCL is a simple way to improve the mechanical properties of P(3HB-co-3HH)s.

INTRODUCTION

Several kinds of polyhydroxyalkanoates (PHAs) are biosynthesized by various bacteria as energy-storage materials.[1–5] They may be produced from renewable natural resources and have biodegradability. Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HH)] is part of the PHA family.[6] Doi et al.[7] have found that the content of the 3HH unit greatly affected the thermal and mechanical properties of P(3HB-co-3HH), but had little effect on the crystalline structure of 3HB-rich P(3HB-co-3HH)s because of the formation of the P(3HB)-homopolymer-type crystalline phase and the exclusion of the 3HH unit from the crystalline lattice. P(3HB-co-3HH) was found to show improved mechanical properties and thermal plasticity over those of known PHAs.[8,9] One of the notable advantages of P(3HB-co-3HH)s is their adjustable mechanical properties, from soft to hard material, depending on the comonomer-unit composition; this allows for the tailoring of P(3HB-co-3HH) to various societal applications, such as in green and sustainable polymeric materials.

However, P(3HB-co-3HH) becomes brittle after aging at room temperature, thus restricting its practical applications. Although P(3HB-co-3HH) with 10 mol% 3HH, which we will hereafter denote as [P(3HB-co-10 mol% 3HH)], has good toughness even after 2 months of aging when it is solvent cast into a film,[10] the brittle nature appears after aging for several days when the film is cast from the melt state. Furthermore, films of P(3HB-co-3HH)s with a 3HH unit content <7 mol% show brittleness after aging, regardless of how they are formed. The unfavorable aging effect limits the processing method and the available copolymer composition of P(3HB-co-3HH). Therefore, it is desirable to develop effective ways to overcome this aging problem to extend the applicability of P(3HB-co-3HH)s as industrial materials.

Polymer blending is a widely used method to improve the mechanical properties of polymeric materials due, at least in part, to its lower cost and relatively wide range of possible of polymer–polymer combinations.

A number of blends have been prepared to improve the mechanical properties of brittle PHAs, such as poly(3-hydroxybutyrate) [P(3HB)] and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV)]. Bio- or petroleum-based polymers, for example, poly(lactide),[11]

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polysaccharides,[12,13] polyethyleneoxide,[14] poly(epichlorohydrin),[15] poly(vinylacetate),[16] poly(methylmethacrylate),[17] poly(ε-caprolactone) (PCL)[18] and ethylene-propylene rubber,[19] have been blended with P(3HB) or P(3HB-co-3HV). The miscibility, morphology and mechanical properties have been studied, and some improvements in the mechanical properties of some blends have been reported. According to these studies, the morphology, which is related to the miscibility between the blend components, is considered to be important in determining the mechanical properties of the final products. For example, domain size, crystallization state and phase continuity of the blend components dramatically affect the mechanical properties of the blends. Although many reports regarding mechanical properties of PHA blends have been published, studies aimed toward overcoming the brittleness of P(3HB-co-3HH)s after aging are few in number,[20] despite the potential of these blends as green, sustainable materials.

In this study, to overcome brittleness resulting from aging, a series of blends of P(3HB) or P(3HB-co-3HH)s with 7 and 11 mol% 3HH and PCL, respectively, were prepared and their properties investigated. PCL is a biodegradable and flexible semi-crystalline polymer. Owing to its biodegradability, PCL is a favorable candidate as a blend partner for P(3HB-co-3HH).

There have been many studies on the P(3HB)/PCL blend.[18,21–24] Interestingly, although most of them have concluded that this blend system is immiscible,[18,21–23] a result, which implies that this blend is miscible, has also been obtained.[24] These contradictory results may indicate a small amount of solubilization of one component in the other, although they seem to be immiscible on the bulk scale. It is expected that, due to such solubilization, PCL is more or less compatible with P(3HB). Compatibility is also expected for the blends of PCL and P(3HB-co-3HH) with a high 3HB unit content. Thus, the morphology, crystallization state and the mechanical properties are expected to be controllable by simply changing the blend composition of P(3HB-co-3HH)/PCL blends. In this study, we shall investigate a series of PHA/PCL blends to clarify how the PCL component affects the mechanical properties of the blends by tensile test, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), polarized optical microscopy (POM) and dynamic mechanical thermal analysis (DMTA).

EXPERIMENTAL PROCEDURE
Materials
Bacterial P(3HB-co-3HH)s with 3HH molar fractions of 7 mol% ($M_w=1.2\times10^5$, $M_w/M_n=3.2$) (M_w, weight-average molecular weight; M_n, number-average molecular weight; M_w/M_n, polydispersity) and 11 mol% ($M_w=8.9\times10^4$, $M_w/M_n=3.9$), bacterial P(3HB) ($M_w=7.3\times10^4$, $M_w/M_n=5.8$) and PCL (Cellgreen; $M_w=7.4\times10^4$, $M_w/M_n=2.5$) were supplied by Kaneka (Osaka, Japan), PHB Industrial S/A (São Paulo, Brazil) and Daicel Chemical (Osaka, Japan), respectively. For purification, each sample was dissolved in chloroform and reprecipitated from ethanol for P(3HB-co-3HH)s and P(3HB) and from n-hexane for PCL; this was followed by drying in vacuum at 23 °C overnight.

Preparation of blend samples
The cast PHA/PCL samples containing 0, 2.5, 5, 10 or 20 wt% of PCL were prepared by casting from chloroform solutions on Petri dishes, allowing the solvent to evaporate at room temperature, and then drying in vacuum at room temperature for 12 h. The obtained cast films were stored in a desiccator at 23 °C for 1 month before testing to allow them to achieve equilibrium in their crystallized state. The melt-pressed samples were prepared by compression molding the corresponding cast films at 160 °C for P(3HB-co-3HH)/PCL blends and at 180 °C for P(3HB)/PCL blends for 2 min between Teflon sheets

with a c.a. 0.1-mm spacer under a pressure of 3–5 MPa using a laboratory press Toyo Mini Test Press-10 (Toyoseiki, Tokyo, Japan); this was followed by keeping the samples in an oven at 60 °C for 2 h and testing them. The thickness of each film was 0.1–0.2 mm.

Tensile test
Tensile properties were measured at room temperature using an EZ test machine (Shimadzu, Tokyo, Japan) with a cross-head speed of 10 mm per min. Dumbbell-type specimens, with a gauge length and width of 22.25 and 4.76 mm, respectively, were prepared from the samples.

Differential scanning calorimetry
Thermal analysis of the samples encapsulated in aluminum pans was carried out on Seiko DSC-220 assembled with a SSC-580 thermal controller (Seiko Instrument and Electronics, Tokyo, Japan). DSC thermograms were recorded from −100 to 200 °C at a scanning rate of 10 °C per min.

Dynamic mechanical thermal analysis
The dynamic mechanical properties of the samples were measured at 1 Hz using DMS210 (Seiko Instrument, Tokyo, Japan) at a heating rate of 3 °C per min. The gauge length and width of the specimens were 20 and 10 mm, respectively.

Scanning electron microscopy
Samples before and after extraction of PCL with acetone were dried in vacuum, coated with gold using an ion coater (IB-3, Eiko, Ibaraki, Japan) and observed under a scanning electron microscope JSM-5200 (Jeol, Tokyo, Japan). For observation of the cross-section of the samples, they were frozen and fractured in liquid nitrogen before the aforementioned procedure.

Polarized optical microscopy
Polarized optical microscopy observation was performed using an Olympus BX90 polarizing microscope (Olympus, Tokyo, Japan) equipped with a digital camera system.

RESULTS AND DISCUSSION
Mechanical properties
The stress-strain curves of P(3HB), P(3HB-co-7 mol% 3HH), P(3HB-co-11 mol% 3HH) and their blends with PCL, which were aged at 23 °C for 1 month, are shown in Figure 1 for the cast films and in Figure 2 for the melt-pressed films. Young's modulus and the maximum stress σ_m that appeared in the region under 30% strain, in which large deformation such as brittle fracture or yielding occurs, are summarized in Table 1. The elongation at break is shown in Figure 3.

It is known that an aging effect related to secondary crystallization causes PHAs to become brittle materials.[10,25,26] Actually, for most neat PHAs used in this study, the elongation at break was small, except for the P(3HB-co-11 mol% 3HH) cast film, as shown in Figures 1 and 2.

As plausible reasons for the embrittlement of PHAs after aging, the formation of cracks (or voids) causing brittle failure and intraspherulitic yielding for the ductile failure, both of which have been frequently observed in semi-crystalline polymers, should be considered.[27] As bulk mechanical responses are considered to result from the competition between brittle and ductile failure processes, an important question is which failure mode is dominant.

The brittleness of a semi-crystalline polymer can be caused by cracks and/or voids that may be formed at interspherulite or intraspherulite regions as the polymer crystallizes or strains. At the initial stage of crystallization, spherulites are formed, followed by spherulite boundaries, which consist of uncrystallized amorphous material. The polymer in the interspherulite region still has the potential to crystallize, and indeed, it gradually crystallizes with aging time. Simultaneously, the density of the interspherulite region should decrease, and
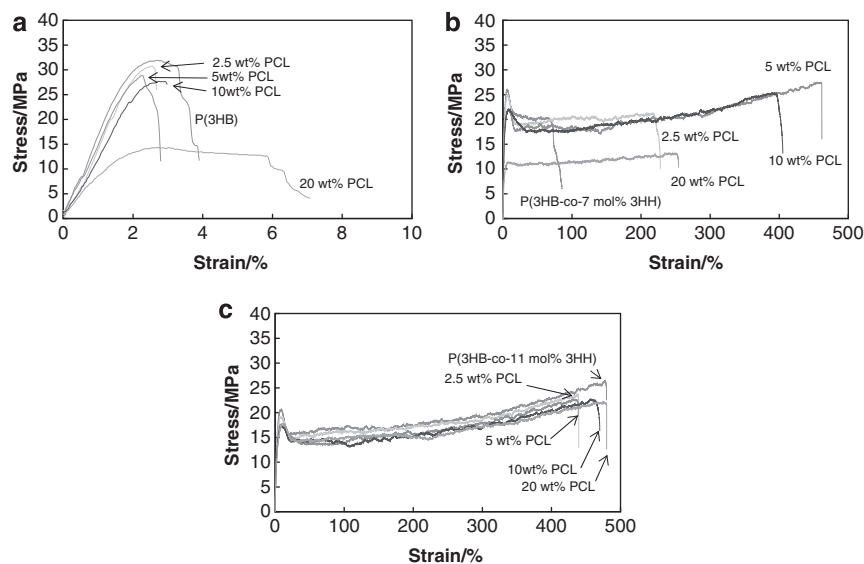
Figure 1 Stress-strain curves of cast films aged for 1 month. (**a**) P(3HB) and P(3HB)/PCL blends, (**b**) P(3HB-co-7 mol% 3HH) and P(3HB-co-7 mol% 3HH)/ PCL blends and (**c**) P(3HB-co-11 mol% 3HH) and P(3HB-co-11 mol% 3HH)/PCL blends. PCL, poly(ε-caprolactone); P(3HB), poly(3-hydroxybutyrate); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).
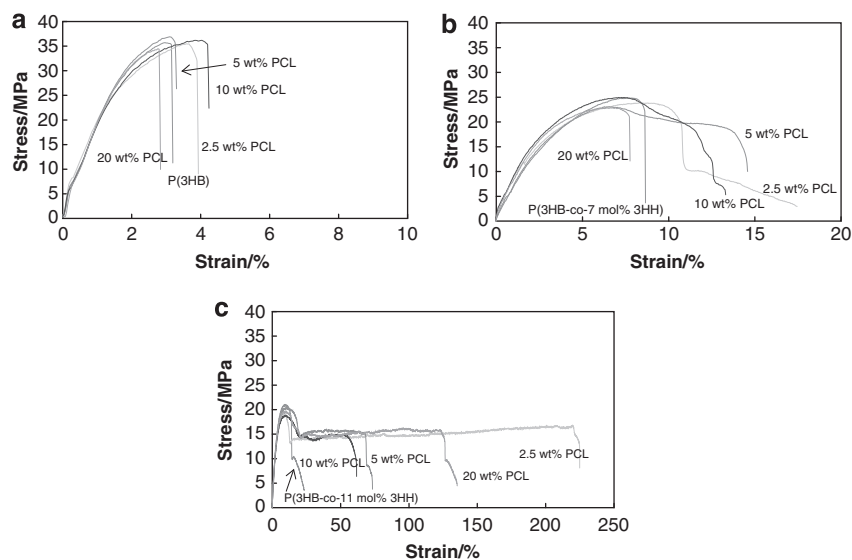
Figure 2 Stress-strain curves of melt-pressed films aged for 1 month. (**a**) P(3HB) and P(3HB)/PCL blends, (**b**) P(3HB-co-7 mol% 3HH) and P(3HB-co-7 mol% 3HH)/PCL blends and (**c**) P(3HB-co-11 mol% 3HH) and P(3HB-co-11 mol% 3HH)/PCL blends. PCL, poly(ε-caprolactone); P(3HB), poly(3-hydroxybutyrate); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).

therefore, voids and/or cracks might grow there. Voids and/or cracks can have deleterious effects on the ultimate mechanical properties.[28]

The formation of types of defect can occur when the material is strained. As spherulites are geometrically anisotropic on the microscopic level due to the orientation of lamellar crystals, the microscopic mechanical responses of the spherulites are also anisotropic. When stress is applied to the material, the spherulites locally change their shape in different ways, leading to elastic discontinuity, especially at the spherulite boundaries or nodes.[27] If the shape accommodation by intraspherulitic flow, namely yielding, becomes difficult when stress increases, the spherulites fracture internally or the spherulite boundaries break to produce voids or cracks to accommodate them in response to the shape change.[27] Aging, which advances secondary

crystallization, might make the spherulites stiffer and thus may prevent them from flowing. As a result, interspherulite or intraspherulite fracture might become a more favorable process; therefore, the material might show brittle behavior upon the application of strain. To overcome the problem of brittleness, it seems to be important to understand how to induce ductile deformation in the presence of mechanical defects. As a biodegradable flexible polymer that shows ductile deformation, PCL was expected to induce the ductile deformation of P(3HB-co-3HH) in the P(3HB-co-3HH)/PCL blend.

As seen in Figures 1 and 2, ductility was not improved for the melt-pressed films of P(3HB) and P(3HB-co-7 mol% 3HH) nor for the cast films of P(3HB) by blending with PCL. In addition, the ductility of the cast films of P(3HB-co-11 mol% 3HH), which intrinsically

Table 1 Young's modulus and the maximum stress σ_m in the region under 30% strain of (a) cast and (b) melt-pressed films of PHA/PCL blends
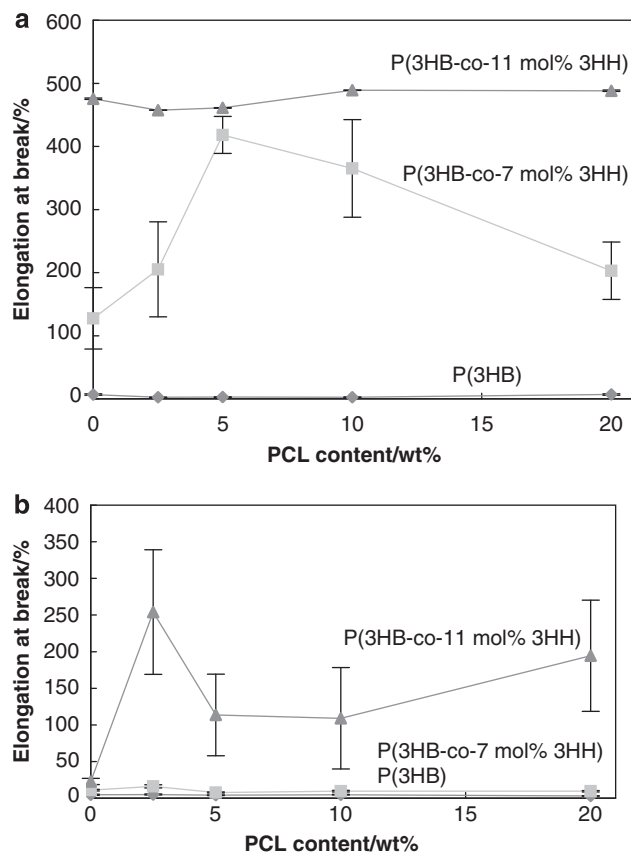
(a)

Matrix	PCL/wt%	Young's modulus/MPa	σ_m/MPa
P(3HB)	0	1534 ± 118	30.1 ± 1.3
	2.5	1584 ± 73	30.0 ± 0.5
	5	1368 ± 87	26.4 ± 0.9
	10	1358 ± 95	27.1 ± 1.7
	20	756 ± 62	14.3 ± 0.7
P(3HB-co-7 mol% 3HH)	0	980 ± 57	26.3 ± 0.3
	2.5	953 ± 53	24.7 ± 0.2
	5	884 ± 25	22.1 ± 0.2
	10	826 ± 49	22.0 ± 0.2
	20	477 ± 36	11.3 ± 0.5
P(3HB-co-11 mol% 3HH)	0	705 ± 56	20.6 ± 0.2
	2.5	685 ± 29	19.3 ± 0.2
	5	629 ± 30	17.5 ± 0.2
	10	599 ± 45	17.6 ± 0.3
	20	520 ± 34	17.9 ± 0.3

(b)

P(3HB)	0	1826 ± 11	35.7 ± 1.7
	2.5	1664 ± 23	35.8 ± 1.0
	5	1780 ± 17	36.4 ± 1.0
	10	1756 ± 78	36.7 ± 0.5
	20	1805 ± 67	34.7 ± 0.3
P(3HB-co-7 mol% 3HH)	0	679 ± 23	24.8 ± 0.4
	2.5	707 ± 35	24.0 ± 0.2
	5	699 ± 56	23.3 ± 0.5
	10	746 ± 30	24.8 ± 0.5
	20	757 ± 38	23.5 ± 0.3
P(3HB-co-11 mol% 3HH)	0	575 ± 20	20.7 ± 0.5
	2.5	569 ± 12	19.7 ± 0.2
	5	591 ± 8	20.0 ± 0.2
	10	555 ± 18	18.7 ± 0.3
	20	586 ± 15	19.3 ± 0.1

Abbreviations: PCL, poly(ε-caprolactone); PHA, polyhydroxyalkanoate; P(3HB), poly(3-hydroxybutyrate); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).

Figure 3 Elongation at break of (**a**) cast and (**b**) melt-pressed films of the blends aged 1 month as a function of PCL content. PCL, poly(ε-caprolactone); P(3HB), poly(3-hydroxybutyrate); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).

showed high elongation at break, was not significantly affected by PCL. In contrast, for the cast films of P(3HB-co-7 mol% 3HH) and the melt-pressed films of P(3HB-co-11 mol% 3HH), the stress-strain behavior was significantly affected by the PCL component. The characteristic lower stress on the cast films of the P(3HB)/PCL blend and the P(3HB-co-7 mol% 3HH)/PCL blend with 20 wt% PCL derive from their void-containing structure formed during preparation, which will be discussed later.

In Table 1, Young's modulus and the σ_m of the cast films of PHA/PCL blends are shown to decrease as the PCL content increases. This is an indication that PHAs were diluted by soft PCL domains and/or voids. In contrast, the nearly constant Young's modulus and σ_m values indicate that the PCL in the melt-pressed films of PHA/PCL blends behave differently. The crystallinity of PCL and the presence of voids are considered to be related to the differences in Young's modulus and σ_m values observed between the various films.

Figure 3 shows elongation at break of the blends as a function of the concentration of the PCL component. In the P(3HB-co-7 mol% 3HH)/PCL cast films and P(3HB-co-11 mol% 3HH)/PCL melt-

pressed films, ductility was effectively improved by adding a small amount of PCL, from 2.5 to 5 wt%. Interestingly, additional PCL led to a reduction in the elongation at break.

Crystals of blend components
The crystalline states of blend components were investigated by DSC. Figure 4 shows DSC thermograms of the P(3HB-co-7 mol% 3HH)/PCL cast films and P(3HB-co-11 mol% 3HH)/PCL melt-pressed films. In each curve, the PCL melting peak at ∼60 °C shifts to lower temperatures as PCL concentration decreases, probably due to the confinement of PCL and the formation of thin lamellar crystals. The thermal properties of the blends are summarized in Table 2. As P(3HB-co-3HH)s show what is called an 'annealing peak,'[29] which partially overlaps with the PCL melting peak at ∼60 °C, the melting enthalpy of PCL, ΔH_{PCL}, was calculated by subtracting the enthalpy of the annealing peak from the enthalpy of the peak of the blend samples in the range from 30 to 70 °C. The enthalpy of the annealing peak was obtained from the peak area from 40 to 70 °C in the DSC curve of the neat P(3HB-co-3HH). The calculation was performed based on the assumption that the shapes of the annealing peaks of each sample were almost the same. The enthalpy of melting of P(3HB-co-3HH), $\Delta H_{P(3HB-co-3HH)}$, was calculated by subtracting ΔH_{PCL} from the enthalpy obtained from the area in the temperature range from 30 to 160 °C, which covers the broad melting peak of P(3HB-co-3HH).

Crystallinity was measured as the ratio between ΔH_m and ΔH_0, where ΔH_m is the melting enthalpy of the material under study and

ΔH_0 the melting enthalpy of a perfectly crystallized material (=142 J g^{-1} for PCL[30] and =146 J g^{-1} for P(3HB)[31]). The ΔH_0 of P(3HB) was also used to measure the crystallinity of P(3HB-co-3HH)s because only the P(3HB)-type crystal forms in P(3HB-co-3HH)s.[7] In each blend, the crystallinity of P(3HB-co-3HH) was almost the same for any composition, whereas that of PCL decreased as its concentration was reduced. These results suggest that PCL does not have much influence on the crystallization of P(3HB-co-3HH); however, the crystallization of PCL is significantly affected by the blend composition.
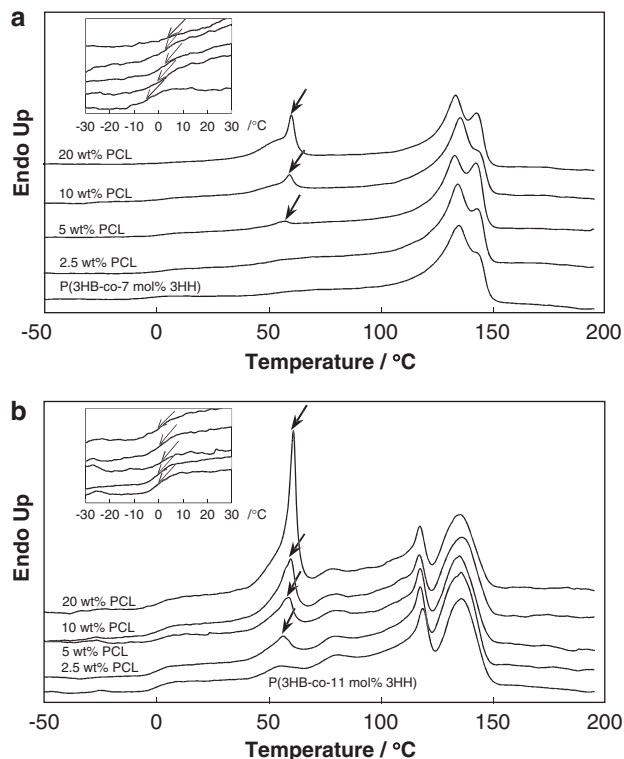
Figure 4 DSC thermograms of (**a**) P(3HB-co-7 mol% 3HH)/PCL cast films and (**b**) P(3HB-co-11 mol% 3HH)/PCL melt-pressed films after 1 month of aging. Magnified curves of the glass transition area of PHAs ∼0 °C are shown in the upper left. DSC, differential scanning calorimetry; PCL, poly(ε-caprolactone); P(3HB), poly(3-hydroxybutyrate); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).

Miscibility

The miscibility of a polymer blend should have great influence on the blend's mechanical properties; therefore, the miscibilities of P(3HB)/PCL, P(3HB-co-7 mol% 3HH)/PCL and P(3HB-co-11 mol% 3HH)/PCL were investigated by measuring the glass transition temperature (T_g) of their cast films by DSC and DMTA. As it is difficult to detect the T_g of PCL because of its low composition, the transition temperatures of PHAs were measured in a temperature range of ∼0 °C.

Figure 4 shows DSC thermograms of P(3HB-co-7 mol% 3HH) and P(3HB-co-11 mol% 3HH) that were obtained to observe the glass transition at ∼0 °C. As the glass transition of P(3HB) was undetectable by DSC (data not shown) probably because of its high crystallinity, DMTA was also performed to observe the glass transition more clearly. Figure 5 shows DMTA tanδ curves of the blend samples. A peak corresponding to the T_g of PHAs, including P(3HB) can be observed.
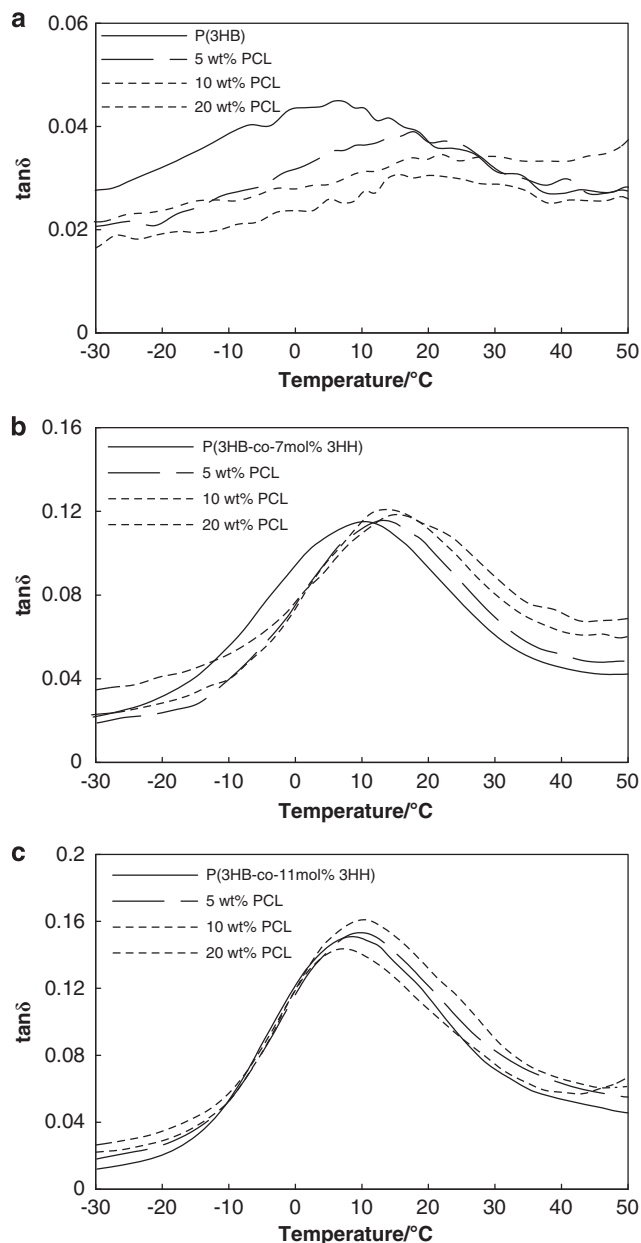
In general, a binary miscible polymer blend shows a T_g between those of each component polymer 1 and 2, T_{g1} and T_{g2}, according to, for example, the Fox-Flory equation:[32]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

where w_1 and w_2 are the weight fractions of component polymers 1 and 2, respectively. Owing to the low T_g of PCL (c.a. −60 °C), the T_g of PHAs (c.a. 0) should be shifted to lower temperatures with increasing PCL concentration in the blend, if PHAs and PCL are miscible. However, for P(3HB)/PCL, P(3HB-co-7 mol% 3HH)/PCL and P(3HB-co-11 mol% 3HH)/PCL blends, the T_g values found at ∼0 °C did not shift to lower temperatures and sometimes showed shifts toward higher temperatures with incorporation of PCL, as shown in Figures 4 and 5; this is an indication that these blends are immiscible. Thus, it is reasonable to conclude that the PHA chain mobility in the amorphous phase is not enhanced by blending with PCL. That is, the enhancement in the mobility of the PHA molecular chain in the amorphous phase with the change in the deformation mode is not a cause of the improvement in the mechanical properties of P(3HB-co-3HH). Therefore, another cause should be suggested.

Microscopic observation

Figure 6 shows SEM cross-sections of cast and melt-pressed films of PHA/PCL blends with 2.5, 10 and 20 wt% PCL after 1 month of aging. Each sample was observed before and after selective extraction of PCL with acetone. Characteristic void-containing structures were found in the cast films of the P(3HB-co-7 mol% 3HH)/PCL blend before PCL

Table 2 Thermal properties of the blends obtained from DSC thermograms shown in Figure 4

Sample	PCL/wt%	Peak$_{PCL}$/°C	ΔH_{PCL}/J g^{-1}	Crystallinity of PCL/%	$\Delta H_{P(3HB-co-3HH)}$/J g^{-1}	Crystallinity of P(3HB-co-3HH)/%
P(3HB-co-7 mol% 3HH) (cast)	0				70.7	53.3
	2.5	ND	ND	ND	66.7	50.3
	5	57.1	15.2	10.7	70.8	53.5
	10	59.1	38.0	26.8	73.1	55.1
	20	59.9	55.2	38.9	78.5	59.3
P(3HB-co-11 mol% 3HH) (melt press)	0				58.6	46.8
	2.5	56.5	50.5	35.6	62.1	49.6
	5	58.7	53.6	37.8	61.4	49.0
	10	59.6	56.1	39.5	62.1	49.6
	20	60.8	78.6	55.3	61.9	49.4

Abbreviations: PCL, poly(ε-caprolactone); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); ND, not detected.

Figure 5 DMTA tanδ of blend cast films aged for 1 month. (a) P(3HB)/PCL, (b) P(3HB-co-7 mol% 3HH)/PCL and (c) P(3HB-co-11 mol% 3HH)/PCL. DMTA, dynamic mechanical thermal analysis; PCL, poly(ε-caprolactone); P(3HB), poly(3-hydroxybutyrate); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).

the structural differences between PHA/PCL blends. Moreover, their characteristic structures should affect their mechanical properties.

There did not seem to be a great difference in the size of PCL domains between the cast and the melt-pressed samples, except for the P(3HB-co-7 mol% 3HH)/PCL blend with 20 wt% PCL. In addition, the size of the PCL domains did not seem to be significantly affected by the 3HH content. In all of the blend systems we studied, the domain size of the PCL phase in the blends became finer as PCL concentration decreased.

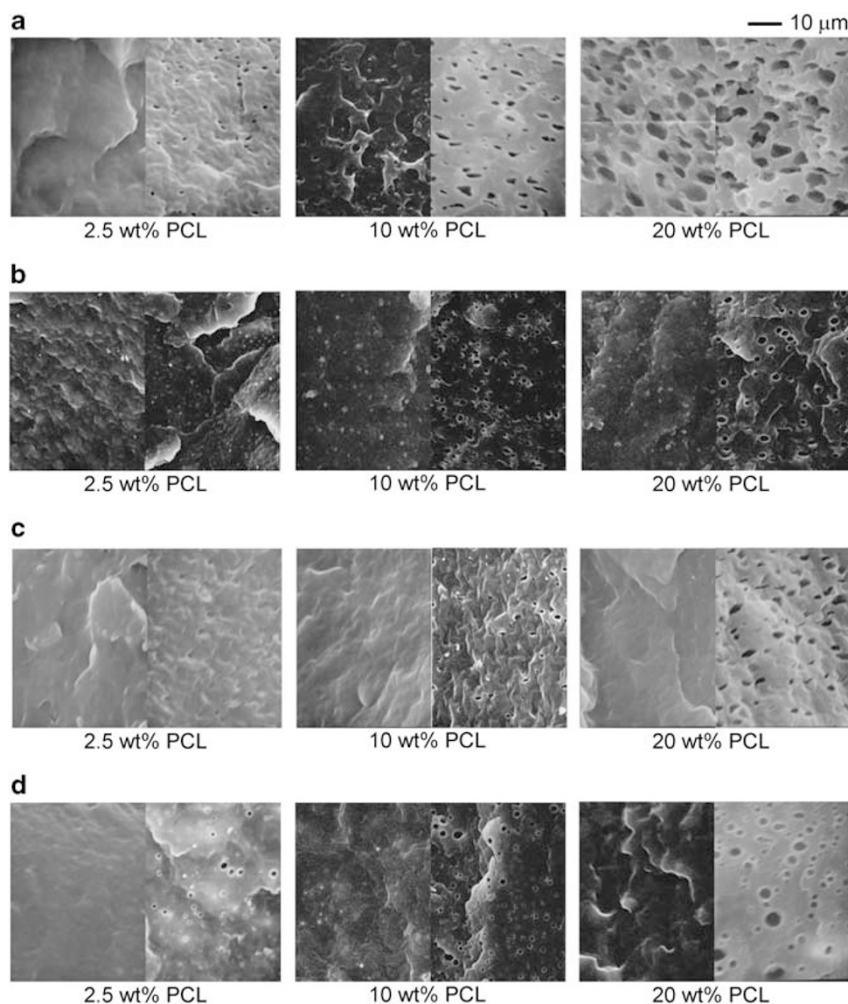## Plausible effect of PCL on mechanical properties

As discussed above, the microstructure and crystalline state are expected to be important for the improvement in toughness. Similar results have been reported by Noda et al.[36] They investigated the properties of blends of poly(lactic acid), which is hard and brittle, and a class of PHAs called Nodax. It was found that the addition of a small amount of PHAs effectively improved the toughness of poly(lactic acid) by inducing crazing deformation rather than the typical brittle fracture. This interesting result was assumed to derive from the finely dispersed PHAs, the crystallization of which unusually slowed down, and from the inclusion of soft liquid-like particles.

The similarity between Noda's and our cases is the conclusion that a small amount of immiscible semi-crystalline polymer could greatly improve the toughness of a blend. In both Noda's and our cases, soft particles that result from fine dispersion of the heterogeneous polymer in the matrix might deform preferentially, possibly indicating more ductile deformation of the surrounding polymer matrix. Eventually, the blends' toughness might be enhanced. Although PCL obviously crystallized to a certain degree, as observed in the DSC thermograms of Figure 4, the PCL domains are expected to be sufficiently soft to deform easily when their crystals are tiny and the crystallinity is low.

Another possible effect of PCL on the improvement in toughness is the delocalization of stress by the effective deformation of PCL domains. It is possible that toughness is equivalent to delocalization of stress.[37] The incorporation of heterogeneities into polymeric materials should be expected during molding. In addition, micro- or nano-scale cracks or voids might arise from secondary crystallization[38] and mechanical strains. Stress is locally concentrated in areas where polymeric materials are strained. Crazing involving void formation may dominate in these areas. When deformable particles are embedded in a matrix, the local stress will be delocalized, and brittle failure will be suppressed.

Microstructural modification

In consideration of the above, POM and SEM observations were performed in elongated samples to understand the effect of PCL on the modification of the mechanical properties of the blends. POM micrographs are shown in Figure 7 of elongated cast films of neat P(3HB-co-7 mol% 3HH) and P(3HB-co-7 mol% 3HH)/PCL blends; Figure 8 shows POM micrographs of the melt-pressed films of P(3HB-co-11 mol% 3HH) and P(3HB-co-11 mol% 3HH)/PCL blends at the tip of the neck. An obvious change in appearance was observed for the elongated cast films on going from the neat P(3HB-co-7 mol% 3HH) to the blends with 10 wt% PCL. For the neat P(3HB-co-7 mol% 3HH), the tip of the elongated sample became white with countless lines, indicating the occurrence of a crazing-cracking-type fracture. It is known that, under this deformation mode, micro-voids form inside a material which can be identified as the source of the characteristic whitening.[39,40] These micro-voids might easily be converted into cracks when the applied stress increases. This crazing is often observed in stiff and brittle materials.[41,42] The P(3HB-co-7 mol% 3HH) cast

extraction. Void size increased as PCL concentration increased. These voids were formed during preparation. Void formation was also observed in the cast films of P(3HB)/PCL blends (their micrographs are not shown). This may be due to the phase separation of the solution from a homogeneous phase to a PHA- and PCL-rich solution phase during evaporation of the solvent.[33–35] When PHA crystallizes and the material structure is set with the remaining PCL-rich domains of sufficient size, voids may form after evaporation of the residual solvent. Therefore, the formation of void-containing structures may depend on the crystallizability of PHAs. In general, the rate of crystallization and crystallinity of P(3HB) and P(3HB-co-3HH) decreases as the 3HH content increases.[7] This may be a source of

Figure 6 SEM cross-sections of (**a**) cast films of P(3HB-co-7 mol% 3HH)/PCL blends, (**b**) melt-pressed films of P(3HB-co-7 mol% 3HH)/PCL blends, (**c**) cast films of P(3HB-co-11 mol% 3HH)/PCL blends and (**d**) melt-pressed films of P(3HB-co-11 mol% 3HH)/PCL blends, with 2.5, 10 and 20 wt% PCL after 1 month of aging. Each sample was observed before (left) and after (right) extraction of PCL by acetone. PCL, poly(ε-caprolactone); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); SEM, scanning electron microscopy.

film became stiff and brittle over the aging period, and thereby showed crazing-cracking-type breaking. In contrast, PCL-containing blend films, even those in which the amount of PCL was small, showed good elongation and a reduced degree of whitening, indicating that shear yielding, usually observed in flexible materials,[43,44] occurred instead of crazing. From the appearance of the elongated cast films of P(3HB-co-7 mol% 3HH)/PCL blends, it was suggested that PCL, if its concentration was small, transformed the deformation mode of P(3HB-co-7 mol% 3HH) from crazing cracking to shear yielding. The white appearance of the cast film of the P(3HB-co-7 mol% 3HH)/PCL blend with 20 wt% PCL is due to its preexisting porous structure. Although it was impossible to determine whether whitening by crazing had or had not occurred, the surface of the deformed film was so smooth that the neck region could not be easily discerned, and the low yield stress in the stress-strain curve shown in Figure 1b indicates that the delocalization of the applied stress and the deformation of the film were effectively induced by the porous structure. As shown in Figure 3, although the elongation at break of the cast films of P(3HB-co-7 mol% 3HH)/PCL blends increased by PCL content up to 5 wt%, it decreased when more PCL was added. This may be due to the size of the voids in the films. As the PCL concentration increased,

the sizes of voids that formed during preparation increased. Although P(3HB-co-7 mol% 3HH) in the blends showed ductile deformation, the enlargement of the voids may have led to inhomogeneous stress delocalization. That is, the applied stress was too localized around the large voids to deform the entire material, thus possibly reducing the elongation at break. The modification of the mechanical properties of the melt-pressed films of the P(3HB-co-11 mol% 3HH)/PCL blend seemed to be different from the cast films of the P(3HB-co-7 mol% 3HH)/PCL blend. The melt-pressed film of neat P(3HB-co-11 mol% 3HH) broke immediately upon the first sign of crazing; blending with PCL changed its brittle deformation behavior to plastic flow with the production of the white elongation region. This would indicate that the applied stress, which was localized in the small crazing region in neat P(3HB-co-11 mol% 3HH), was delocalized by PCL to prevent crack propagation and to induce an increase in the number of craze-initiation sites. The cloud of craze initiation may have caused the improvement in the ductility of melt-pressed P(3HB-co-11 mol% 3HH).
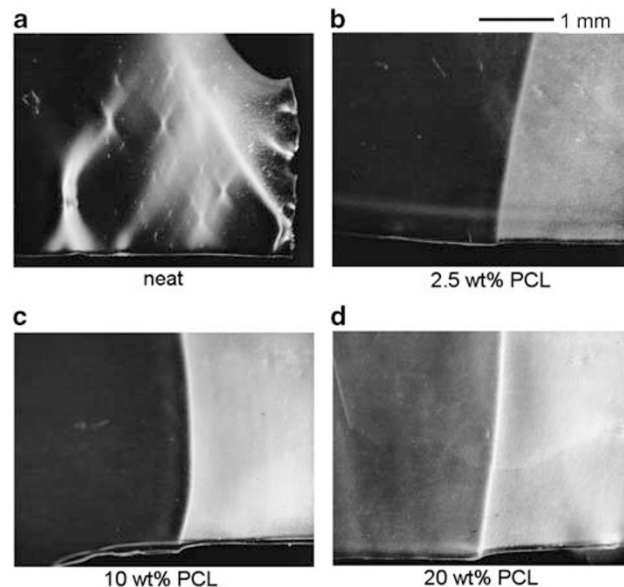
Figure 9 shows SEM micrographs of the elongated films. Blend samples were observed before and after extraction of PCL. In the cast films of P(3HB-co-3HH 7 mol% 3HH)/PCL blends, ellipsoidal voids

and similarly shaped PCL domains can be seen before and after PCL extraction, respectively. This suggests that both PCL domains and voids contributed to the delocalization of the stress applied to the samples and the beginning of plastic deformation around them. The cooperative effects of PCL and the voids may have effectively induced the change in the deformation mode of P(3HB-co-7 mol% 3HH) from crazing to shear yielding. In contrast, the melt-pressed films of P(3HB-co-11 mol% 3HH)/blends did not show such a structure. In SEM micrographs of the elongated melt-pressed films in which PCL was not extracted, on the left in Figure 9, each melt-pressed film showed such smooth surfaces that we could not detect any characteristic structural change. Figure 9 (right) shows the blend samples after

PCL extraction. Although ellipsoidal structures, which could be seen in the cast films of the P(3HB-co-7 mol% 3HH)/PCL blend, were not observed, the shape of the P(3HB-co-11 mol% 3HH)/PCL blend with 2.5 wt% PCL, the elongation of which at break was effectively improved, suggests that deformation of the film was initiated around the finely dispersed PCL domains to delocalize the stress applied to the sample. This might lead to a cloud of craze initiation. Although the structure of the melt-pressed film of the P(3HB-co-11 mol% 3HH)/ PCL blend with 2.5 wt% PCL was well regulated, by increasing the PCL content to 5 or 10 wt%, regularity was reduced and the matrix structure became disrupted, probably due to an enlargement of the PCL domains as seen in Figure 6. Therefore, delocalization of the
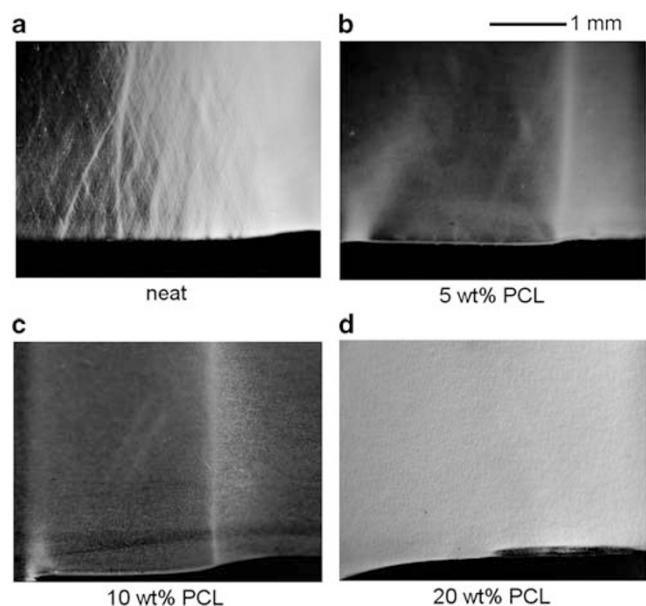
Figure 7 POM micrographs of elongated cast films at the tip of the neck after elongation. (a) P(3HB-co-7 mol% 3HH) and blends with (b) 5 wt% PCL, (c) 10 wt% PCL and (d) 20 wt% PCL. Each sample was aged for 1 month before elongation. PCL, poly(ε-caprolactone); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); POM, polarized optical microscopy.

Figure 8 POM micrographs of elongated melt-pressed films at the tip of the neck after elongation. (a) P(3HB-co-11 mol% 3HH) and blends with (b) 2.5 wt% PCL, (c) 10 wt% PCL and (d) 20 wt% PCL. Each sample was aged for 1 month before elongation. PCL, poly(ε-caprolactone); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); POM, polarized optical microscopy.
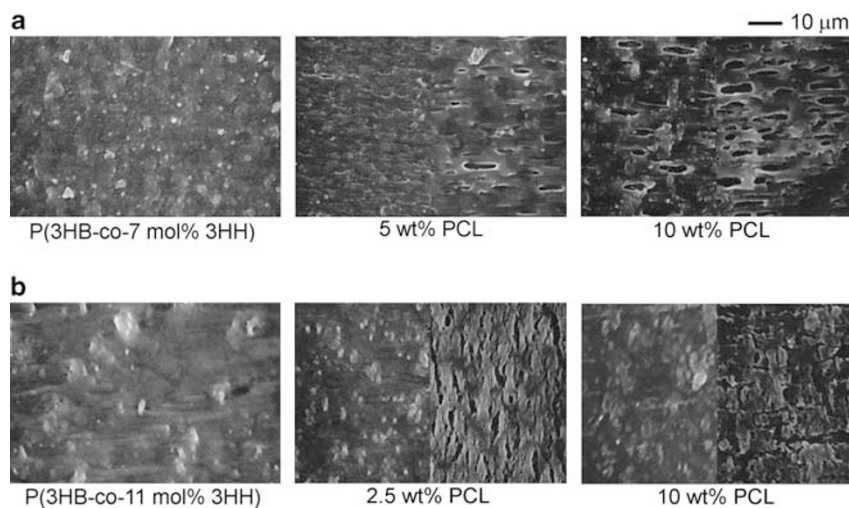
Figure 9 SEM micrographs of elongated (a) cast films of P(3HB-co-7 mol% 3HH) and blends with 5 and 10 wt% PCL and (b) melt-pressed films of P(3HB-co-11 mol% 3HH) and blends with 2.5 and 10 wt% PCL. Each sample was aged for 1 month before elongation. PCL, poly(ε-caprolactone); P(3HB-co-3HH), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); SEM, scanning electron microscopy.

applied stress became less effective and elongation at break decreased, as shown in Figure 3. The difference in the microstructural deformation change between the cast films of P(3HB-co-7 mol% 3HH)/PCL blends and the melt-pressed films of P(3HB-co-11 mol% 3HH)/PCL blends might be related to the deformability of the P(3HB-co-3HH) matrix formed by the corresponding copolymer composition and the preparation process.

CONCLUSIONS

Polyhydroxyalkanoates/PCL polymer blends were developed to improve the toughness of brittle PHAs after aging. Although miscibility of blend components could not be observed, it was interesting that only a small amount of PCL could increase the ductility of the PHA. The melting peak of PCL in DSC thermograms and SEM micrographs of the blends indicated that a small amount of PCL was finely dispersed and confined, therefore restricting its crystallization. Voids were observed in P(3HB-co-7 mol% 3HH)/PCL cast films. The fine PCL particles and voids seemed to deform preferentially with the transition from crazing to shear deformation. In the case of P(3HB-co-11 mol% 3HH)/PCL melt-pressed films, finely dispersed PCL seemed to deform preferentially to initiate a cloud of craze initiation and contributed to the improvement in the toughness of the blends.

These results suggest that the change in deformation mechanisms and the delocalization of applied stress are important for enhancing the toughness of aged P(3HB-co-3HH)s. A polymer blended with a small amount of PCL that is immiscible with P(3HB-co-3HH)s is a simple way to improve the mechanical properties and, thereby, to extend the applicability of PHAs.

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