

Control of Structure and Mechanical Properties for Binary Blends of Poly(3-hydroxybutyrate) and Cellulose Derivative

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ABSTRACT: Structure and mechanical properties for binary blends composed of a poly(3-hydroxybutyrate) (PHB) and a cellulose derivative, such as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB), have been studied by means of dynamic mechanical analysis, isothermal crystallization measurements, and tensile testing. It is found that β relaxation temperature due to glass transition of PHB or PHB-rich phase in the blends, in which the cellulose derivative has lower molecular weight, is almost the same as that of the pure PHB. On the other hand, the peak location is shifted to even lower temperature than that of the pure PHB

by blending the cellulose derivative with higher molecular weight, although the cellulose derivative is a glassy polymer with high glass transition temperature. Further, the blend with lower β relaxation temperature exhibits ductile behavior with low modulus in uniaxial deformation. The difference in the structure and mechanical properties for the blends are found to be determined by the crystallization rate. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3447–3452, 2007

Key words: biodegradable; blends; crystallization; miscibility; viscoelastic properties

INTRODUCTION

In these days, many pilot and/or commercial plants for poly(3-hydroxybutyrate) (PHB) and its copolymer are being constructed because of the attractive properties of PHB.^{1–4} In particular, mechanical and heat-resistant properties of PHB are somewhat similar to those of polypropylene (PP), one of the most successful polymers in the current petrochemical industry. As similar to PP, however, brittle behavior of PHB as well as the thermal degradation^{5–7} has to be improved to widen the application. Therefore, considerable efforts have been paid for blends with rubbery materials.^{8,9}

Meanwhile, miscibility of PHB with other polymers has been studied extensively to control the morphology of blends. In particular, cellulose derivatives, such as cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP), have been often employed for the investigation on the miscibility after the pioneering works by Scandola et al.^{10–13} and Buchanan et al.^{14,15} Scandola et al. demonstrated that PHB is miscible with CAB and CAP in the molten state by dynamic mechanical analysis and differential scanning calorimetric measurements. Furthermore, in blends having more than 50% of PHB, there are double peaks in the $\tan \delta$

curve due to glass transition, suggesting phase separation. According to them, this type of phase separation takes place during the crystallization of PHB from the homogeneous molten state.¹⁰ Buchanan et al. also found similar results by dynamic mechanical analysis. Further, they showed that blending 20–30 wt % of CAB enhances the tensile modulus as well as tensile strength.¹⁴ Furthermore, El-Shafee et al. revealed that Flory-Huggins interaction parameter between PHB and CAB is negative by the measurement of melting point depression of PHB.¹⁶ Moreover, Wang et al. investigated the mechanical properties of the blends composed of PHB and CAB and found that some blends show ductile behavior to some degree whereas the individual pure components are brittle materials.¹⁷ Finally, Park et al. studied the deformation process from spherulite texture into fibrous structure by X-ray diffraction for PHB/CAB blends.^{18,19} These previous works, however, have not revealed the effect of chemical composition, i.e., the species and/or amounts of substitution, as well as the molecular weight for cellulose derivatives on the miscibility and thus the structure of blends, although various types of cellulose derivatives are manufactured.

In this study, we employed various kinds of cellulose derivatives and studied the structure-properties relationship of the blends with PHB considering the kinetics of crystallization. Further, unique tensile properties for the blends composed of two brittle polymers are demonstrated.

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TABLE I
Characteristics of Raw Materials

	Composition (%)				Molecular weight	
	Acetyl	Propionyl	Butyryl	Hydroxyl	M_n	M_w
PHB	–	–	–	–	3.6×10^5	7.0×10^5
CAP46	2.5	46.0	–	1.8	7.7×10^4	2.0×10^5
CAB52	2.0	–	52.0	1.8	2.0×10^4	7.9×10^4
CAB38	13.5	–	38.0	1.3	2.5×10^4	6.1×10^4
CAB37	13.5	–	37.0	1.8	7.7×10^4	1.8×10^5

EXPERIMENTAL

Materials

The polymers employed in this study were a microbial poly(3-hydroxybutyrate) homopolymer, kindly supplied by PHB Industrial S/A in Brazil, and four types of cellulose derivatives produced by Eastman Chemical, such as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). The nomenclature used in this study is as follows: e.g., CAP46 is CAP with 46% of propionyl and CAB52 is cellulose acetate butyrate with 52% of butyryl. The contents of propionyl, butyryl, acetyl, and hydroxyl are listed in Table I. Further, the molecular weight and its distribution, evaluated by a gel permeation chromatograph, (GPC), (Tosoh, HLC-8020) with TSK-GEL[®] GMHXL, are also shown in Table I as a polystyrene standard. In GPC measurements, the concentration of the sample was 1.0 mg/mL. The measurements were carried out at 40°C at a flow rate of 1.0 mL/min employing chloroform as an eluant.⁷

The polymers were mixed together with small amounts of thermal stabilizers at 180°C for 1.5 min in an internal batch mixer (Toyoseiki, Labo-plastmil) at a rotor rate of 40 rpm. The blend ratio was 8/2 (PHB/cellulose derivative, w/w). Flat sheets of the blends were prepared by a compression-molding machine (Tester Sangyo, SA303IS) at 180°C for 3 min. The molten samples were cooled down in another compression-molding machine kept at 40°C for 5 min to crystallize PHB fraction.

Measurements

The oscillatory tensile moduli, such as tensile storage modulus E' , loss modulus E'' , and loss tangent $\tan \delta$, were measured employing a rectangular sample with 4 mm × 20 mm × 0.3 mm by a dynamic mechanical spectrometer (UBM, DVE E4000) conducted at 10 Hz. The heating rate was 2°C/min.

The growth rate of a spherulite radius was also measured by a polarizing optical microscope (Leica, DMPLP) equipped with a hot stage (Mettler, FP90). The sample set between cover glasses was cooled down from 200 to 120°C at a rate of 20°C/min. Then, the ra-

dius of a spherulite was measured isothermally as a function of the residence time at 120°C.

Tensile testing was carried out by a tensile machine (Tokyo Testing Machine, Little Senstar) at room temperature. The sample specimens with ASTM D1822L were cut out from the plate with 0.3 mm thickness by a razor blade. The stretching speed was 100 mm/min and the initial distance between the crossheads was 35 mm.

RESULTS AND DISCUSSION

Dynamic mechanical properties in solid state

Figure 1 illustrates the temperature dependence of oscillatory tensile moduli, such as storage modulus E' , loss modulus E'' , and loss tangent $\tan \delta$, for PHB, CAB52, PHB/CAB52 (8/2), CAP46, and PHB/CAP46 (8/2).

As depicted in Figure 1(a), PHB exhibits typical dynamic mechanical properties for semicrystalline polymers. The broad peak in the E'' and $\tan \delta$ curves in the temperature range between 70 and 150°C is attributed to α relaxation, which is ascribed to the relaxation of crystalline-grain boundaries, such as dislocation of lamellae with a frictional resistance related to disordered interface layers.²⁰ Further, β relaxation peak, due to the glass transition, is also identified at around 20°C. The storage modulus E' decreases around room temperature and then falls off sharply at 170°C due to melting. The locations of the relaxation temperature are quite similar to those of a conventional polypropylene.

In case of CAB52, as shown in Figure 1(b), typical dynamic mechanical properties for glassy polymers are observed. The modulus keeps almost constant and drops off around 110°C due to glass transition. CAP46 also shows similar dynamic mechanical properties, although the modulus falls off at a higher temperature, i.e., ~150°C [Fig. 1(d)].

Further, the oscillatory moduli for the blends with 20% of a cellulose derivative are exemplified in Figures 1(c) and 1(e). As seen in the figure, dynamic mechanical properties for PHB/CAB52 are quite similar to those of the pure PHB, whereas PHB/

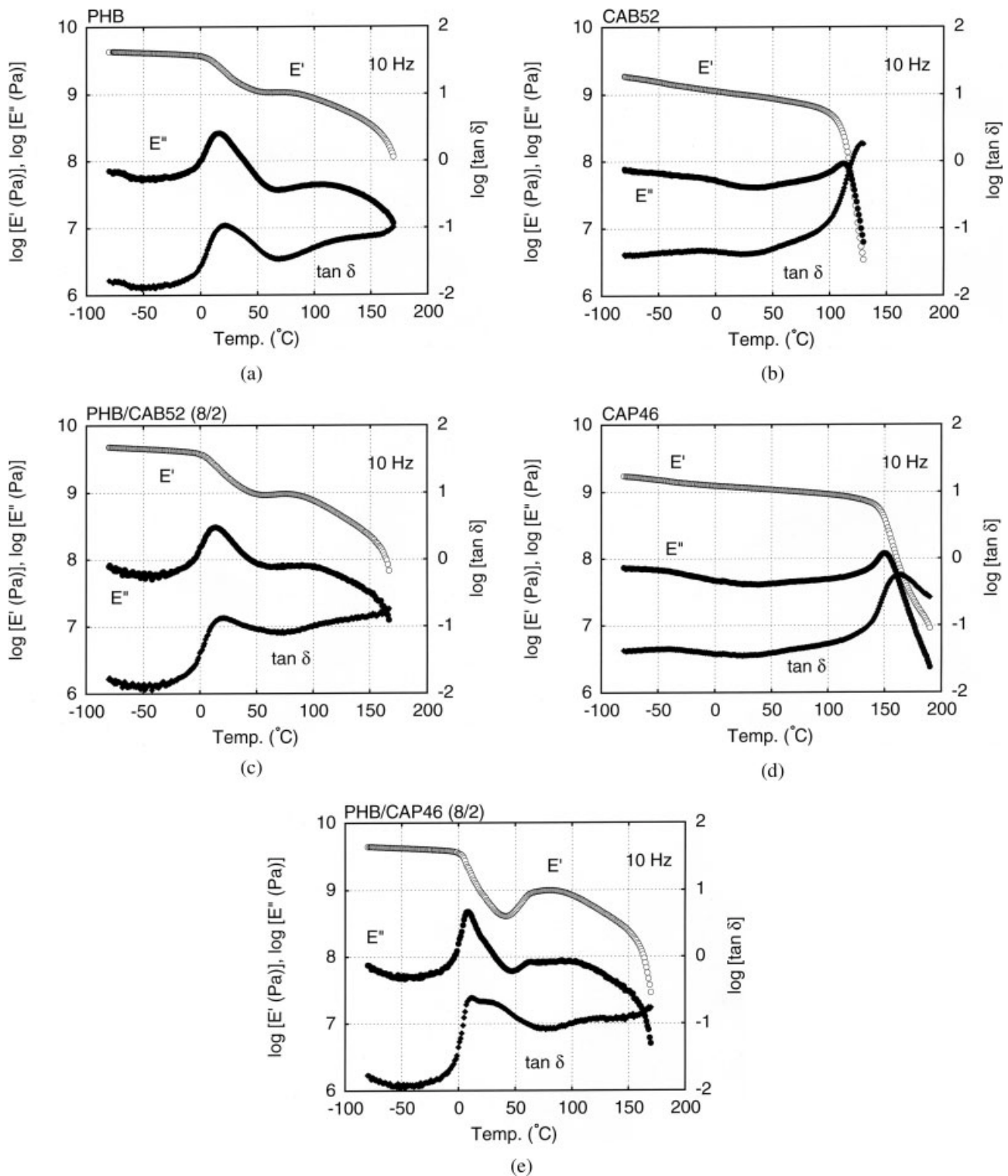


Figure 1 Temperature dependence of oscillatory tensile moduli, such as storage modulus E' (○), loss modulus E'' (●), and loss tangent $\tan \delta$ (◆), at 10 Hz for (a) PHB, (b) CAB52, (c) PHB/CAB52 (80/20), (d) CAP46, and (e) PHB/CAP46 (80/20).

CAP46 exhibits considerably different curves especially around β relaxation.

For the better understanding of the difference in dynamic mechanical properties, the oscillatory moduli, such as storage modulus E' and loss modulus

E'' , in the temperature range around β relaxation are plotted for all blends in Figure 2. It is obvious that the level of E' for PHB/CAP46 and PHB/CAB37 is lower than that of PHB, especially around at room temperature, i.e., β relaxation temperature, and then

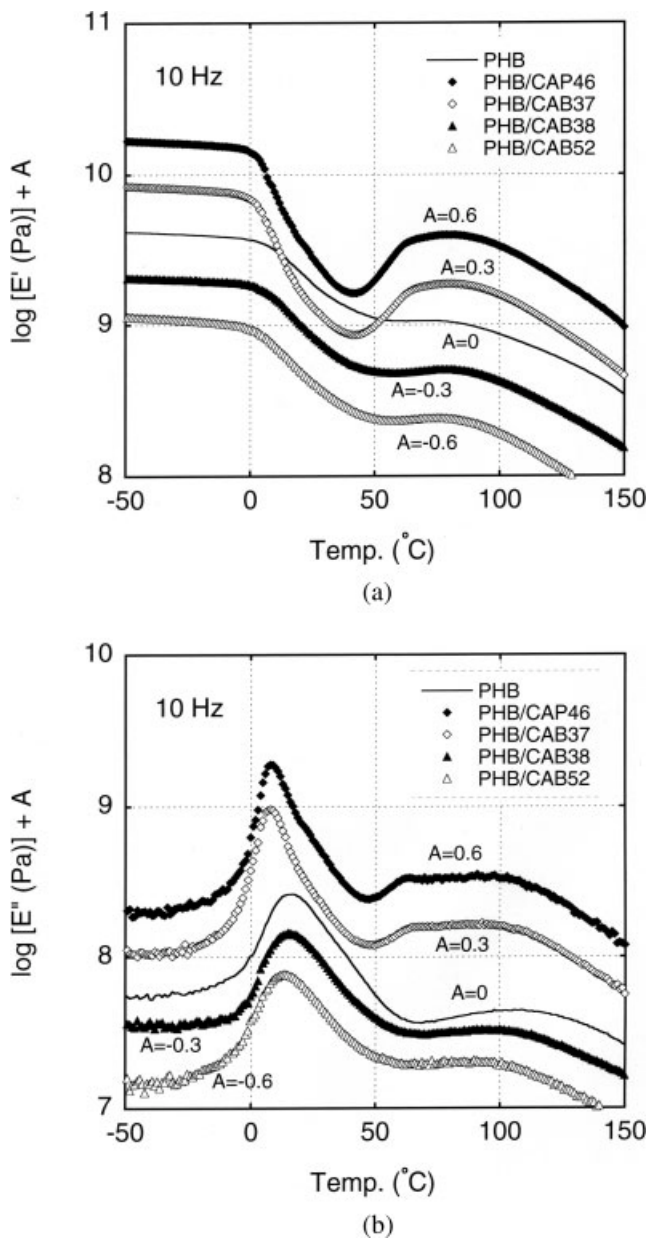


Figure 2 Temperature dependence of oscillatory tensile moduli, such as (a) storage modulus E' and (b) loss modulus E'' at 10 Hz for the pure PHB and blends with 20% of a cellulose derivative; (—) PHB, (◆) PHB/CAP46, (◇) PHB/CAB37, (▲) PHB/CAB38, and (△) PHB/CAB52.

increases with temperature after taking a minimum around at 40°C, which is quite different from that of PHB/CAB38 and PHB/CAB52. The increase in E' will be attributed to the crystallization of PHB fraction during the measurement, indicating the original specimens, i.e., the sample sheets processed by compression-molding have low degree of crystallinity. Further, it is demonstrated in the E'' curves that the peak temperatures due to β relaxation for PHB/CAP46 and PHB/CAB37 are located even at lower temperature than that of the pure PHB, although the

blends are composed of a higher T_g fraction; 140°C for CAB37 and 150°C for CAP46 as a peak temperature in the E'' curve. Moreover, the peak seems to be even sharp when compared with that of the pure PHB. On the other hand, β relaxation for PHB/CAB38 and PHB/CAB52 are located at almost the same temperature as that for the pure PHB.

Crystallization rate

The spherulite growth rate at isothermal crystallization is measured to evaluate the effect of blending a cellulose derivative on the crystallization rate of PHB in the blends. As shown in Figure 3, blending a cellulose derivative leads to a great depression of the spherulite growth rate, i.e., the slope in the figure, demonstrating that a cellulose derivative and PHB are miscible in the molten state. It is also seen from the figure that the radius of a spherulite increases linearly with crystallization time, suggesting that the concentration of PHB in the molten region is constant. These results correspond with the literature.¹³

Further, the figure demonstrates that the depression of crystallization rate is prominent for the blends with CAP46 and CAB37, as compared with the other ones. The difference in the growth rate would be mainly attributed to the molecular weight, because CAB37 has a similar chemical composition to CAB38. Higher molecular weight of CAP46 and CAB37, which are miscible with PHB in a molten state, is responsible for higher viscosity and then the reduction of the molecular diffusion of PHB chains during crystallization.

Considering the kinetics of crystallization, the low degree of crystallinity of PHB fraction will be the or-

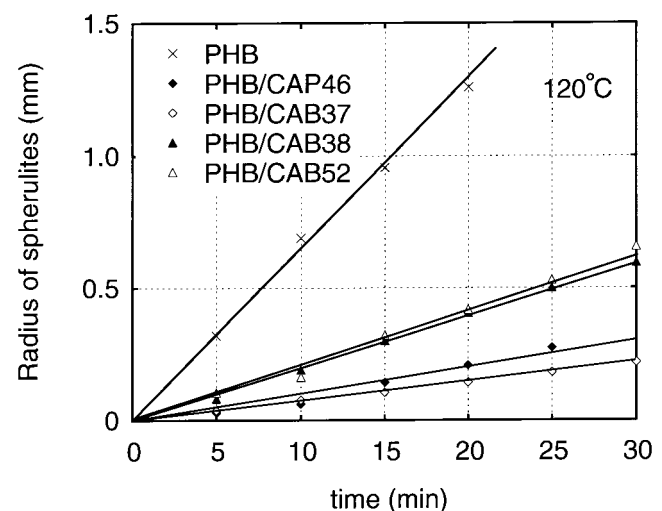


Figure 3 Growth curves for radius of spherulite during isothermal crystallization at 120°C for (×) PHB, (◆) PHB/CAP46, (◇) PHB/CAB37, (▲) PHB/CAB38, and (△) PHB/CAB52.

origin of the anomalous viscoelastic behavior, i.e., depression of β relaxation temperature and the low level of storage modulus around β relaxation, for the blends with CAP46 and CAB37. It is generally believed that there are various types of amorphous chains, such as loop chain, tie chain, cilia chain, and floating chain, in a semicrystalline polymer from the viewpoint of molecular motions.^{21,22} For loop chains and tie chains, both ends are trapped in crystallites, one end is trapped for cilia chains, and both ends are free for floating chains. The variation of molecular mobility for amorphous chains leads to a broad relaxation peak as compared with that of fully amorphous polymers. Further, as higher population in floating chains, which increases with decreasing the degree of crystallinity, β relaxation peak shifts to lower temperature because of the enhanced mobility. This would be responsible for the anomalous viscoelastic properties in this study.

The effect of chemical composition of cellulose derivatives is, however, not clarified in this study. Further experiments considering the diffusion constant at crystallization temperature will be required to discuss the effect of chemical composition on the miscibility with PHB, because this study has proved that the molecular weight of cellulose derivatives affects the blend structure to a great extent.

Tensile properties

The tensile properties for PHB, PHB/CAP46, and PHB/CAB52 are illustrated in Figure 4. As for cellulose derivatives, it is impossible to cut the specimens out from the plate because they are too brittle. In the figure, the engineering stress is plotted against the nominal strain. Although both CAP46 and CAB52 are quite brittle materials, the blends show larger elongation at break than the pure PHB. Further, there is a significant difference in tensile properties between PHB/CAP46 and PHB/CAB52, yet the amount of a cellulose derivative is the same. The ductile property with low modulus for PHB/CAP46 is attributed to the low degree of crystallinity.

CONCLUSIONS

The structure and properties for the binary blends of PHB with a cellulose derivative are studied employing four types of cellulose derivatives. It is found that the blend of PHB and the cellulose derivative with high molecular weight shows slow crystallization rate, which leads to the increase in amorphous chains of PHB fraction. The β relaxation temperature due to glass transition for such type of blends is located at lower temperature than that of the pure PHB, although the cellulose derivative has high glass

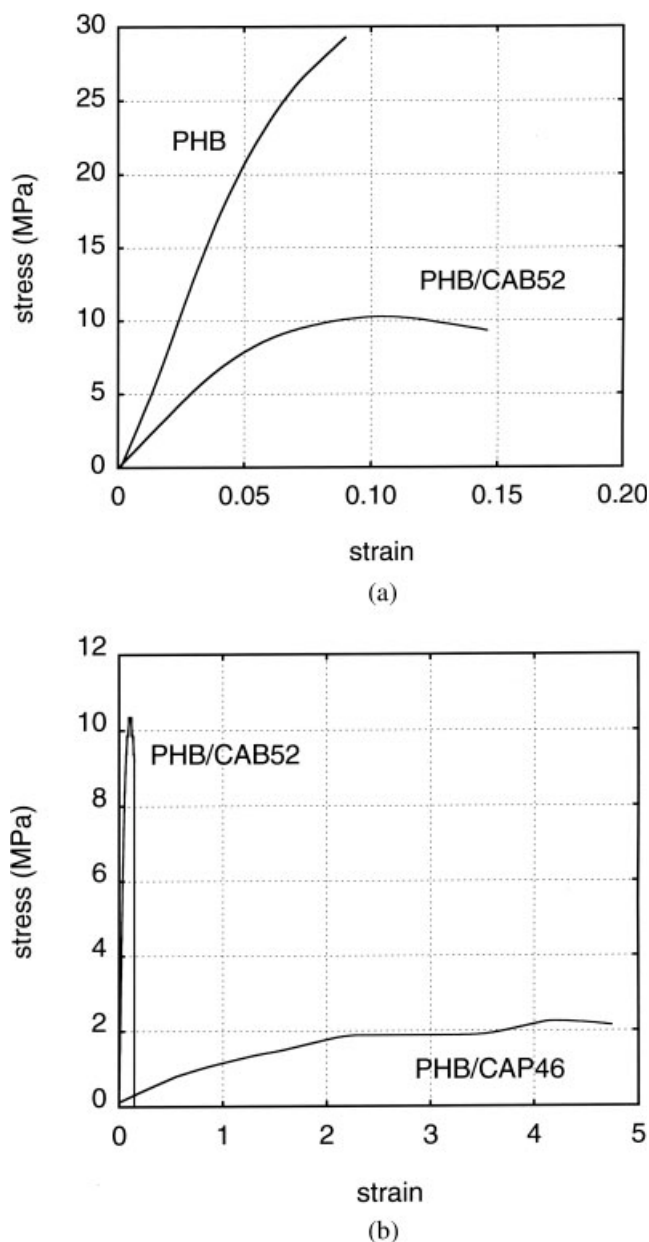


Figure 4 Stress-strain curves at 23°C for (a) PHB and PHB/CAB52 (8/2) and (b) PHB/CAB52 (8/2) and PHB/CAP46 (8/2).

transition temperature. These anomalous dynamic mechanical behaviors are explained considering the enhanced mobility of amorphous PHB chains by the reduction of crystallites, which act as a constraint. Consequently, the blend of the cellulose derivative with high molecular weight deforms largely in a ductile manner. In other words, mechanical toughness of PHB would be improved by controlling the amorphous fraction, which is attained by blending the cellulose derivative with high molecular weight.

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