Preparation of Cellulose Acetate Butyrate and Poly(ethylene glycol) Copolymer to Blend with Poly(3-hydroxybutyrate)

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ABSTRACT: A two-step procedure was used to synthesize the cellulose acetate butyrate and poly(ethylene glycol) graft copolymer (CAB-*g*-PEG). By choosing the appropriate composition, the crosslinked graft copolymer or not could be obtained. Then, the CAB-*g*-PEG copolymer was blended with poly(3-hydroxybutyrate) (PHB), to further improve the mechanical properties of PHB. The results indicated that PHB and CAB-*g*-PEG that were not crosslinked were miscible over the entire composition range. As the CAB-*g*-PEG copolymer increased in the PHB/CAB-*g*-PEG blends, the melting temperature of the blends decreased, the crystallization of PHB became more difficult, and the crystallinity of the blend and PHB phase all decreased. The tensile properties and impact strength of the PHB/CAB-*g*-PEG blends were superior to the PHB/CAB blends. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1471–1478, 2006

Key words: poly(3-hydroxybutyrate); graft copolymers; blends; miscibility; mechanical properties

INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is a very useful biodegradable thermoplastic polymer that can be used in many fields.[1] However, its application is limited, because it is very brittle, with a low elongation at break, and easily degrades at the temperature slightly higher than its melting point. To improve the inferior properties of PHB, there have been many attempts to copolymerize PHB with other hydroxyalkanoates, resulting in various poly(hydroxyalkanoate)s (PHA), ranging from thermoplastic polymers to rubbery elastomers.[2,3]

Blending of PHB with other polymers has also been studied extensively. These polymers include poly(vinyl acetate),[4] poly(ε-caprolactone),[5] poly(vinyl alcohol),[6] chitin and chitosan,[7] etc. To get the blends that can be completely degradable, study on blends of PHB with degradable polymer has also been reported. For example, PHB has been used in blends with poly(ethylene oxide)[8] and cellulose derivatives,[9–11] such as cellulose propionate, cellulose acetate butyrate (CAB), and cellulose acetate propionate, etc.

Our team also studied the PHB/CAB blends before.[12] Our purpose is to find the relationship between the blend morphology and physical properties, but more important is to seek a means of making the best use of this degradable polyester. Unfortunately, we found that the mechanical properties of PHB/CAB blends were not greatly improved to meet the needs of practical use. To further improve the properties of PHB, the graft copolymer of CAB and poly(ethylene glycol) (CAB-*g*-PEG) was first prepared, and then blended with PHB. In this article, the miscibility, crystallization behavior, mechanical properties and biodegradability of PHB/CAB-*g*-PEG blends were studied, and the synthetic procedures and characterization of CAB-*g*-PEG copolymer were also investigated.

EXPERIMENTAL

Materials

PHB was kindly supplied by Tianjin Tianlu Food Co., Ltd (Tianjin, China), with $M_n = 4.3 \times 10^5$ and $M_w/M_n = 1.49$ (obtained by gel-permeation chromatography in chloroform at 30°C). CAB was purchased from Wuxi Chemical Industry Institute (Wuxi, China), with $M_n = 3.0 \times 10^4$. The content of butyryl was 55%, acetyl 4%, and hydroxyl 2% (the content of hydroxyl obtained by titration method using pyridine and acetic anhydride as cosolvent), and the limiting inherent viscosity was 0.4 Pa s. PEG ($M_n = 1000$), acetone, methanol, 2,4-toluene diisocyanate, dibutyl tin dilau-

TABLE I
The Synthetic Recipe of Graft Copolymer CAB-g-PEG

	TD (mL)	PEG (g)	CAB (g)
Recipe I	2.852	10	4.25
Recipe II	0.7131	2.5	4.25

rate were all AR grade and obtained from Tianjin chemicals Co., Ltd.

Synthesis of PHB-g-PEG copolymer

A two-step procedure was used to obtain the CAB-g-PEG copolymer: the first step was reaction between PEG and TDI, to get the prepolymer NCOPEG, and then grafting of NCOPEG on the CAB.

PEG, CAB, and acetone were first dried, and then PEG (1:5 wt) and CAB (1:10 wt) were dissolved in acetone, respectively.

TDI and a small amount of dibutyl tin dilaurate (catalyst) were dissolved in acetone at 55°C, under stirring and nitrogen atmosphere. After the solution was stirred for 0.5 h, PEG solution was introduced dropwise (the quantity of TDI is twice as much as PEG), after which the temperature was raised to 60°C and maintained at this temperature for 0.5 h, to obtain the prepolymer NCOPEG. Then, CAB solution was added to the NCOPEG solution. The reaction proceeded under stirring and N_2 atmosphere, at 60°C for 1–2 h. At last, some methanol was added to eliminate the unreacted isocyanate group. Then, the product mixture was precipitated in distilled water and extracted for 24 h by distilled water. The CAB-g-PEG copolymer thus obtained was dried under vacuum at 60°C. Table I was the synthetic recipe of the graft polymer CAB-g-PEG.

Characterization of PHB-g-PEG copolymer

Fourier transform infrared (FTIR) spectra of CAB-g-PEG and CAB were recorded on Nicolet MAGNA IR-550 (Series II) spectrometer.

Nuclear magnetic resonance (13C NMR) spectra of CAB-g-PEG and CAB were recorded on Varian UNITY-plus 400 spectrometer at 400 MHz, using tetramethylsilane as an internal reference and $CDCl_3$ as the solvent.

Preparation of blends

Weighed amounts of the two components were first mixed in the HL-28 smash machine (Shanghai Hailin Ltd., Shanghai, China). PHB/CAB and PHB/CAB-g-PEG blends were obtained by melt-mixing at 170–180°C (according to the blend composition). The temperature was controlled precisely to minimize thermal degradation of PHB. The blend compositions were denoted as PHB along with the weight percentage of PHB and the code name of CAB-g-PEG synthetic recipe. For example, PHB90(I) indicated PHB was blended with CAB-g-PEG, obtained from the synthetic recipe I, and the weight percentage of PHB was 90%.

Analytical procedure

A DSC-204 thermal analyzer (Netzsch Ltd., Germany) was used to study the thermal properties of the PHB/CAB-g-PEG blends. To eliminate the influence of different thermal histories, the samples were first heated from room temperature to 190°C (run I). After being held for 1 min at 190°C, the samples rapidly quenched to −100°C, and this was followed by heating from −100 to 220°C (run II). A scan rate of 10°C/min was used.

The shapes of the PHB spherulites in the blends were observed by polarizing optical microscopy (POM). The samples were first heated to 190°C and were kept at this temperature for 1 min. The temperature was then lowered to room temperature, and then the PHB was allowed to crystallize. An Olympus POM (Japan) equipped with a hot stage was used.

Dumbbell-shaped samples of PHB/CAB and PHB/CAB-g-PEG blends were used for tensile tests. The stress at break (MPa) and elongation at break (%) of the tested samples were measured with an M500–25KN universal testing machine (Testometric Co. Ltd., UK) at room temperature. The extension rate was 10 mm/min. The fracture surfaces of the blends were investigated with SEM (Hitachi X-650, Japan). Standard samples of PHB/CAB and PHB/CAB-g-PEG blends were used for impact tests. The impact resistance was tested with a CHAPPY XCJ-500 impact tester (Ceast Ltd., Italy). All the results were derived, averaging five experimental values, for each composition.

The degradation studies were conducted at 25°C in natural lake water (Youth Lake, Tianjin, China) and stored in glass containers. The blends were taken out from water over a period of time, washed with distilled water, and subsequently dried at 100°C for 2 h. The degradation rate was determined by the following equation:

$$S = (W_0 - W_t)/W_0$$

where S was the rate of weight loss, W_t and W_0 were the weights after drying and the initial weight of the blends, respectively.
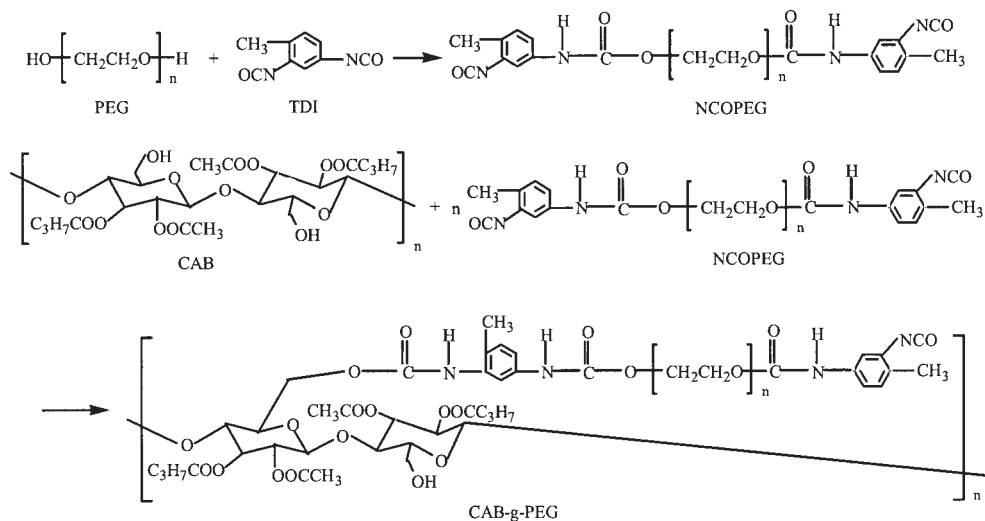
Figure 1 The two-step synthetic route of graft copolymer CAB-g-PEG.

RESULTS AND DISCUSSION

Synthesis and characterization

The choice of composition in synthesis

Figure 1 shows the two-step synthetic route of copolymer CAB-g-PEG. Hydroxyl end groups of PEG react with TDI to form NCOPEG, with isocyanate end groups. No chain propagation reaction occurs in this process, because the PEG solution is added dropwise and the quantity of TDI is twice as much as PEG. The hydroxyl end groups of PEG are changed to isocyanate groups, and the prepolymer NCOPEG, in which the average degree of functionality per polymer chain (for isocyanate group) is 2, is obtained.

The number average molecular weight of CAB is 3.0 $\times$ 10^4. The hydroxyl content of CAB is 2% (1.176 $\times$ 10^{-3} mol OH/g CAB). From these, we can know the average degree of functionality per CAB chain (for hydroxyl group) is 35.3. So, the grafting reaction of NCOPEG on the CAB is a multifunctional group system. By choosing different composition, the crosslinked graft copolymer or not could be obtained.

According to Carothers equation,

$$f = 2N_A f_A / (N_A + N_B) \qquad (1)$$

where f is the total average degree of functionality; N_A, N_B, and f_A, f_B are the mole fraction and the average degree of functionality per polymer chain of component A and B, and the total of A functional group is less than B functional group in the reaction system ($N_A f_A < N_B f_B$).

The critical extent of reaction P at gel point is given as follows:

$$P = 2/f = (N_A + N_B)/N_A f_A \qquad (2)$$

Now, keeping the quantity of CAB constant (4.25 g, 1.417 $\times$ 10^{-4} mol, the hydroxyl groups was 0.005 mol), the change of gel point P with the quantity of PEG (W) is studied:

1. $W < 2.5$ g: The total of isocyanate group is less than hydroxyl group in the reaction system, and the gel point is given as follows:

$$P = 2/f = (N_A + N_B)/N_A f_A = (W/1000 + 1.417$$
$$\times\ 10^{-4})/(2W/1000) = 0.07085/W + 0.5 \qquad (3)$$

2. $W > 2.5$ g: The total of isocyanate group is more than hydroxyl group in the reaction system, and the gel point is given as follows:
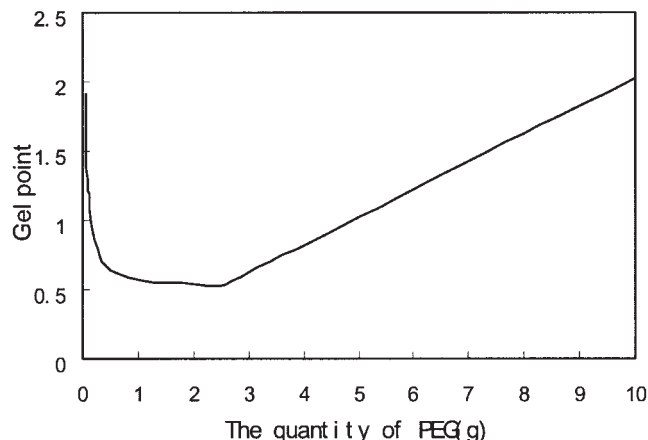

Figure 2 Gel point of grafting reaction versus the quantity of PEG (CAB 4.25 g, 1.417 $\times$ 10^{-4} mol; the hydroxyl groups was 0.005 mol).
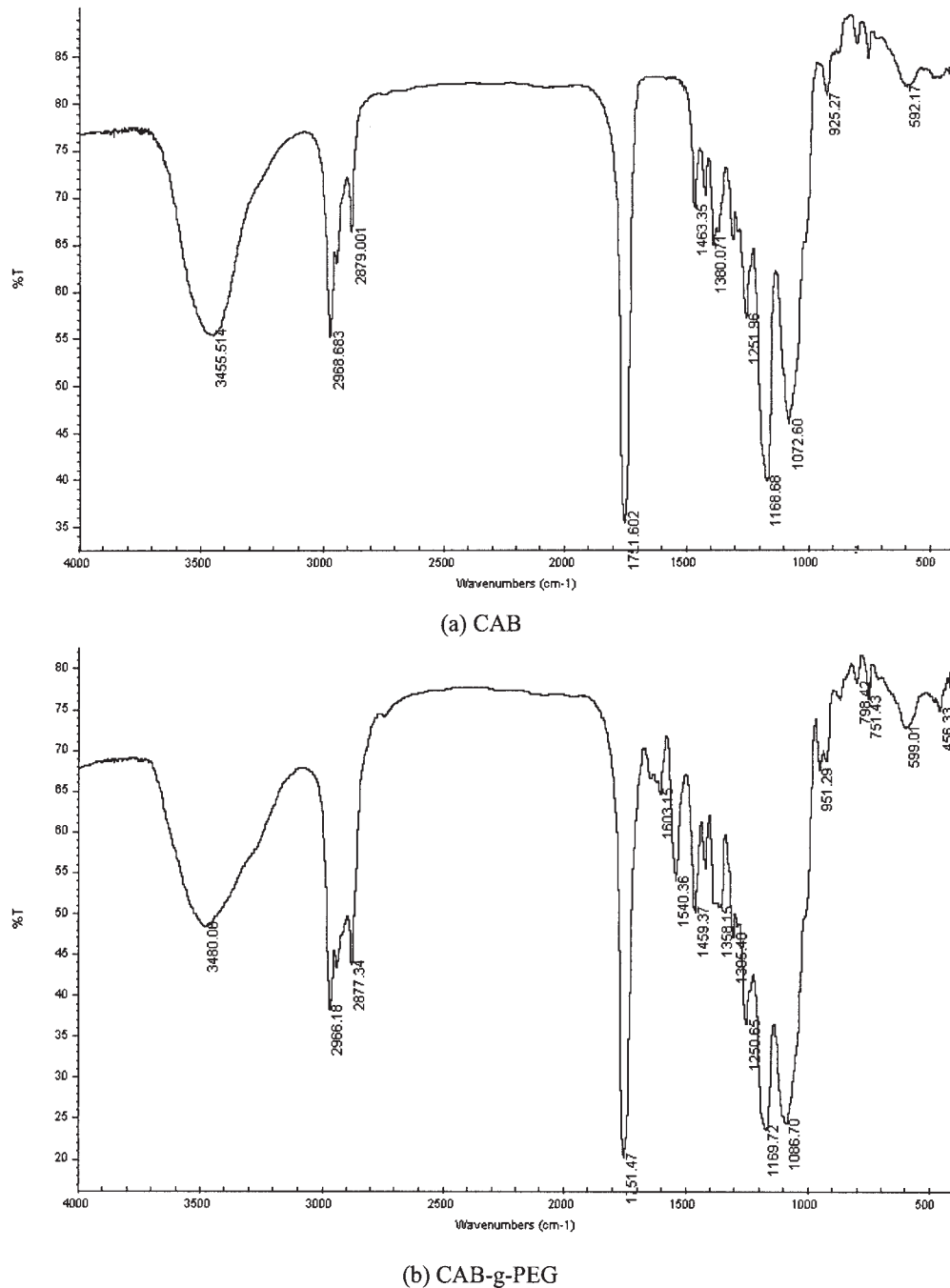
(a) CAB

(b) CAB-g-PEG

Figure 3 The infrared spectra of CAB and CAB-*g*-PEG.

$$P = 2/f = (N_A + N_B)/N_A f_A = (1.417 \times 10^{-4}$$
$$+ W/1000)/(35.3 \times 1.417 \times 10^{-4}) = 0.2W$$
$$+ 0.02833 \quad (4)$$

3. $W = 2.5$ g: eq. (4) is equal to eq. (5).

Figure 2 shows the change of gel point with the quantity of PEG. In the synthetic recipe I, the gel point is 2.0283, and no crosslinking reaction occurs. While in the recipe II, the gel point is 0.5283, with lowest gel point, and crosslinking reaction occurs most easily. In the following sections, blending of PHB with these two kinds of graft copolymers are discussed.

Characterization of PHB-*g*-PEG copolymer

The FTIR spectra of CAB and the purified copolymer CAB-*g*-PEG are shown in Figure 3. For the graft copolymer, the spectrum shows three absorption bands
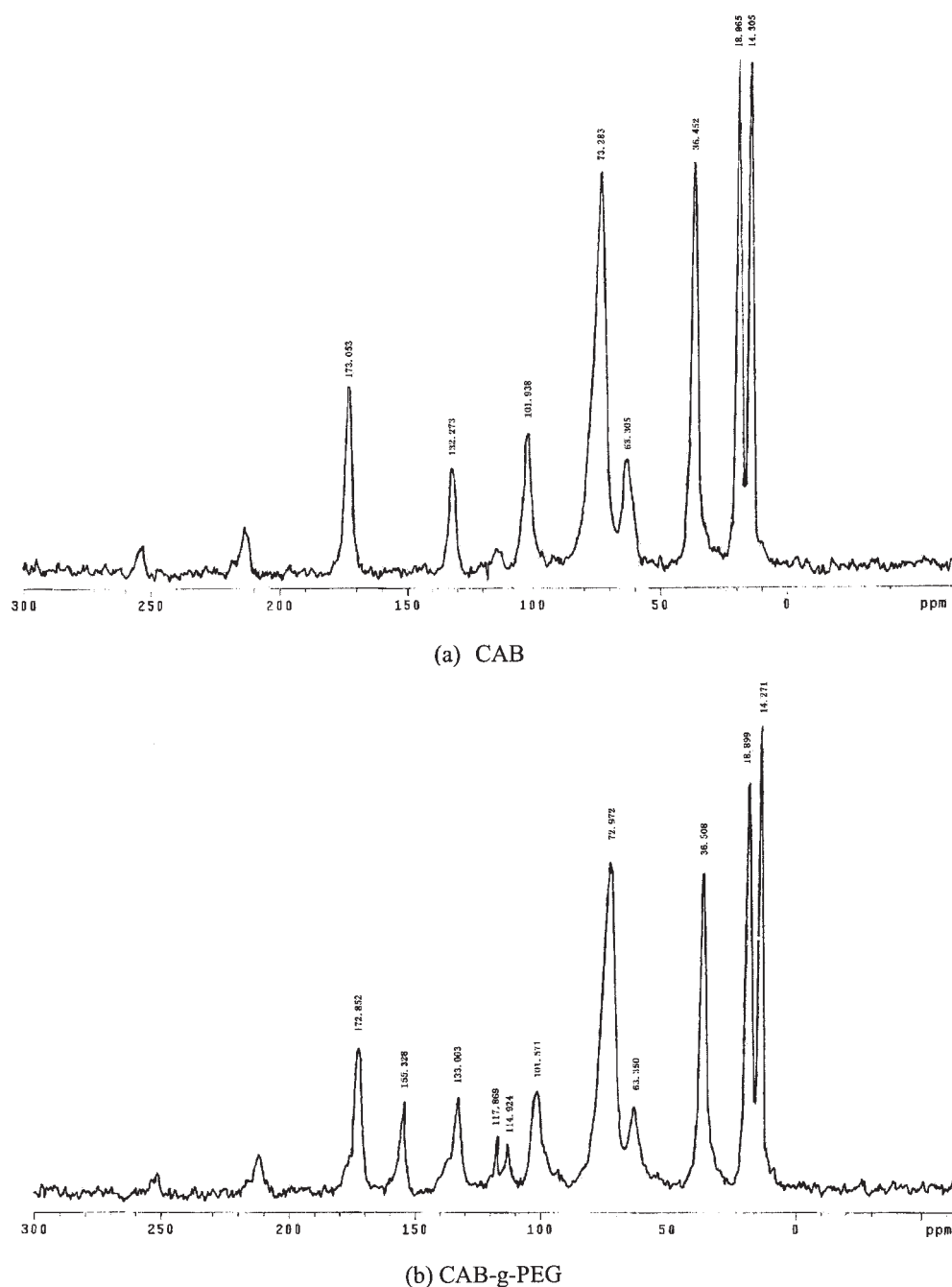
(a) CAB

(b) CAB-g-PEG

Figure 4 The ^{13}C NMR spectra of CAB and CAB-*g*-PEG.

that cannot be seen in CAB spectrum. At 1650 cm^{-1} and 1540 cm^{-1} for acid amide groups, and at 1603 cm^{-1} for C=C of benzene ring. The FTIR analysis indicates that carbamate was obtained by the reaction between CAB and PEG.

In Figure 4 ^{13}C NMR spectrum of CAB is compared with that of CAB-*g*-PEG copolymer. Carbon peaks at 114.9 and 117.8 ppm were attributed to the carbons of benzene ring. The carbon peak at 155.3 was attributed to the carbonyl of carbamate.

The FTIR and ^{13}C NMR analysis confirm the synthesis of the copolymer CAB-*g*-PEG.

On PHB/CAB-*g*-PEG blends

Miscibility and crystallization behaviors

The DSC thermograms of PHB/CAB-*g*-PEG (recipe I) blends are shown in Figure 5 (run II). Glass transition temperature (T_g), melting temperature (T_m), cold crystallization temperature (T_{cc}), and crystallinity (W), obtained in Figure 5, are listed in Table II.

The CAB-*g*-PEG copolymer is rubbery at room temperature, and no melting peak can be seen in the DSC thermogram. When the content of PHB in the blends is higher than 40 wt %, an obvious melting peak can be
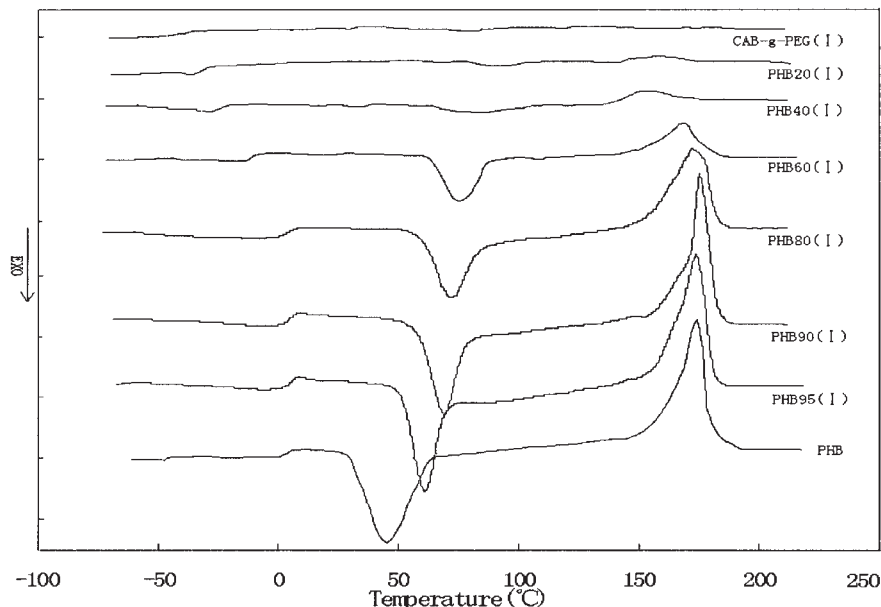
Figure 5 DSC thermograms of PHB/CAB-g-PEG blends.

seen. With increasing copolymer in the blends, the T_m of PHB phase decreases. The decrease in observed T_m, with an increase in CAB-g-PEG content, is what one would expect for a miscible system.[13,14]

T_g of the blends is plotted in Figure 6 as a function of composition. The line drawn in Figure 6 was calculated using the Fox equation[15]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \qquad (5)$$

where W_1, W_2 and T_{g1}, T_{g2} are the weight fraction and T_g of components 1 and 2, respectively. The fact that the T_g of the blends containing 0–60% of PHB follows the prediction of Fox equation is a good indication that the system is miscible over this composition. The blends containing more than 60% of PHB have nearly a constant T_g, located in proximity to the T_g of PHB.

The overall trend is in agreement with previous study on PHB/CAB blends.[12] In fact, this system is miscible over the entire composition range, for no evidence was found for a second lower temperature, T_g, as the blends contain more than 60% of PHB. The trend in T_g is ascribed to the presence of two mobilization processes in a homogeneous blend.

The crystallinity of the blends and PHB phase listed in Table II was calculated by using the following equation:

$$\chi_{\text{blend}}(\%) = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \qquad \chi_{\text{PHB}}(\%) = \frac{\chi_{\text{blend}}}{W_{\text{PHB}}} \times 100 \quad (6)$$
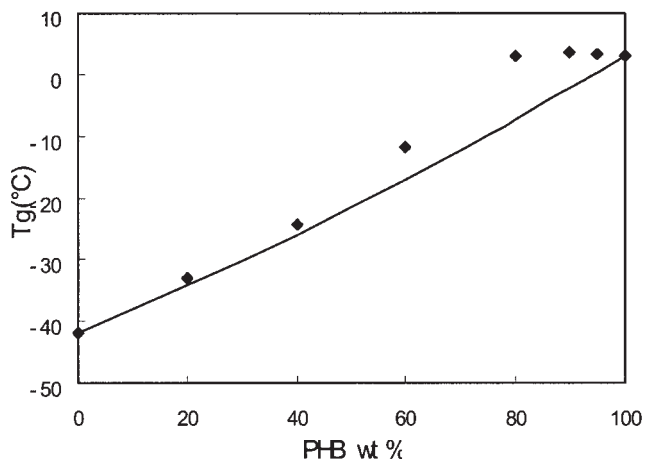
TABLE II
Glass Transition Temperature (T_g), Melting Temperature (T_m), Cold Crystallization Temperature (T_{cc}), and Crystallinity (χ) of PHB/CAB-g-PEG Blends

	T_g (°C)	T_m (°C)	T_{cc} (°C)	χ_{blend} (%)	χ_{PHB} (%)
PHB	3.0	183.1	47.4	62.1	62.1
PHB95(I)	3.4	180.6	60.6	52.9	55.7
PHB90(I)	3.7	178.9	68.7	48.7	54.1
PHB80(I)	2.9	176.3	73.9	40.1	50.1
PHB60(I)	−11.9	171.5	82.4	18.7	31.2
PHB40(I)	−24.2	162.9	90.1	9.3	23.3
PHB20(I)	−33.1	—	—	—	—
PHB-g-CAB(I)	−42.0	—	—	—	—

Figure 6 Glass transition temperature (T_g) of PHB/CAB-g-PEG blends (The line is calculated from T_g, using the Fox equation).
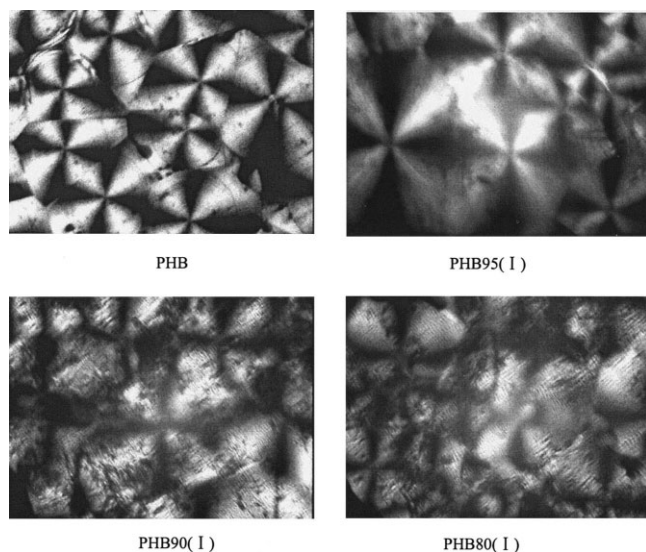
Figure 7 Optical micrographs of PHB/CAB-*g*-PEG blends (×200).

where ΔH_f^0 is the thermodynamic enthalpy of fusion per gram of PHB (146.6 J/g), ΔH_f is the apparent enthalpy of fusion per gram of blend, which is calculated from the area of melting peak, and W_{PHB} is the weight fraction of PHB in the blend. Both the crystallinity of the blends and PHB decrease with the increase of CAB-*g*-PEG contents. This is different from the maintenance of constant level of PHB crystallinity that has been reported previously for the PHB/CAB blends.[10]

The implication is that CAB-*g*-PEG copolymer behaves simply as a polymeric diluent like CAB. There must be some kind of intermolecular force between PHB and CAB-*g*-PEG copolymer. Certainly, the long PEG side chain of CAB-*g*-PEG copolymer would be expected to enhance the intermolecular force and the miscibility, with PHB.

As far as crystallization of PHB is concerned, the cold crystallization temperatures of PHB are dependent on blend composition, as shown in Table II. Compared with that of pure PHB, the T_{cc} of the blends shift to higher temperature, indicating the difficulty in crystallization of PHB in the blend. The heats of crystallization of the blends are also significantly dependent on the blend composition. These results confirm the effect of CAB-*g*-PEG copolymer on crystallization of PHB. Figure 7 shows the POM micrographs of PHB and PHB/CAB-*g*-PEG blends. PHB is able to crystallize according to a spherulitic morphology, which shows the Maltese cross birefringent pattern and exhibits concentric extinction bands. With the increase of the CAB-*g*-PEG copolymer, the PHB spherulites become imperfect, and this influence is enhanced with the increase in the CAB-*g*-PEG content.

Mechanical properties

The tensile strength, elongations at break and impact strength of PHB/CAB blends and PHB/CAB-*g*-PEG blends are shown in Tables III and IV. Compared with PHB and PHB/CAB blends, the mechanical properties of the PHB/CAB-*g*-PEG blend (recipe I) were greatly improved. The CAB-*g*-PEG (recipe I) copolymer is rubbery at room temperature. Its elongation at break (%) is about 110% and Impact strength is 30,268 J/m². With increase the CAB-*g*-PEG content, the elongations at break and impact strength of the blends increase. But when the copolymer is above 20%, the tensile strength of the blends decreases for the tensile strength of CAB-*g*-PEG is only 10.66 MPa. Figure 8 is the fracture surface observed by SEM. The section of PHB sample indicates that PHB is a very brittle material. However, the photograph of the PHB/CAB-*g*-PEG (recipe I) blend shows obvious characteristic of tenacity fracture.

The toughening mechanism of PHB blending with CAB-*g*-PEG is as follows: the graft polymer CAB-*g*-PEG is much more tenacious than CAB and processes the similar property as rubber. After blending, the

TABLE III
Mechanical Properties of PHB/CAB Blends

PHB/CAB	Tensile strength (MPa)	Elongation at break (%)	Impact strength (J/m²)
100/0	25.70	2.17	2774
90/10	26.80	2.22	3109
80/20	29.30	3.34	4161
70/30	20.39	2.04	4855
60/40	16.99	2.05	5548
50/50	13.33	7.29	5687
0/100	5.57	0.59	1109

TABLE IV
Mechanical Properties of PHB/CAB-*g*-PEG Blends

|	Tensile strength (MPa)	Elongation at break (%)	Impact strength (J/m²)
PHB	25.70	2.17	2,774
PHB95(I)	24.99	7.32	6,355
PHB90(I)	32.70	16.28	8,329
PHB80(I)	28.43	19.24	7,024
PHB60(I)	23.32	25.77	10,058
PHB40(I)	18.54	28.66	12,689
PHB20(I)	14.68	50.30	18,206
PHB-*g*-CAB(I)	10.66	110.9	30,268
PHB95(II)	20.58	4.16	3,328
PHB90(II)	18.34	3.10	2,857
PHB80(II)	16.84	3.22	2,961
PHB60(II)	15.23	3.74	2,834
PHB40(II)	15.68	4.03	3,142
PHB-*g*-PEG(II)	19.70	5.99	1,504
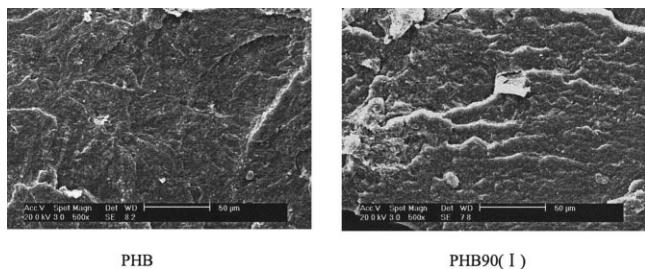
Figure 8 Scanning electron micrographs of the fracture surface of PHB and PHB/CAB-*g*-PEG blends.

introduction of a discrete CAB-*g*-PEG rubbery phase within the PHB brittle matrix can induce the production of silver streaks that absorb most of the impacting energy for the impact experiment. In the PHB/CAB blends, CAB is brittle similar to PHB at normal temperature, for its T_g (about 113°C) is very high. So the tenacity of PHB/CAB blends is inferior to PHB/CAB-*g*-PEG blends.

The PHB/CAB-*g*-PEG blends (recipe II) are also very brittle like PHB. The main reason for this is the CAB-*g*-PEG (recipe II) is crosslinked copolymer. PHB is not miscible with it. As shown in Figure 9, the clear phase separation can be seen in the fracture surface photos for these blends. When drawn, the copolymer is easy to depart from the PHB matrix and left a cavern, the crack can grow up quickly from the cavern and cause the fracture of the blends.

Biodegradability

As far as PHB is concerned, one of the most important advantage is its biodegradability. If this property is destroyed in the modification, the superiority of PHB materials is greatly weakened. Figure 10 shows the degradation rate of PHB/CAB-*g*-PEG blends in natural water. The CAB-*g*-PEG copolymer has a little influence on the degradation rate of the blends. The PHB/CAB-*g*-PEG blends have almost the same degradation rate, with PHB.

CONCLUSIONS

In this article, the graft copolymer of CAB-*g*-PEG was first synthesized, and then blended with PHB. The
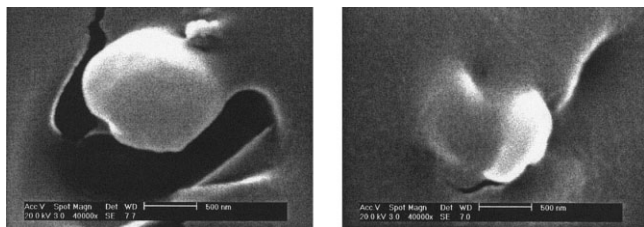

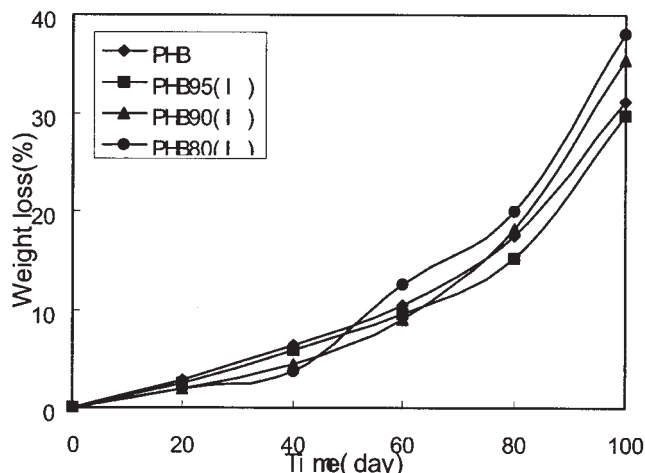**Figure 9** Scanning electron micrographs of PHB90(II) blends.

Figure 10 Weight loss of PHB/CAB-*g*-PEG blends in the natural water.

synthetic procedures and characterization of CAB-*g*-PEG copolymer, the miscibility, crystallization behavior, mechanical properties, and biodegradability of PHB/CAB-*g*-PEG blends were studied. The results indicated that PHB and CAB-*g*-PEG that were not crosslinked were miscible over the entire composition range. As the CAB-*g*-PEG copolymer increased in the PHB/CAB-*g*-PEG blends, the melting temperature of the blends decreased. The crystallization of PHB became more difficult, and the crystallinity of the blend and PHB phase were all decreased. The tensile properties and impact strength of the PHB/CAB-*g*-PEG blends were superior to the PHB/CAB blends.

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