Study of Miscibility, Crystallization, Mechanical Properties, and Thermal Stability of Blends of Poly(3-hydroxybutyrate) and Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)

Rongcong Luo, Kaitian Xu, Guo-Qiang Chen

Multidisciplinary Research Center (MRC), Shantou University, Shantou, Guangdong 515063, China

ABSTRACT: Natural amorphous polymer poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB) containing 41 mol % of 4HB was blended with poly(3-hydroxybutyrate) (PHB) with an aim to improve the properties of PHB. The influence of P3HB4HB contents on thermal and mechanical properties of the blends was evaluated with differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, stress–strain measurement and thermo gravimetric analyzer. Miscibility of PHB/ P3HB4HB blends was mainly decided by the contents of P3HB4HB. When P3HB4HB exceeded 50 wt %, the two polymer phases separated and showed immiscibility. The addition of P3HB4HB did not alter the crystallinity of PHB, yet it diluted the PHB crystalline phase as revealed by DSC studies. DSC and FTIR results showed that the overall crystallinity of the blends decreased remarkably with increasing of P3HB4HB contents. Decreased glass transition temperature and crystallinity imparted desired flexibility for the blends. The ductility of the blends increased progressively with increasing of P3HB4HB content. Thus, the PHB mechanical properties can be modulated by changing the blend composition. P3HB4HB did not significantly improve the thermal stability of PHB, yet it is possible to melt process PHB without much molecular weights loss via blending it with suitable amounts of P3HB4HB. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3402–3408, 2007

Key words: PHB; P3HB4HB; blends; miscibility; crystallization

INTRODUCTION

A wide variety of microorganisms are known to synthesize an optically active polyester, poly(3-hydroxybutyrate) (PHB), as their intracellular carbon and energy reserved materials.[1] Because of its biocompatibility and biodegradability, PHB has attracted industrial attention as an environmental friendly polymer for agricultural, marine, and medical application.[2] However, the application of PHB in these areas is restricted owing to its brittleness attributed to its high crystallinity.[3] Furthermore, the PHB melting temperature is close to its thermal decomposition temperature, thus leaving a very narrow window for its processing.[4] To lower the crystallinity and melting temperature of PHB, copolymerization of 3HB units with other 3-hydroxyalkanoate (3HA) units is an effective way. The copolymerization of 3HB with 3HV (3-hydroxybutyrate) (PHBV),[5,6] 3HP (3-hydroxypropionate) (PHBP),[7] 4HB (4-hydroxybutyrate) (P3HB4HB),[8] 3HHx (3-hydroxyhexanoate) (PHBHHx),[9] and 3HO (3-hydroxyoctanote) (PHBO),[10] respectively, has been successfully carried out by microbial fermentation. In addition, over 90 different types of PHA consisting of various monomers have been reported and the number is still increasing.[11]

P3HB4HB produced by *Ralstonia eutropha*, *Alcaligenes latus*, and *Comamonas acidovorans* has been shown to have a wide range of physical properties and morphologies ranging from highly crystalline to elastic rubber like depending on the molar fraction of 4HB and their melting points associated with 4HB content.[12–14] As the 4HB monomer has one more backbone carbon atom than those of 3HB, 3HV, 3HHx, and 3HP, it was found that P3HB4HB copolymer shows unique crystallization behaviors.[15–17]

Compared with copolymerization, blending is a more convenient and well-developed technology with lower cost for improving polymer properties. Among PHA families, two blending systems, PHB/PHBV[18–20] and PHB/PHBHHx,[21–24] had been studied. PHBV maintains its high crystallinity throughout whole range of composition from 0 to 100 mol % 3HV because of the isomorphous behaviors; thus, PHB/ PHBV blends are regarded as crystalline–crystalline blending systems.[18] It was found that PHB is miscible

with PHBV when the relative 3HV content is less than 12 mol %.[19] Meanwhile, the binary blend of PHB/PHBV was found to have cocrystallization phenomenon and thus the improvement of physical properties for PHB by blending with PHBV is marginal.[20] PHBHHx, already produced in industrial scale, showed much better mechanical properties, biodegradability, and biocompatibility than that of PHB.[21–23] PHBHHx with about 12 mol % 3HHx is completely miscible with PHB, and the blend improved the brittle feature of PHB: elongation to break of the PHB/PHBHHx blend films increased from 15 to 106% when the PHBHHx contents in the blend increased from 40 to 60%.[24]

P3HB4HB (41 mol % 4HB) in this study is a totally natural amorphous polymer with a low glass transition temperature of −17.7°C. It behaves as an elastomer at room temperature. In this study, for the first time, P3HB4HB was selected to blend with PHB with an aim to improve the application properties of PHB. Binary blends of PHB/P3HB4HB in this study can be regarded as a crystalline-amorphous blending system. Miscibility, crystallization behaviors, mechanical properties, and thermal stability of the blending system were investigated.

EXPERIMENT

Materials

PHB was purchased from Jiangsu Lantian Group (Jiangsu, China). The number-average molecular weight (M_n) is 350,000 and polydispersity (M_w/M_n) 1.75, as revealed by gel permeation chromatography (GPC). PHB sample was purified using chloroform extraction process to dissolve PHB under elevating temperature at 100°C for 20 min, and filtration was employed to remove possible undissolvable components. PHB was precipitated with addition of absolute ethanol. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of purified PHB is 350,000 and 1.60, respectively, as revealed by GPC (GPC chromatgrams not shown). P3HB4HB containing 41 mol % 4HB with $M_n = 420,000$ and $M_w/M_n = 1.62$ was generously donated by Tianjin Guoyun Biotech (Tianjin, China). The P3HB4HB sample was purified using chloroform as a solvent at elevated temperature (100°C). The insoluble components were removed by filtration. P3HB4HB was precipitated by addition of absolute ethanol. The purified P3HB4HB sample contains less than 1% impurities as revealed by ^{1}H NMR, Fourier transform infrared (FTIR), and gas chromatography (GC) (data not shown). The 4HB molar fraction in P3HB4HB copolymer was determined to be 41% through the 400 MHz ^{1}H NMR spectra recorded on a Bruker Advance-400 spectrometer at 30°C in CDCl₃ solution.

Blend preparation

All the blend films were prepared through the conventional solvent-casting method. That is, appropriate amounts of the two polymers were dissolved in hot chloroform with a total concentration of 5% (w/v). The solution was cast on glass Petri dishes, and the solvent was evaporated at room temperature over night. All films obtained were vacuum dried at 40°C for 72 h to completely remove the residual chloroform. The films were stored in a glass desiccator with silica gel at room temperature for more than 2 weeks to reach crystallinity equilibrium before further studies.

Differential scanning calorimetry (DSC) was performed with a TA-Q100 DSC analyzer equipped with a mechanical cooler system. It was calibrated with an indium standard. Each sample weighted 2–3 mg encapsulated in an aluminum pan was heated from −60 to 200°C as the first scan corresponding to "as-cast films." After maintaining at 200°C for 1 min, the molten sample was quenched to −60°C. The cooling rate was estimated to be 50°C min⁻¹. Subsequently, the sample was again heated from −60 to 200°C as the second scan corresponding to "melt-quenched films." A heating rate of 10°C min⁻¹ was used throughout the process. The apparent heat of fusion (ΔH_m) was determined from the DSC endothermal peaks in the second scan. The glass transition temperature (T_g) was taken as the inflection point of the specific heat increment at the glass-rubber transition.

Fourier transform infrared spectroscopy was used to confirm the change of crystallinity for the PHB/P3HB4HB blends. Infrared study was carried out with a Nicolet IR 200 (Thermo Electron, USA) spectroscope. A total of 32 scans at a resolution of 4 cm⁻¹ were recorded for each sample. Thin films of copolymers were cast from 10 mg mL⁻¹ solution in CHCl₃ on a KBr plate. All the films were dried at room temperature. Complete removal of chloroform was confirmed by FTIR.

Tensile mechanical analysis was conducted on the blend films. The films were cut into dumbbell-shape specimen with a width of 4 mm and a thickness of about 100 μm. The stress–strain measurements of films were carried out using a CMT-4000 universal testing machine (Shenzhen SANS, China) at room temperature. Speed of the cross-head was 5 mm min⁻¹.

Thermal stability of the blend films was determined with a TA-Q50 thermo gravimetric analyzer (TGA). The temperature range was 40–400°C in a nitrogen atmosphere. Four to five milligrams of samples were loaded and the heating rate was set at 10°C min⁻¹ each run.

RESULTS AND DISCUSSION

Miscibility of PHB/P3HB4HB

Glass transition temperatures T_g of PHB and P3HB4HB were 0.5 and −17.7°C, respectively (Table I

TABLE I
Physical properties of PHB/P3HB4HB

P3HB4HB (% wt)	T_g (°C)[a]	ΔH_m (Jg^{-1})[b]	X_{c1} (%)[c]	X_{c2} (%)[d]	CI[e]	E (Mpa)[f]	ε_t (Mpa)[g]	δ_s (Mpa)[h]	σ_b (%)[i]	$T_{d(5\%)}$ (°C)[j]
0	0.5	95.0	65.0	65.0	0.36	1317.4	15.2	13.6	1.8	235.0
10	−1.0	90.9	62.5	69.2	0.31	1021.9	9.8	7.6	2.0	236.8
20	−2.6	83.7	57.3	71.6	0.28	999.5	7.8	7.0	2.5	237.7
30	−5.3	53.6	36.7	52.4	0.24	413.2	6.5	6.3	7.9	240.3
40	−9.0	59.7	40.8	68.2	0.20	211.3	3.9	3.9	18.5	239.4
50	−9.8	48.7	33.3	66.7	0.18	112.8	2.8	2.7	27.5	241.3
60	−17.0 – 1.0	31.0	21.2	53.1	0.15	32.9	1.2	0.3	34.2	246.3
100	−17.7	−[k]	−	−	0.07	/[l]	/	/	/	254.3

[a] Glass transition temperature.
[b] Apparent melting enthalpy of PHB/P3HB4HB blends determined by calculating the intensities of the endothermal peaks in the second scan of DSC.
[c] Crystallinity degree of PHB/P3HB4HB blends (±5%) estimated from the ratio of the apparent melting enthalpy of PHB/P3HB4HB blends to that of 100% crystalline PHB (146 J g^{-1}).
[d] Crystallinity degree per gram of PHB (±5%) in PHB/P3HB4HB blends determined from the DSC thermograms.
[e] CI: crystallinity index defined as the ratio of the intensities of 1453 cm^{-1} peak and that of 1185 cm^{-1} peak in the FTIR spectra.
[f] E: Young's modulus.
[g] ε_t: tensile strength.
[h] δ_s: stress at break.
[i] σ_b: elongation at break.
[j] Temperature at 5% weights loss determined by the TGA curves.
[k] Not detected.
[l] Not determined.

and Fig. 1). Blends of PHB/P3HB4HB with weight ratios of 90/10, 80/20, and 70/30 showed a single intermediate T_g located between the T_g of PHB and P3HB4HB. The T_g decreased with increasing amounts of P3HB4HB in the blends (Table I), reflecting a good miscibility of PHB/P3HB4HB in the composition ranges investigated. In two blends of PHB/P3HB4HB with weight ratios of 60/40 and 50/50, T_g with long and smooth shoulders spanned over a wide temperature range were observed (Fig. 1). When using lower heating rate (5 and 2°C min^{-1}, respectively), the T_g changes of these two blends were still similar with that obtained by using a heating rate of 10°C min^{-1} (curves not shown). These results suggested partial miscibility of P3HB4HB with PHB and a single T_g most possibly indicates that these two polymer phases coexist, they disperse into each other evenly, and thus show no phase separation in the process of glass-to-rubber transition. In the blend of PHB/P3HB4HB (40/60), two temperature-constant glass transitions were observed. The lower temperature one at −17.0°C is related to the P3HB4HB phase whereas the higher one at 1.0°C to PHB phase. Two constant temperatures independent of the composition ratio may imply that these two components were immiscible. Generally, ratios of blend compositions have strong effect on the miscibility of a blend system. In PHB/P3HB4HB, the weight ratio of 50/50 may represent the solubility limit for P3HB4HB in PHB. All blends containing more than 50% of P3HB4HB such as PHB/P3HB4HB (40/60) will show

phase separation, as indicated by the two constant glass transition temperature T_g (Fig. 1 and Table I).

Melting and crystallization behaviors of PHB/P3HB4HB

No melting peak was detected for pure P3HB4HB in both the as-cast and melt-quenched films, indicating the totally amorphous nature of P3HB4HB (Fig. 2). Both the as-cast films [Fig. 2(a)] and melt-quenched films [Fig. 2(b)] of pure PHB showed a single melting
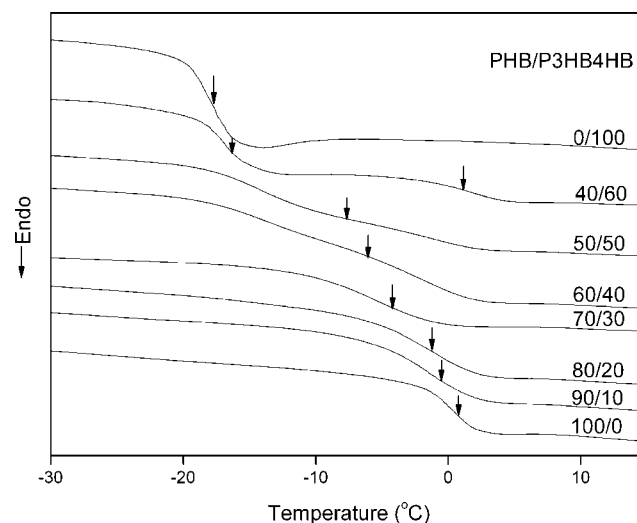

Figure 1 Detailed comparision of glass transition temperature T_g for blends of PHB/P3HB4HB.
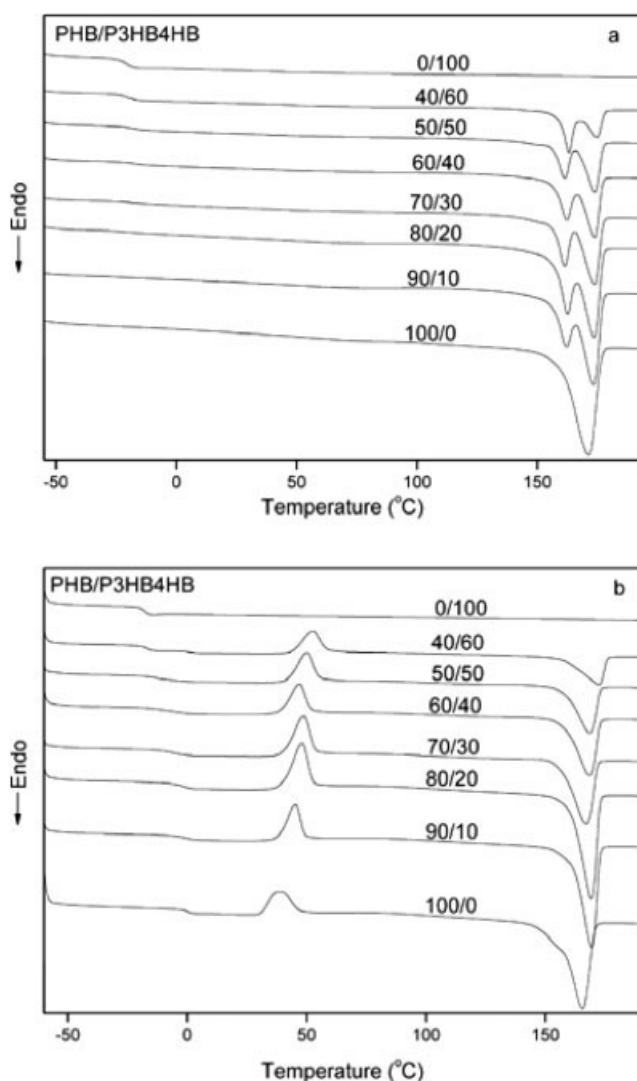
Figure 2 DSC thermograms of PHB/P3HB4HB blends. (a) First scan of DSC thermogram (corresponding to ''as-cast films'') of the blends (b) second scan of DSC thermogram (corresponding to ''melt-quenched films'') of the blends.

peak at 170 and 165°C, respectively. However, blends of PHB/P3HB4HB as-cast films showed double melting peaks [Fig. 2(a)]. Generally, double melting peaks imply a decrease in lamellar thickness or degree of crystallinity[25] and multiple melting peaks in the first DSC scan also reflects a melt-recrystallization process happened in the DSC measurement.[26] All the samples of melt-quenched films showed single melting peaks [Fig. 2(b)], implying better crystallinity of the PHB/P3HB4HB blends after the melt-quenched treatment in the DSC measurement. The apparent heats of fusion (ΔH_m) of the blends were also determined by integrating the endothermal peaks.

The crystallinity of PHB/P3HB4HB blends was estimated from the second scan of DSC run. It was defined as the ratio of the apparent melting enthalpy (ΔH_m) of PHB/P3HB4HB blends to that of a 100%

crystalline PHB which calculated as 146 J g^{-1} according to Deng et al.[25] The crystallinty of PHB/P3HB4HB blends (X_{c1}) decreased steeply with increasing P3HB4HB content in the blends (Table I). The decreased crystallinity of the PHB/P3HB4HB blends may be attributed to the presence of an amorphous P3HB4HB which just simply dilutes the crystalline phase of PHB that does not change its own crystallization ability at all. On the other hand, it is also possible that the amorphous P3HB4HB inhibits the crystallization of PHB directly and thus reduces the crystallization ability of PHB in the blends. The latter case was reported in the blends of PHB with some other components that exhibit certain molecular interactions such as hydrogen bonding, dipole et al.[27,28] The alteration of PHB crystalline structure and crystallization ability was also observed in some PHB-based copolymers.[7,10,15–17] For example, the incorporation of other non 3HB 3-hydroxyalkanoates (3HA) monomers such as 4HB, 3-hydroxyoctanoate (3HO) and 3HP etc, alter the crystalline structure of PHB molecular segments and thus reduces the PHB crystallinity. In the case of PHB/P3HB4HB blends, it is very likely that not the molecular interaction between the two components but the ''dilution effects'' of P3HB4HB that decreased crystallinity of the blends. To confirm the suggestion more clearly, the crystallinity per gram of PHB (X_{c2}) was calculated. The values obtained were relatively constant independent of the P3HB4HB weight contents in the blend (Table I). These results are similar with that obtained by Dufresne and Vincendon, who blended PHB with poly(3-hydroxyoctanote) PHO.[29] The relatively constant X_{c2} values suggested that crystallization ability of PHB in the blends remained unchanged in the whole blend composition ratios investigated.

FTIR study of PHB/P3HB4HB

FTIR study further confirmed the decreased crystallinity of PHB/P3HB4HB blends. The bands at 980, 1230, 1278, and 1722 cm^{-1} [Fig. 3(a,b)], respectively, are characteristic of the crystalline phase in the PHB/P3HB4HB blends while those at 1185 and 1738 cm^{-1} are characteristic of the amorphous phase [Fig. 3(a,b)]. The band at 1722 cm^{-1} representing the stretching vibration of carbonyl groups (C=O) changed shapes dramatically with increasing contents of P3HB4HB [Fig. 3(a)]. The intensity of the spectra at 1722 cm^{-1} attributed to the crystalline C=O groups decreased dramatically with increasing content of P3HB4HB [Fig. 3(a)], while that at 1738 cm^{-1} corresponding to the amorphous C=O groups increased steadily [Fig. 3(a)]. The band at 1722 cm^{-1} corresponding to crystalline C=O groups in 100% (wt) P3HB4HB was not detectable, yet a very strong absorbance peak at 1738 cm^{-1} appeared, reflecting its totally amorphous na-
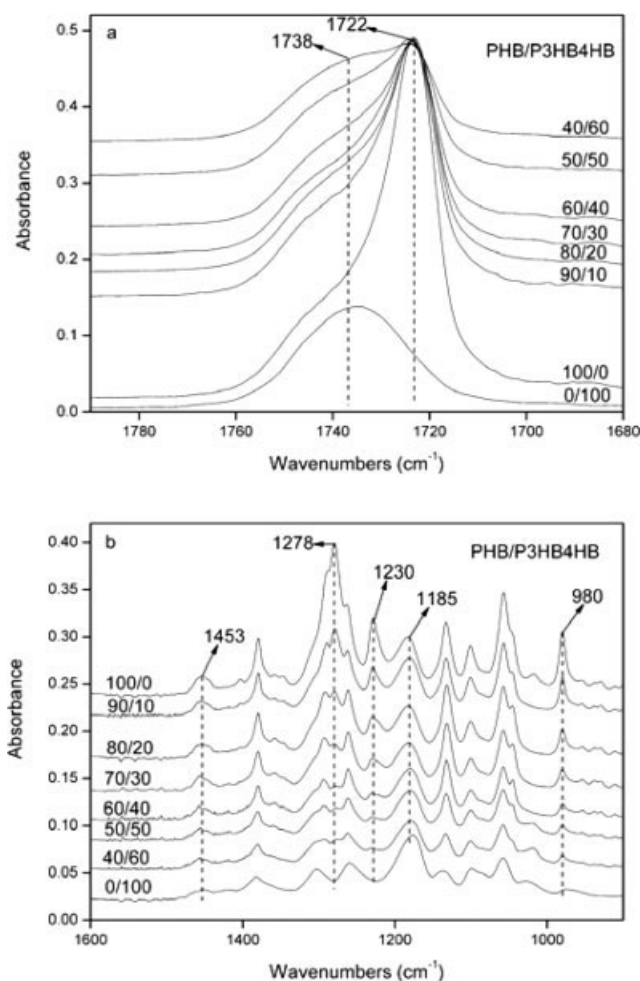
Figure 3 FTIR spectra of PHB/P3HB4HB blends. (a) Variance of the stretching bands of carbonyl groups (C=O) in PHB/P3HB4HB (b) Variance of the stretching bands of other characteristic groups in PHB/P3HB4HB.

ture. For the 100% (wt) PHB, band at 1722 cm^{-1} appeared with the sharpest shape, together with another band at 1738 cm^{-1} corresponding to the amorphous C=O groups emerging as a smooth shoulder, indicating a semicrystalline nature of PHB with a high crystallinity degree [Fig. 3(a)]. For an overall view, the band shapes in the wavelength region of 1720–1750 cm^{-1} became broader and broader. This may demonstrate the existence of more molecular freedom in the PHB/P3HB4HB blends with increasing contents of P3HB4HB.

Decrease of crystallinity of PHB/P3HB4HB blends was also demonstrated by FTIR spectra of other characteristic groups. Absorbance of all the crystalline bands at 980, 1230, and 1278 cm^{-1} showed steady decrease while that of the amorphous band at 1185 cm^{-1} showed steeply increase with increasing contents of P3HB4HB [Fig. 3(b)]. As suggested by Xu et al.,[30] a crystallinity index (CI) defined as the ratio of the intensity of a band at 1453 cm^{-1} which is insensitive to the crystallinity and composition to that of

the band at 1185 cm^{-1}, was used to quantitatively measure the crystallinity of PHB/P3HB4HB blends, pure PHB and P3HB4HB components, respectively. It was observable that CI decreased constantly with increasing contents of P3HB4HB (Table I), reflecting the decreased crystallinity of PHB/P3HB4HB blends.

Stress–strain measurements of PHB/P3HB4HB

Stress–strain curves of PHB/P3HB4HB blends were recorded in Figure 4. Relevant data including Young's modulus (E), tensile strength (ε_t), stress at break (δ_s) and elongation at break (σ_b) are summarized in Table I. The data on tensile mechanical properties of pure P3HB4HB could not be obtained because of the amorphous nature of P3HB4HB that is sticky, elastic, and not suitable for solvent-casting. Pure PHB displayed typical brittle feature with an elongation to break at around 1.8% (Fig. 4). Depending on composition ratios, the binary blends exhibited various tensile mechanical properties, e.g., PHB-rich samples (up to 80 wt %) are characterized with a brittle feature and a relatively high Young's modulus (E), tensile strength (ε_t), stress at break (δ_s), combined with a very low elongation to break (σ_b) (Table I).

Values of E, ε_t, δ_s, and σ_b of the blend films were almost the same with those of PHB homopolymer when the PHB contents in the blend are 90 and 80% (Table I). An obvious yield point was observed when the PHB contents were less than 80%, reflecting the appearance of ductile property. When the contents of P3HB4HB increased from 30 to 60%, the E, ε_t, and δ_s characterizing the brittleness nature of the polymers decreased from 413.2, 6.51, and 6.29 Mpa to 32.8, 1.2, and 0.3 Mpa, respectively, while the σ_b indicating material flexibility increased from 7.9 to 34.2%. Consequently, we can modulate mechanical properties of the blends by changing the blend composition. The improved mechanical properties of PHB via blending
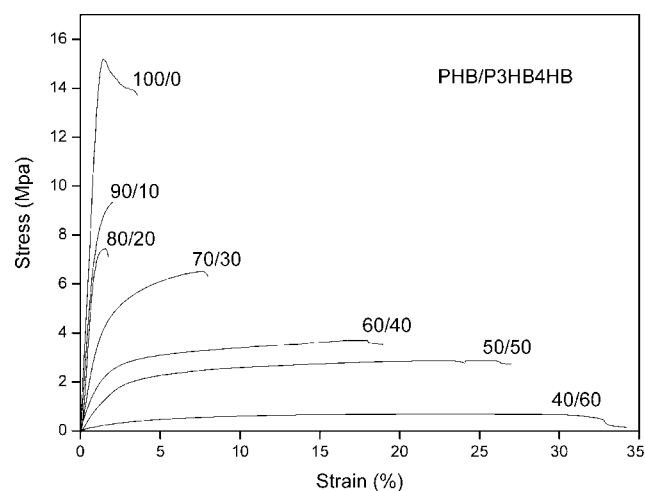

Figure 4 Stress–strain curves of PHB/P3HB4HB blends.

with P3HB4HB were also correlated with the changes of their thermal properties (Table I). T_g of PHB/P3HB4HB blends decreased with the increase of P3HB4HB contents like shown in Figure 1. A decreased T_g may indicate the increased mobility of the molecular chains in the blends under the test temperature of 25°C, which will help improve the brittleness nature of polymers. Therefore, decreased E, ε_t, δ_s, and increased σ_b with increasing contents of P3HB4HB in the blends were observed. The decreased crystallinity of the blends may also impart desired toughness for the blend films. The crystallinity of PHB is as high as 65% after crystallization from chloroform solution (Table I). Moreover, it is well-known that PHB will form very large size of spherulites during the crystallization process. The large PHB spherulites will easily crack and it is brittle as films when it is drawn. P3HB4HB containing 41% mole 4HB-units in this study is an amorphous polymer with a relatively low T_g of −17.7°C. The presence of the amorphous P3HB4HB component did not alter the crystallization ability of PHB although it diluted and dispersed in the PHB crystalline phase as demonstrated by the DSC measurement (Table I). The "dilution effects" of the amorphous P3HB4HB in the blends may reduce the continuity and regularity of PHB crystalline phase and thus enhanced the conformation freedom of the blends as confirmed by FTIR (Fig. 3). Consequently, when the blend films were dawn, the molecular segments of the blend films are easier to reorient, they begin to display ductility. The more the P3HB4HB in the blends, the more flexible the blend films were.

Thermal stability of PHB/P3HB4HB

Thermal stability is of particular importance for any materials in the melting-process. While it is well-known that PHB suffers serious thermal decomposition at a temperature above 170°C, which is near the melting point of PHB, this has brought difficulties for melting-process of PHB. The temperature termed $T_{d(5\%)}$ at which a 5% weight loss occurs to the polymer was employed to evaluate the polymer thermal stability. PHB had the lowest thermal stability with a lowest $T_{d(5\%)}$ located at 235.0°C while P3HB4HB had the highest thermal stability with a $T_{d(5\%)}$ of 254.3°C (Fig. 5 and Table I). Unlike the usual binary blend systems which always exhibit a two-step degradation process, the PHB/P3HB4HB blends showed a single one-step degradation process [Fig. 5(a)]. A possible reason could be that the thermal decomposition temperatures of PHB and P3HB4HB were too close to be distinguished at the heating rate of 10°C min⁻¹. However, the selected PHB/P3HB4HB (50/50) blend films subjected to a lower heating rate of 2°C min⁻¹ exhibited again a one-step degradation process [Fig. 5(b)].
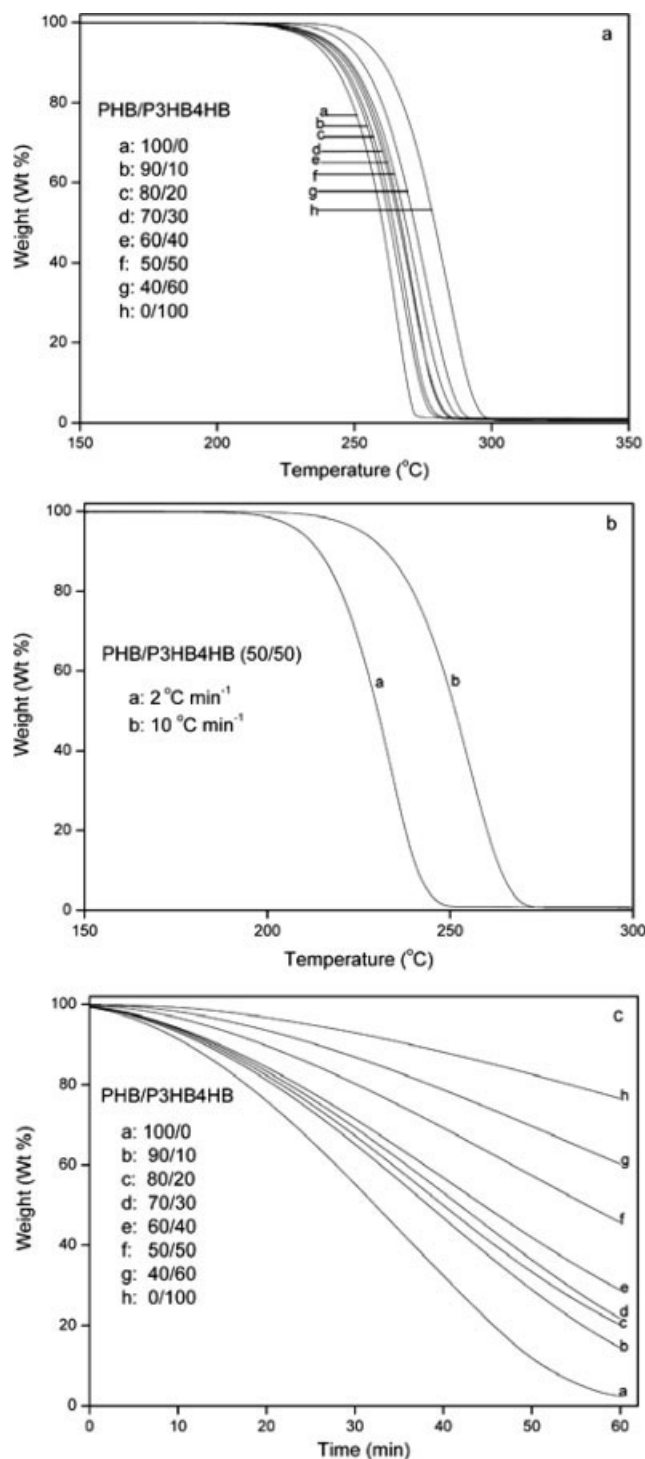

Figure 5 TGA and isothermal TGA thermograms for PHB/P3HB4HB blends. (a) TGA thermograms of PHB/P3HB4HB, (b) Comparison of TGA thermograms for PHB/P3HB4HB (50/50) at different heating rates, (c) Isothermal TGA thermograms obtained at 200°C for 1 h for PHB/P3HB4HB.

Shuai et al. showed that a binary blend forming inclusion complex displayed a one-step degradation process in their TGA tests.[31] Inclusion complex formation will not likely happen in the PHB/P3HB4HB blends and further research to make this problem more

clearly is in progress. The $T_{d(5\%)}$ slightly increased from 235.0 to 241.3°C when P3HB4HB contents increased from 0 to 50%.

The thermal stability of PHB was not significantly improved by blending with P3HB4HB [Fig. 5(a)] like the normal TGA curves shown. To investigate the thermal stability of PHB/P3HB4HB blends more clearly, isothermal TGA was carried out. It was clearly observed that the residual weights under 200°C for 20 min in isothermal TGA curve increased slightly when P3HB4HB contents increased from 0 to 40% [Fig. 5(c)]. When the P3HB4HB component weights increased from 50 to 60%, the residual weights at 20 min increased from 89.7 to 93.5%. While it has been generally reported that the temperature and time-scale of melting-process for PHB are less than 200°C and 20 min, respectively, therefore, it becomes possible to melt process PHB without much molecular weight loss when PHB is blended with suitable amounts of amorphous P3HB4HB.

CONCLUSIONS

When P3HB4HB (with 40 mol % 4HB) exceeded 50 wt %, PHB/P3HB4HB exhibited phase separation. The crystallinity of PHB/P3HB4HB blends decreased from 65.0 to 21.2% while that for per gram PHB in the blends remained relatively stable when P3HB4HB increased its content to 60% in the blends, indicating that P3HB4HB did not change the crystallization ability of PHB yet dilute its crystalline phase. Defined CI measuring polymer crystallinity using FTIR showed a decrease from 0.36 to 0.15 as P3HB4HB increased in the blends from 0 to 60%, confirming the decreasing crystallinity in the blends. With the decrease of T_g and reduced crystallinity of PHB/P3HB4HB blends, the mechanical parameters E, ε_t, and δ_s characterizing the brittleness of the blends decreased with increasing P3HB4HB contents, together with an increasing σ_b characterizing material ductility. P3HB4HB did not significantly improve the thermal stability of PHB, yet it is possible to melt process PHB without much molecular weights loss via blending it with suitable amounts of P3HB4HB.

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