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ORIGINAL CONTRIBUTION

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Effect of poly(vinyl acetate) (PVAc) on thermal behavior and mechanical properties of poly(3-hydroxybutyrate)/poly(propylene carbonate) (PHB/PPC) blends

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Abstract To assess the compatibility of blends of synthetic poly(propylene carbonate) (PPC), with a natural bacterial poly(3-hydroxybutyrate) (PHB), a simple casting procedure of blend was used. poly(3-hydroxybutyrate)/poly(propylene carbonate) blends are found to be incompatible according to DSC and DMA analysis. In order to improve the compatibility and mechanical properties of PHB/PPC blends, poly(vinyl acetate) (PVAc) was added as a compatibilizer. The effects of PVAc on the thermal behavior, morphology, and mechanical properties of 70PHB/30PPC blend were investigated. The results show that the melting point and the crystallization temperature of PHB in blends decrease with the increase of PVAc content in blends, the loss factor changes from two separate peaks of 70PHB/30PPC blend to one peak of 70PHB/30PPC/12PVAc blend. It is also found that adding PVAc into 70PHB/30PPC blend can decrease the size of dispersed phase from morphology analysis. The result of tensile properties shows that PVAc can increase the tensile strength and Young's modulus of 70PHB/30PPC blend, and both the elongation at break and the tensile toughness increase significantly with PVAc added into 70PHB/30PPC.

Keywords Poly(3-hydroxybutyrate) · Poly(propylene carbonate) · Poly(vinyl acetate) · Compatibilizer

Introduction

Microbially generated poly(3-hydroxybutyrate) (PHB) is a biodegradable engineering polymer with tensile properties similar to polypropylene [1]. But the application of PHB has two main limitations. One is a narrow processing window. The polymer is thermally unstable at temperature above the melting point (about 453 K), and a drastic reduction in molecular weight occurs during processing in the temperature range 453–473 K [2–4]. The other is a relatively low impact resistance. Injection-molded PHB shows a high crystallinity with a brittle behavior. Especially after storage at room temperature, the polymer suffers a dramatic loss in extension-to-break and in impact strength, which levels off after 150 days [5]. In order to overcome the shortcomings of PHB, efforts have been made to bacterially co-polymerize 3 HB repeating units with other monomers such as 3-hydroxyalknoates [6–10], 4-hydroxybutyrate [11–13], and so on, but the considerable high cost impeded broader application of the bacterial polyester. One approach to obtain a less expensive thermoplastic polymer with improved mechanical properties is to blend PHB with a suitable polymer. Much work on blending PHB with a second polymer component has been reported. It has been known that PHB is miscible with poly(ethylene oxide) (PEO) [14, 15], poly(vinyl acetate) (PVAc) [16–18], poly(*p*-vinylphenol)(PVPh) [19, 20], poly(epichlorohydrin) (PECH) [21, 22], poly(vinylidene fluoride) (PVDF) [23,

24], poly(methyl acrylate) (PMA) [25], respectively. It has also been found that PHB is immiscible or partmiscible with poly(vinyl acetate-co-vinyl alcohol) (PVAc-co-VA) [26], poly(ϵ-caprolactone) (PCL) [27], poly(L-lactide) (PLLA) [28], poly(oxymethylene) (POM) [29], ethylene-propylene rubber (EPR) [30], ethylene-vinyl acetate copolymer (EVA) [31], respectively. But most second polymers are non-biodegradable.

Poly(propylene carbonate) (PPC), first synthesized by Inoue [32], is a new kind of aliphatic polycarbonate. It is composed of carbon dioxide and propylene epoxide with the following molecular structure.

The synthesis of PPC can fix and recycle carbon dioxide, particularly in the environment. PPC is also a synthetic biodegradable polymer [33], which has been proved by our coworkers. PPC is an amorphous polymer [34], which can be used to increase the toughness of epoxy resin [35], but till now no blending of PHB or PHBV with PPC has been reported.

In this work, the compatibility of PHB with PPC was discussed. In order to improve the mechanical properties of PHB/PPC blends, PVAc was added into 70PHB/30PPC blend and the effects of PVAc on the thermal behavior and mechanical properties of 70PHB/30PPC blend were investigated.

Experimental

Materials

Poly(3-hydroxybutyrate) was produced by Beijing Biological Institute. The weight-average molecular weight obtained by measuring its viscosity in chloroform at a temperature of 303 K was 3.9×10^5. Poly(propylene carbonate) was produced by Changchun Institute of Applied Chemistry. The weight-average molecular weight obtained by GPC was 2.3×10^5, and M_w/M_n was 2.3, and the mono-distributed polystyrene was used as a standard and toluene was employed as elution agent.

Preparation of blends

Poly(3-hydroxybutyrate)/poly(propylene carbonate) blends with different weight ratios and 70/30 wt% PHB/PPC blends containing different weight of PVAc were prepared by solution casting from chloroform, and dried under vacuum at 353 K to constant weight and films were obtained. Poly(propylene carbonate) sample used in blend was treated with maleic anhydride in advance [36]. Specimens for tensile test and dynamic mechanical analysis were compression molded and cut into dumbbell shape samples and strips (4 mm in width and 20 mm in length), respectively.

Experimental conditions for measurements

A Perkin-Elmer DSC-7 differential scanning calorimeter was employed to study the glass transition temperature (T_g), melting and crystallization behaviors of the blends. About 10 mg of each sample was heated from room temperature to 463 K (I run) and then maintained at 463 K for 2 min before quenching to 223 K. The samples were then reheated to 463 K (II run). After holding for 2 min at 463 K, the samples were cooled down to 223 K (III run). A scan rate of 20 K/min was used throughout. The midpoints of the transitions in the traces recorded in the second heating scan (II run) were taken as the values of glass transition temperatures T_g. The exothermic and endothermic peaks of the thermograms in the second heating scan were taken as cold crystallization temperature T_{cc} and melting temperature T_m, respectively. The heat of fusion ΔH_m (II run) was estimated as the integral of the endothermic curves. The exothermic peaks of the thermograms by the third heating scan were taken as crystallization temperatures T_c (III run).

The morphology of 70PHB/30PPC solution casting films containing different content of PVAc was examined with JEOL scanning microscope model JAK-840. Samples were sputtered with a coating of gold and palladium by using a Polaron cool sputter coater, in order to obtain a conducting specimen surface. Prior to sputtering samples were etched with acetone for 5 h.

Tensile properties were studied by an Instron 1211 dynamometer on dumbbell shape samples. Testing speed and temperature were 10 mm/min and 293 K, respectively.

A NETZSCH-242 dynamic mechanical analyzer was employed to study dynamic mechanical properties of samples. Testing frequency and heating rate were 3.3 Hz and 3 K/min, respectively.

Results and discussion

Miscibility of PHB/PPC blends

In general, thermal characterization of polymer blends is a well-known method for determining the miscibility of polymer blends. The miscibility between any two polymers in the amorphous state is detected by the presence of a single glass transition temperature (T_g) intermediate between those of the two components polymers [37]. So it is important to establish the T_g behavior of PHB/PPC blends.

The DSC curves of the quenched PHB/PPC blends (II run) is showed in Fig. 1. The T_g of PHB in PHB/PPC blends does not change with the PHB contents. And for the blends with composition 20/80 and 40/60 wt% PHB/

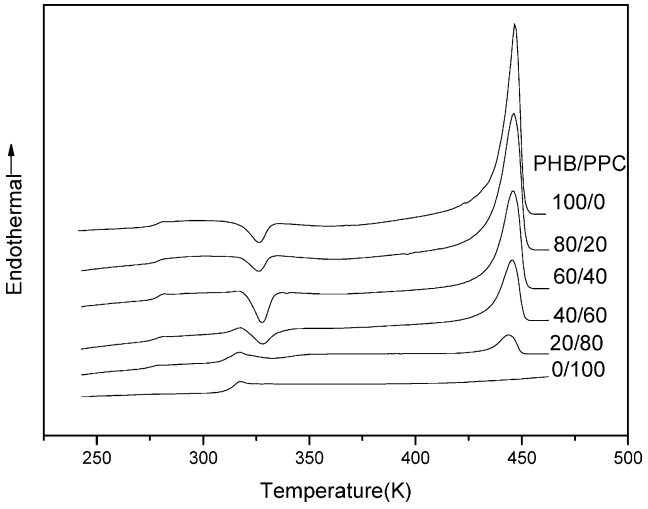

Fig. 1 The DSC curves of quenched PHB/PPC blends

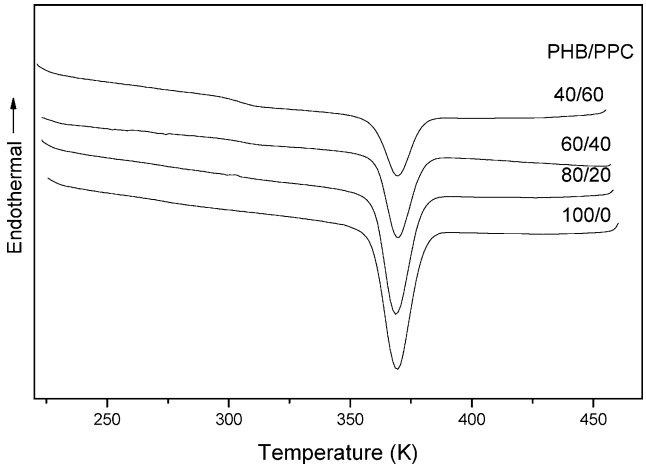

Fig. 2 The DSC curves of PHB/PPC blends cooled from 463 K to 223 K

PPC, there are two glass transition temperatures. One is about 278 K, close to the T_g of PHB. The other is not evident because of being affected by the cold crystallization peak (T_{cc}), which is about 312 K, close to the T_g of pure PPC. In the 60/40 and 80/20 wt% PHB/PPC blends only one T_g (about 278 K) close to the T_g of PHB, was observed. The possible reason was that the T_g of PPC was veiled due to the cold crystallization peak of PHB.

In addition to T_g method, the cold crystallization temperature and melting point in the heating scan of the quenched blends (II run) can be used together to identify the miscibility of the system. In general, cold crystallization takes place at a temperature above the T_g of the blends in which the crystallizable polymer chains possess enough segmental mobility to crystallize. The cold crystallization peak (T_{cc}) of the quenched blends almost does not change with PHB contents. This can be explained that the existence of PPC does not affect the segmental mobility of PHB. In another aspect, the melting point (T_m) of PHB in blends does not change with the increase of PPC in blends either (see Fig. 1).

Poly(3-hydroxybutyrate) is a highly crystalline polymer, which will crystallize when cooled from the melt. Figure 2 shows the curves of non-isothermal crystallization of PHB/PPC blends. The crystallization temperature (T_c) almost remains constant with the increase of PHB content in blends. This indicates that the existence of PPC does not affect the crystallization of PHB in blends.

Further, DMA is a helpful tool to characterize the miscibility of PHB/PPC blends. The peak of loss factor of PHB cannot be found in the curves of the dynamic mechanical loss factor versus temperature of PHB/PPC blends of Fig. 3. PHB is a high crystalline polymer, the peak intensity of loss factor of PHB is much smaller

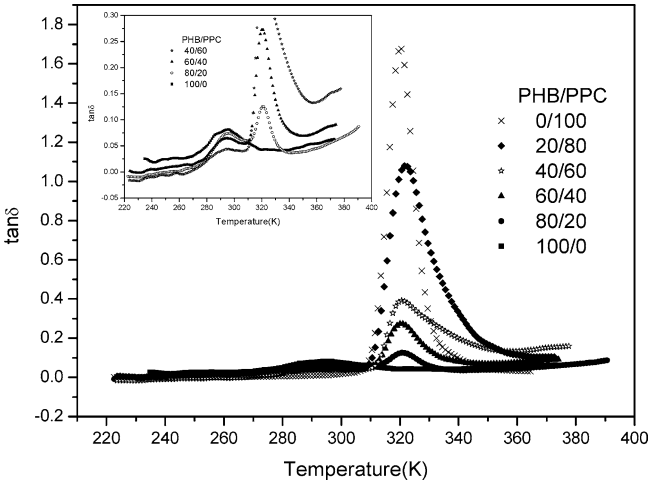

Fig. 3 Loss factor of PHB/PPC blends as a function of temperature

than that of amorphous PPC, so only the peak of loss factor of amorphous PPC can be seen. In general, the loss factor is sensitive to the molecular motions and its peaks are related to the glass transition temperature regions. The peak intensity increases but the peak position does not change with the increase of PPC content in PHB/PPC blends. In other words, the T_g of PPC in blends does not change.

In order to know the change of loss factor of PHB in blends, a new figure (see the inset graph in Fig. 3) can be obtained by changing the scale of tan δ axis in Fig. 3. There are two peaks of loss factor for 80PHB/20PPC, 60PHB/40PPC, 40PHB/60PPC blends in the inset graph. In the above discussion, it can be concluded that the second peak is corresponding to PPC in the blends. It is easy to know that the first peak is corresponding to

PHB. And the first peak position does not change in PHB/PPC blends. That is to say the glass transition temperature does not change with the PHB content. The DMA results are in good agreement with DSC results. From the DSC and DMA results, it can be concluded that the PHB/PPC blends show immiscibility in the melt.

Effect of PVAc on the thermal behavior of 70PHB/30PPC blend

In order to modify the compatibility of two-component blends, usually a third component often named as compatibilizer, is added into the blends. In general, for A/B blends, A–B or A–C block copolymer was used as compatibilizer [38–40]. But here one homopolymer, PVAc, was employed as compatibilizer for PHB/PPC blends, because PVAc is miscible with both PHB and PPC.

Figure 4 shows quenched DSC curves of 70PHB/30PPC blends (second scan) containing different content of PVAc. The T_g of PHB in blends increases with the increase of PVAc content. There are two possible explanations. One is that some PVAc chains dissolved in PHB phase [16–18] make the segmental motion of PHB chains difficult. The other is that adding PVAc may make the immiscible PHB/PPC blend become partial miscible blend, and thus leading the T_g value of PHB moves towards higher temperature. Here it cannot be determined which factor is more important than the other because T_g value is related to the segment mobility of PHB chains. The cold crystallization of PHB in blends also increases with the increase of PVAc content in blends, as can be seen in Fig. 4. The T_g, cold crystallization temperature (T_{cc}), and melting point (T_m) are all listed in Table 1.

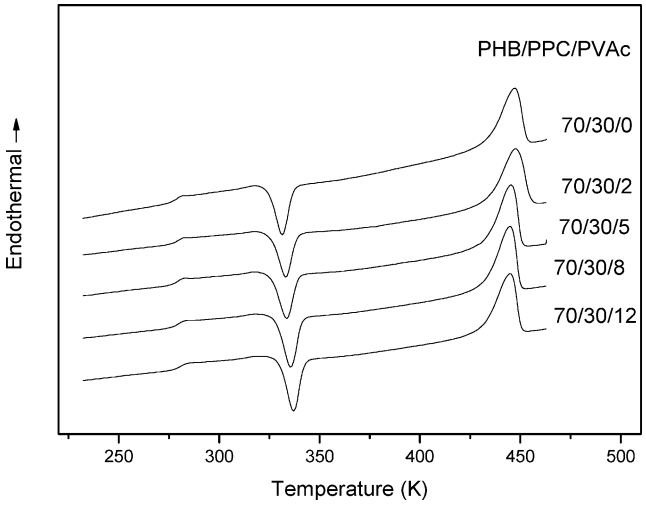

Fig. 4 The DSC curves of quenched 70PHB/30PPC blend containing different content of PVAc

From Table 1, it is seen that the T_m value of PHB decreases with the increase of PVAc content in blends. Thermodynamic considerations predict that the chemical potential of a polymer will decrease by the addition of a miscible diluent. If the polymer is crystallizable, this decrease in chemical potential will result in a decreased melting point. The decrease of melting point of PHB in blends means some miscible components entered PHB phase. Adding PVAc into PHB can decrease the melting point of PHB because PHB/PVAc blends are miscible in the melt, but it is incredible that such small amount of PVAc can result in such a decrease of melting point of PHB in 70PHB/30PPC/12PVAc blend. Probably adding PVAc into PHB/PPC blends can increase the miscibility between PHB and PPC, and then not only PVAc but also PPC contributes to the decrease of melting point of PHB in 70PHB/30PPC blends containing different content of PVAc.

The melting enthalpy of 70PHB/30PPC blend containing PVAc (ΔH_m) and that of the PHB phase in the blends (ΔH_m^{PHB}) are also listed in Table 1. ΔH_m^{PHB} is calculated from the enthalpy of the blends ΔH_m, $\Delta H_m^{PHB} = \Delta H_m / w_{PHB}$.

Then the crystallinity of PHB in blends (X_c) can be calculated according to the following equation:

$$X_c = \frac{\Delta H_m^{PHB}}{\Delta H_m^0}$$

where ΔH_m^0 is the heat fusion of 100% crystalline PHB, which is reported to be 146 J/g [41]. The calculated X_c values are also listed in Table 1. The crystallinity of PHB in blends almost does not change with PVAc content. In other words, the effect of small amount of PVAc on the crystallinity of PHB in blends is not evident.

Table 1 Thermal parameters of quenched 70PHB/30PPC blend containing PVAc determined by DSC

PHB/PPC/PVAc	T_g (K)	T_{cc} (K)	T_m (K)	ΔH_m (J/g)	ΔH_m^{PHB} (J/g)	X_c (%)
70/30	277.6	331.4	447	59.2	84.6	58
70/30/2	278.7	333.1	447.2	59.8	87.1	60
70/30/5	278.4	333.6	445.2	57.4	86.1	59
70/30/8	279	335.6	444.9	56.5	87.1	60
70/30/12	280.2	337.2	444.4	54.6	87.3	60

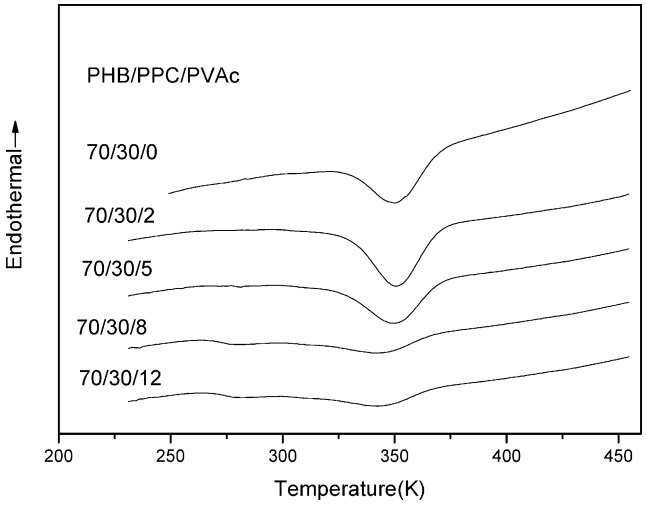

Fig. 5 The DSC curves of 70PHB/30PPC blends containing different content of PVAc cooled from 463 K to 223 K

Figure 5 shows the DSC curves of non-isothermal crystallization of 70PHB/30PPC blend containing PVAc from melt. The crystallization temperature (T_c) of PHB has a trend of decreasing and the temperature range of PHB crystallization becomes wider with the increase of PVAc content . The T_c, the enthalpy of blends (ΔH_c) and the enthalpy of non-isothermal crystallization of the PHB phase in the blends (ΔH_c^{PHB}) are all listed in Table 2. ΔH_c^{PHB} is calculated from the enthalpy of the blends ΔH_c, $\Delta H_c^{PHB} = \Delta H_c / w_{PHB}$. From Table 2 it is seen that with the increasing in content of PVAc of blends, the ΔH_c^{PHB} has a drastic decrease from 61.3 J/g for 70PHB/30PPC blend to 27 J/g for 70PHB/30PPC/8PVAc blend. This indicates that PVAc can affect the crystallization of PHB in blends. This also implies that adding PVAc may make 70PHB/30PPC blend become partially miscible.

Effect of PVAc on the dynamical mechanical properties of 70PHB/30PPC blend

Figure 6 shows the plots of tanδ as a function of temperature for 70PHB/30PPC blends containing different content of PVAc. For 70PHB/30PPC blend, it is evident that there are two separate tanδ peaks for individual component. But after adding PVAc into the blend, the peak of PPC shifts a little towards lower temperature and the peak of PHB disappeared gradually with the increase of PVAc content in blends. This indicates that PVAc can improve the compatibility between PHB and PPC. This result is in a good agreement with that obtained from DSC analysis; and with the increasing PVAc content in blends both the height and area of loss factor for blends increase. This indicates that the maximum

Table 2 Temperature and enthalpy of non-isothermal crystallization from the melt for 70PHB/30PPC blend containing different content of PVAc

PHB/PPC/PVAc	T_c (K)	ΔH_c (J/g)	ΔH_c^{PHB} (J/g)
70/30	350.6	−42.9	61.3
70/30/2	350.2	−43.2	62.9
70/30/5	350	−38.9	58.4
70/30/8	344.5	−17.5	27
70/30/12	344.2	−17.3	27.7

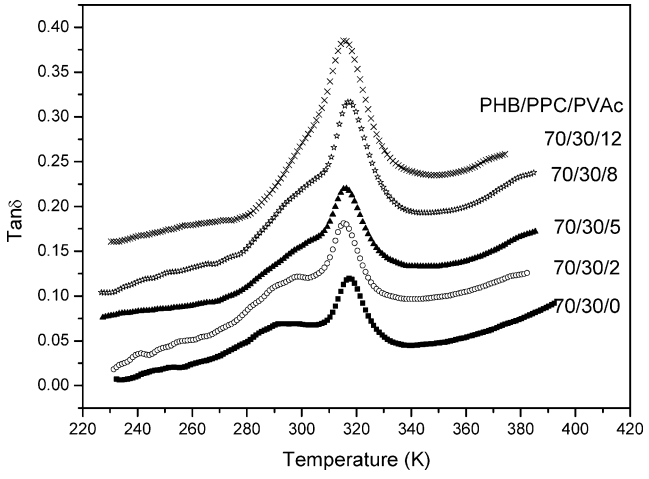

Fig. 6 Loss factor of 70PHB/30PPC blends containing different content of PVAc as a function of the temperature

and total energy dissipated because of viscoelastic relaxation of blends increases. In general, the area of loss factor is somewhat in relation to toughness. In other words, it maybe implies that PVAc can improve its toughness.

Effect of PVAc on the morphology of 70PHB/30PPC blend

The morphology of the blends was investigated by scanning electron microscopy (SEM). Figure 7 shows SEM micrographs for 70PHB/30PPC blends containing different content of PVAc. The dispersed particles in the SEM micrographs are attributed to PPC-rich phase because the surfaces of the PHB/PPC/PVAc blends were etched with acetone, which is a good solvent for PPC and a poor solvent for PHB. Figure 7a presents the surface of a 70PHB/30PPC blend and shows that the dispersed particles are large and circular. On the contrary, by adding two parts of PVAc to 70PHB/30PPC blend, the shape of dispersed particles is not regular circularity as shown in Fig. 7b. By increasing the content of PVAc, the size of dispersed particles decreases, as

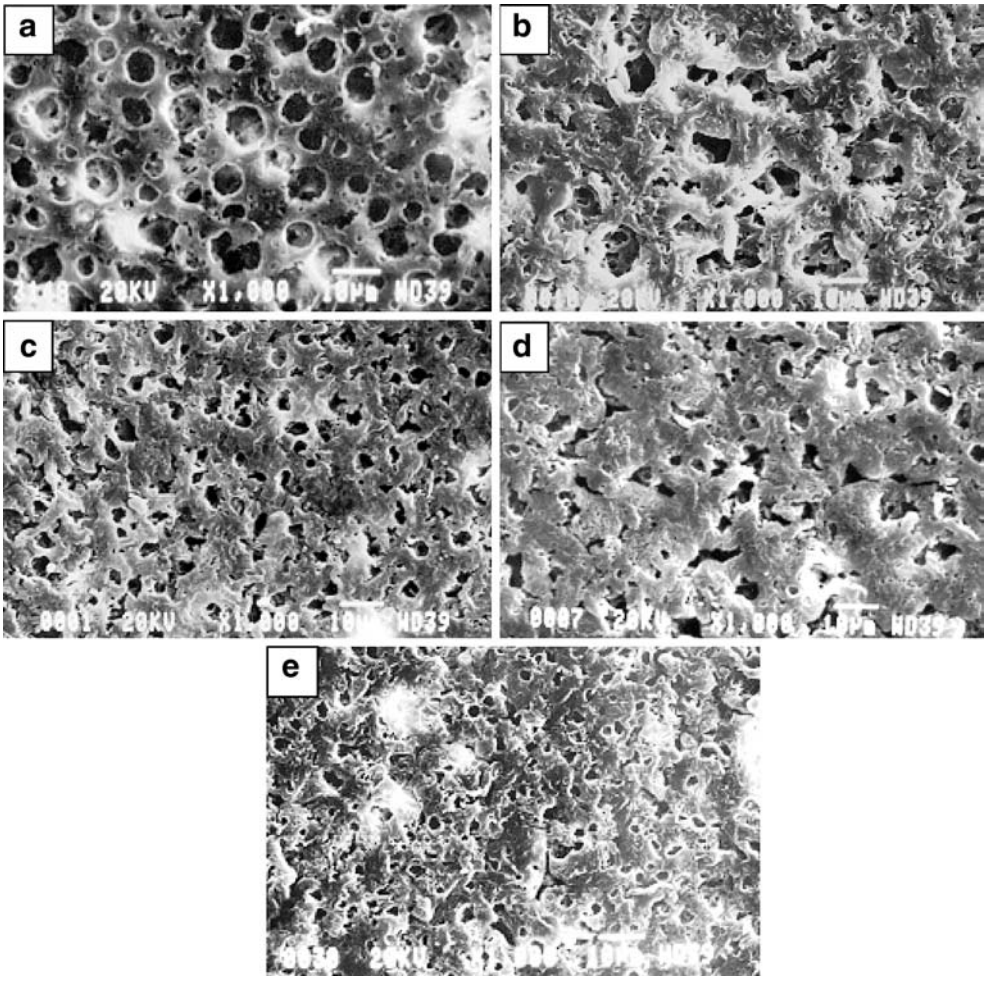

Fig. 7 The SEM photographs of 70PHB/30PPC containing different content of PVAc (content of PVAc: **a** 0%, **b** 2%, **c** 5%, **d** 8%, **e** 12%)

shown in Fig. 7b–e. This indicates that adding PVAc into 70PHB/30PPC blend can modify the interface between PHB phase and PPC phase and decrease the interfacial tension. In other words, the compatibilizing effect of PVAc on PHB/PPC blends is remarkable.

Effect of PVAc on the tensile properties of 70PHB/30PPC blend

Table 3 lists the tensile properties of 70PHB/30PPC blend containing different content of PVAc. The tensile or Young's modulus, which is a measure of the material stiffness, is obtained from the initial linear portion of the stress–strain curve. The fracture stress (tensile strength) and fracture strain (elongation at break) are known as ultimate properties of the material. Tensile toughness, the energy per unit volume required to fracture the material, is obtained from the area under the stress–strain curve. Adding two parts of PVAc into 70PHB/30PPC blend gave a significant improvement in the tensile strength, from 36 MPa to 41 MPa according to Table 3. Further increasing PVAc from 2 parts to 12 parts, the tensile strength decreases a little but is higher than that for plain 70PHB/30PPC. The Young's modulus also increases to a maximum, and then decreases a

Table 3 Tensile properties of 70PHB/30PPC blend containing different content of PVAc

PHB/PPC/PVAc	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)	Toughness (mJ)
70/30	36 ± 2	4.9 ± 1	1,640 ± 80	66 ± 5
70/30/2	41 ± 2	5.5 ± 1	1,900 ± 90	82 ± 6
70/30/5	40 ± 2	13 ± 2	1,700 ± 80	140 ± 7
70/30/8	39 ± 2	20 ± 2	1,700 ± 80	260 ± 14
70/30/12	38 ± 2	30 ± 3	1,600 ± 80	385 ± 20

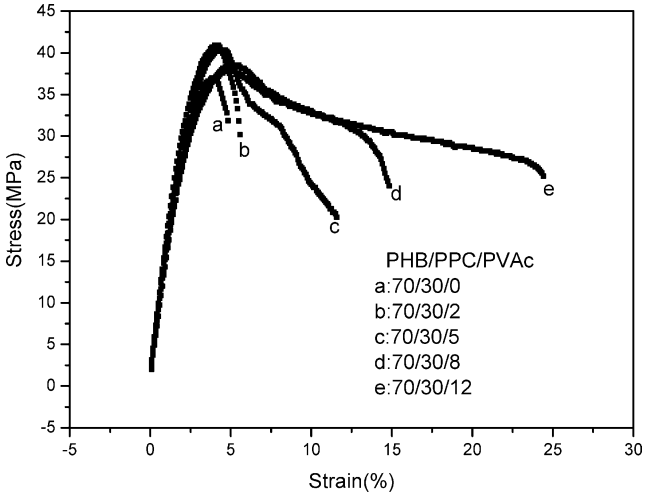

Fig. 8 Stress–strain curves of 70PHB/30PPC containing different content of PVAc

little with the addition of PVAc into 70PHB/30PPC blend. This behavior is quite similar to the results of tensile strength. In general, the mechanical properties of polymer blends are also highly dependent on the morphology as well as the interfacial adhesion. It is reported that the tensile properties of polymer blends are very sensitive to the state of the interface, that is, interfacial adhesion [42, 43]. The poor interface behaves as a flaw, and the failure initiates at the interface, which results in low tensile strength. The increased tensile strength and Young's modulus of all the 70PHB/30PPC blends containing PVAc suggested that the interfacial strength could be improved.

The addition of PVAc can increase the elongation at break and tensile toughness of 70PHB/30PPC blend. The values of elongation at break and tensile toughness for 70PHB/30PPC blend containing 12 parts of PVAc are $30 \pm 3\%$ and 385 ± 20 mJ, respectively. The increase is significant compared with plain 70PHB/30PPC blend, whose corresponding values are $4.9 \pm 1\%$ and 66 ± 5 mJ. For polymer blends, the interface often acts as sites for premature craze breakdown and crack initiation. Because PHB/PPC blends are immiscible, the behavior that the elongation at break and the tensile toughness are dependent on the PVAc content in blends further proves that adding PVAc can improve the interfacial adhesion between PHB phase and PPC phase in blends.

Figure 8 shows the stress–strain curves of 70PHB/30PPC blend containing various content of PVAc. In general, the stress–strain curve of brittle materials extends almost linearly up to a low fracture strain. If the material exhibits ductile behavior, the stress–strain curve passes through a maximum in the stress. For ductile polymers, deformation continues beyond the yield point and fracture eventually occurs. It is seen that the stress–strain curve exhibited by plain 70PHB/30PPC blend is typically that of a brittle polymer. The 70PHB/30PPC blend extends in an almost linear manner up to an elongation at break of about 4%. However, the stress–strain curve for 70PHB/30PPC blends containing PVAc is different from that for plain 70PHB/30PPC blend. Especially for 70PHB/30PPC/12PVAc blend, the stress–strain curve is almost typically that of a ductile polymer. This can be characterized by four different regions: (1) an initial linear region, (2) at a stress of approximately 38 MPa and a strain of about 5%, 70PHB/30PPC/12PVAc blend exhibits a yield point, (3) yielding is followed by a post drop in the stress to about 34 MPa, (4) a final region where the stress gradually decreases with increasing strain and eventually the specimen fractures. This indicates that adding PVAc into 70PHB/30PPC blend can change its fracturing mode.

Conclusion

The miscibility of PHB and PPC blends was studied by DSC and DMA. It is found that glass transition temperature, cold crystallization temperature, melting point and crystallization temperature of PHB do not change with the variation of PPC content in PHB/PPC blends, the peak position of loss factor of PPC also remains constant. This indicates that PHB/PPC blends are immiscible.

In order to improve the miscibility and mechanical properties of PHB/PPC blends, PVAc was employed as a comptibilizer. The effects of PVAc on the thermal behavior, morphology and mechanical properties of 70PHB/30PPC blend were investigated. The results show that the glass transition temperature and cold crystallization temperature of PHB in blends increases and the melting point of PHB in blends decreases, and the crystallization temperature and the enthalpy of non-isothermal crystallization of the PHB phase in the blends decreases with the increase of PVAc content in blends. But the effect of adding small amount of PVAc into 70PHB/30PPC blend on the crystallinity of PHB in blends is not evident. DMA results show that for 70PHB/30PPC blend, it is evident that there are two separate tanδ peaks for individual component, but after adding PVAc into 70PHB/30PPC blend, the peak of PPC shifts a little towards lower temperature and the peak of PHB disappeared gradually with the increase of PVAc content in blends. From morphology analysis, it is found that the size of dispersed phase decreases with the increasing content of PVAc in blends. The result of tensile properties shows that PVAc can increase its tensile strength and Young's modulus. Both the elongation at break and the tensile toughness increase significantly and the fracturing changes from brittle mode to ductile mode with increasing the addition of PVAc into 70PHB/30PPC blend.

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