

Miscibility and crystallization behavior of biodegradable blends of two aliphatic polyesters. Poly(butylene succinate) and Poly(ϵ -caprolactone)

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Abstract

Poly(butylene succinate) (PBSU) and poly(ϵ -caprolactone) (PCL) blends, both biodegradable chemosynthetic semicrystalline polyesters, were prepared with the ratio of PBSU/PCL ranging from 80/20 to 20/80 by co-dissolving the two polyesters in chloroform and casting the mixture. The miscibility and crystallization behavior of PBSU/PCL blends were investigated by differential scanning calorimetry and optical microscopy. Experimental results indicated that PBSU was immiscible with PCL as evidenced by the composition independent glass transition temperature and the biphasic melt. However, during the crystallization from the melt at a given cooling rate, the crystallization peak temperature of PBSU in the blends decreased slightly with the increase of PCL, while that of PCL in the blends first increased and then decreased with the increase of PBSU. Moreover, both the crystallization peak temperature of PBSU and PCL shifted to the low temperature range with the increase of the cooling rate for a given blend composition. Double melting peaks or one main melting peak with a shoulder were found for both PBSU and PCL after the complete crystallization cooled from the melt, and were ascribed to the melting–recrystallization mechanism. It was found that the subsequent melting behavior of PBSU/PCL blends was influenced apparently by the blend composition and the cooling rate used.

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1. Introduction

Biodegradable polymers, which have received more and more attention recently, can be classified into two types in terms of the preparation methods. One is the biosynthetic polymers, such as bacterial polyhydroxyalkanoates (PHAs). The other is the chemosynthetic polymers, such as the linear aliphatic polyesters. Poly(butylene succinate) (PBSU) and poly(ϵ -caprolactone) (PCL) are just two of them. The chemical structures of PBSU and PCL are $(-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}-)_n$ and $(-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}-)_n$, respectively.

Only a few works have been reported on PBSU, mainly on its crystal structure, crystallization and melting behavior

[1–8]. Polymer blending is often performed in order to improve the physical properties and extend the application fields of PBSU. PBSU was found to be miscible with poly(vinylidene fluoride), poly(vinylidene chloride-co-vinyl chloride) and poly(ethylene oxide) [9–12]. On the other hand, PBSU was found to show no miscibility with poly(hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) [14].

PCL is also a biodegradable thermoplastic polymer and has received extensive investigation. PCL is reported to be immiscible with PHB, PHBV, and PEO [15–17]. On the other hand, PCL is found to be miscible with poly(vinyl phenol), bisphenol-A polycarbonate, and phenoxy [18–20]. Recently Eastmond reviewed the polymer blends based on PCL [21].

Blends of two crystalline polymers have received much less attention than fully amorphous or amorphous/crystalline systems. Till now only a small number of works have

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been reported on the miscible polymer blends of two crystalline polymers with different chemical structures, which may be of considerable technological interest and offer the possibility of investigating crystallization and morphological behavior related to blend miscibility [22–27]. On the other hand, it is also possible to determine how the crystallinity of one component affects the morphology, crystallization and mechanical properties of the other in the case of binary immiscible blends of two crystalline polymers [17,28–31].

In this work, we studied the miscibility and crystallization behavior of PBSU/PCL blends on the basis of our previous works of PHB/PBSU, PHBV/PBSU and PEO/PCL blends [13,14,17]. Both of the components are crystalline and biodegradable in PBSU/PCL blends. To the best of our knowledge, no attention has been paid to the blending of PBSU and PCL till now in the literature. It is important to understand their miscibility and the crystallization behavior in a cooling process as a model case of processing a biodegradable crystalline polymer blend material. However, an experimental study is not straightforward to conduct because of the dynamic interplay between crystallization and phase separation, or due to crystallization in phase-separated domain structures [13]. In the present paper, the results of an investigation concerning the miscibility, variation of degree of crystallinity of the two components, nonisothermal crystallization under various cooling rates and subsequent melting behavior of PBSU/PCL blends were reported.

2. Experimental

PBSU ($M_w = 140,000$) was supplied by Showa High Polymer Co., Ltd., and PCL ($M_w = 14,300$) was purchased from Scientific Polymer Products, Inc. (Ontario, NY). PBSU/PCL blends were prepared with mutual solvent chloroform. The solution of both polymers (0.02 g/ml) was cast on a petri dish at room temperature. The solvent was allowed to evaporate in a controlled air stream for one day and the resulting films were further dried in vacuum at 50 °C for three days. In this way, blends were prepared with various compositions ranging from 80/20 to 20/80 in weight ratio, the first number referring to PBSU.

The glass transition temperature (T_g) and melting point temperature (T_m) of the melt-quenched PBSU/PCL blends were measured by a TA Instruments DSC 2910 with a Thermal Analyst 2000 at a heating rate of 20 °C/min. The samples were first annealed at 150 °C for 3 min to destroy any thermal history and subsequently quenched into liquid nitrogen. The crystallization exothermic peak temperature was obtained from the DSC cooling exotherms from the crystal-free melt at 2, 5 and 10 °C/min. The subsequent melting behavior was then studied at a heating rate of 20 °C/min after the completion of the nonisothermal crystallization at various cooling rates from the melt.

A polarizing microscope (Olympus BHA-P) with a temperature controller (Linkam LK-600PM) was used to study the miscibility and crystallization of PBSU/PCL blends.

3. Results and discussion

3.1. Study of the miscibility of PBSU/PCL blends by DSC

Binary polymer blends can be classified into three types in terms of the miscibility between the two components: namely completely miscible, partially miscible and completely immiscible polymer blends. The miscibility of binary polymer blends can be determined easily by measuring the T_g of the blends if the difference in the T_g s of the two components is not less than 20 °C. If polymer blends exhibit one single composition-dependent T_g , the two components are completely miscible polymer blends. If polymer blends exhibit two composition-independent T_g s close to those of neat components, the two components are completely immiscible polymer blends. If polymer blends exhibit two composition-dependent T_g s which locate between those of neat components, the two components are partially miscible polymer blends.

In the present work the difference in the T_g s between neat PBSU (around –34 °C) and neat PCL (around –65 °C) is more than 30 °C, so the miscibility of PBSU/PCL blends can be investigated by the determination of T_g . DSC measurements were performed to characterize the melt-quenched PBSU/PCL blends. However, it should be noted here that the crystallization rates of both PBSU and PCL are very fast during the cooling process from the melt to the amorphous phase. The crystallinity of PBSU and PCL formed during the cooling process must have a significant negative influence on the accuracy of the measured value of the T_g . In order to avoid or diminish to the least extent such a negative influence on the accurate measurement of the value of the T_g , we quenched the samples directly into liquid nitrogen as quickly as possible after they were melted at 150 °C for 3 min with a hot stage to destroy any thermal history. Then the samples were transferred to the DSC cell, which had been set at around –100 °C in advance, as quickly as possible to measure the T_g of the PBSU/PCL blends at a heating rate of 20 °C.

Fig. 1 shows the DSC traces of PBSU/PCL blends. Neat PBSU exhibits a T_g at around –34 °C, an exothermic cold crystallization peak at around –5 °C, and a T_m at around 118 °C. Neat PCL exhibits a T_g at around –66 °C, an exothermic cold crystallization peak at around –54 °C, and a T_m at around 60 °C. In the PBSU/PCL blends, a T_g at around –36 °C, which is close to that of neat PBSU, can be found for 80/20 and 60/40 blends, while the glass transition corresponding to PCL is not so apparent that it cannot be determined accurately for 80/20 and 60/40 blends. On the other hand, a T_g at around –65 °C, which is close to that of

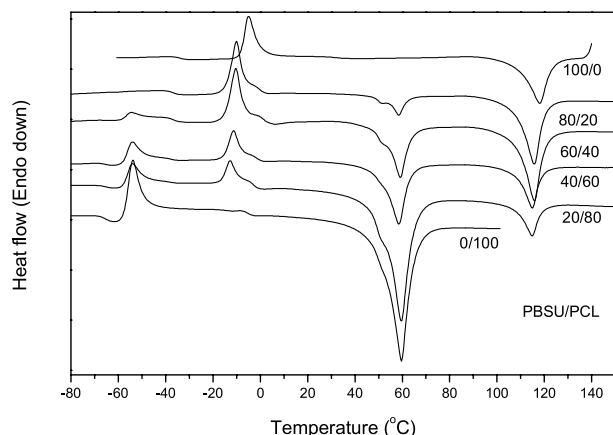


Fig. 1. DSC traces of PBSU/PCL blends after melt quenching at a heating rate of 20 °C/min.

neat PCL, can be found for 40/60 and 20/80 blends, while the glass transition corresponding to that of PBSU cannot be found since it is masked by the cold crystallization peak temperature of PCL. The cold crystallization peak temperature of PBSU in the blends is found to shift to around -10 °C from around -5 °C for neat PBSU and is almost composition-independent, indicating that the cold crystallization of PBSU in the PBSU/PCL blends is enhanced by the addition of PCL. This is probably because that the cold crystallization of PCL is prior to that of PBSU on heating from the amorphous phase of the PBSU/PCL blends, and the crystals of PCL may have a positive effect on the nucleation of the crystallization of PBSU. The cold crystallization peak temperature of PCL is found to remain around -54 °C for both the neat and the blended PCL, indicating that the addition of PBSU does not have a significant influence on the cold crystallization of PCL in the blends. It should be pointed out that the cold crystallization of PCL is not apparent for 80/20 blend due to the very low content of PCL in the blends. The T_m of PBSU remains almost the same in the blends. Compared with the value of the T_m of neat PBSU, the decrease of the T_m of PBSU in the blends is no more than 3 °C. The T_m of PCL remains also unchanged in the blends. The decrease of the T_m of PCL in the blends is no more than 2 °C compared with that of neat PCL. All the results mentioned above lead us to the conclusion that PBSU is immiscible with PCL in the blends.

Two separate melting peaks can be found in Fig. 1 for the melt-quenched PBSU/PCL blends, which correspond to the melting of PBSU and PCL, respectively. On the basis of the heat of fusion of 100% crystalline PBSU (200 J/g) [6] and PCL (136 J/g) [32], the degree of crystallinity of both PBSU and PCL components were calculated from the melting endotherms of the melt-quenched sample and normalized with respect to the composition of each component in the blend. Fig. 2 summarizes the variation of degree of crystallinity of PBSU and PCL as a function of blend composition. The degree of crystallinity of PBSU for

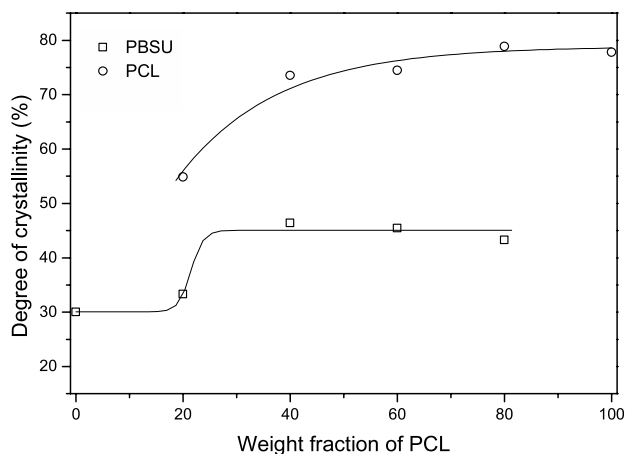


Fig. 2. Variation of degree of crystallinity of PBSU and PCL for the melt-quenched PBSU/PCL blends as a function of blend composition.

80/20 blend is comparable to that of neat PBSU. However, the degree of crystallinity of PBSU increases from around 30% for neat PBSU and 80/20 blend to around 45% for the rest of the blended PBSU, indicating that the addition of PCL enhanced the crystallization of PBSU, which is consistent with the trend of the cold crystallization of PBSU with the addition of PCL mentioned above. On the other hand, compared with that of neat PCL, the degree of crystallinity of PCL in the blends varies slightly with the addition of PBSU up to 60 wt%. This is also consistent with the tendency of the cold crystallization of PCL in the blends mentioned above. However, the degree of crystallinity of PCL for 80/20 blend decreases sharply to around 55% from around 75–80% for the neat and the rest of the blended PCL, indicating that the crystallization of PCL is suppressed by the high PBSU content for 80/20 blend.

3.2. Optical microscopy study

Optical microscopy was also used to investigate the miscibility and crystallization of PBSU/PCL blends. If PCL is miscible with PBSU, the single-phased melt should be observed. Otherwise, if PCL is immiscible with PBSU, the biphasic melt should be observed. PBSU/PCL blends samples were first melted at 150 °C and then were observed by optical microscopy. For all of the samples studied, biphasic separation was observed, indicating that PCL was not miscible with PBSU in the melt. Fig. 3 shows the spherulitic morphology of PBSU and PCL for 40/60 blend observed by polarizing optical microscopy using two-step crystallization process. Shown in Fig. 3a are the PBSU spherulites which were crystallized at 80 °C in the matrix of the PCL melt since the crystallization temperature 80 °C was higher than the T_m of PCL. Shown in Fig. 3b are the PCL spherulites which were crystallized at 30 °C in the presence of the PBSU spherulites formed previously at 80 °C.

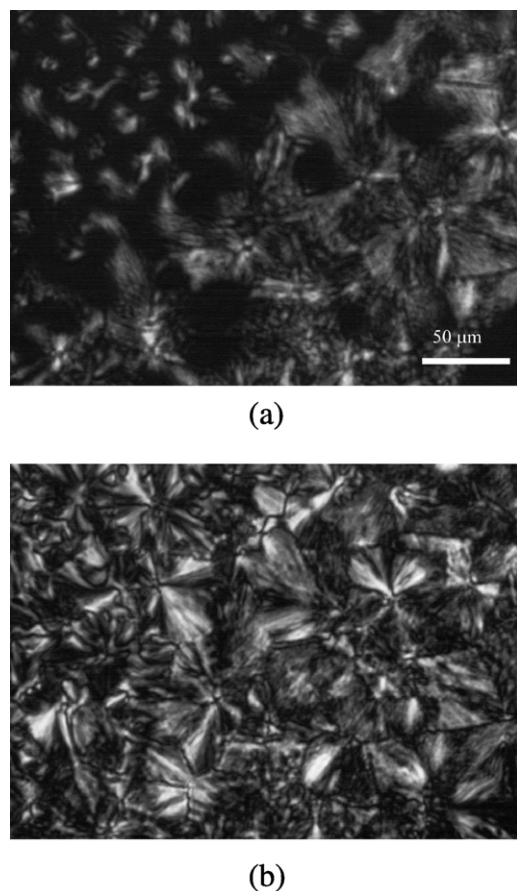


Fig. 3. Polarizing optical micrographs of PBSU/PCL 40/60; (a) Crystallization of PBSU at 80 °C and (b) crystallization of PCL at 30 °C in the presence of PBSU spherulites formed previously at 80 °C.

3.3. Nonisothermal crystallization and subsequent melting behavior

It is important to study the crystallization behavior of PBSU/PCL blends in a cooling process as a model case of

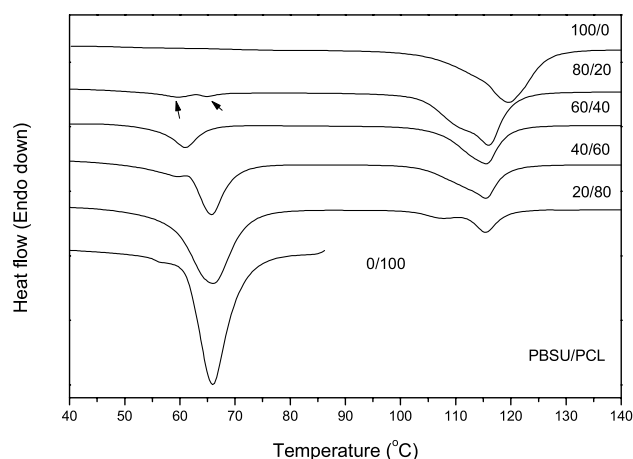


Fig. 4. DSC traces of PBSU/PCL blends at a heating rate of 20 °C/min for the as cast samples

processing a biodegradable crystalline polymer blend material. However, it is expected that an experimental study is not straightforward to conduct because of the crystallization in phase-separated domain structures. In the present paper, the nonisothermal crystallization and subsequent melting behavior of PBSU/PCL blends were also studied by DSC. As introduced in the experimental part, PBSU/PCL blends were cooled from the melt at various cooling rates of 2, 5 and 10 °C/min. The subsequent melting behavior was then investigated at a heating rate of 20 °C/min.

Before studying the nonisothermal crystallization and subsequent melting behavior of PBSU/PCL blends, we first studied the melting behavior of PBSU/PCL blends for the as cast samples. Fig. 4 shows the melting behavior of PBSU/PCL blends for the as cast samples. Similar to those of the melt-quenched samples, two separate melting endotherms are found for the as cast samples. The one located at low temperature corresponds to the melting of PCL, while the other located at high temperature corresponds to the melting of PBSU. The T_m s of PBSU and PCL in the blends are lower than those for the neat polymers. In some cases, double melting behavior can be found for the T_m s of PCL and PBSU, which are often found for the melting behavior of biodegradable polymer blends for the as cast samples [14].

The degree of crystallinity of PBSU and PCL were also investigated for the as cast samples. Fig. 5 summarizes the variation of degree of crystallinity of PBSU and PCL as a function of blend composition. The degree of crystallinity of PBSU remains almost 60% and is independent of the blend composition, which is higher than that of the melt-quenched sample. On the other hand, the degree of crystallinity of PCL is around 85% and varies slightly for the 0/100, 20/80 and 40/60 samples. The degree of crystallinity of PCL for 60/40 blend decreases sharply to around 65%, and that for 20/80 decreases sharply to around 40%, indicating that the presence of high PBSU content has a significant negative

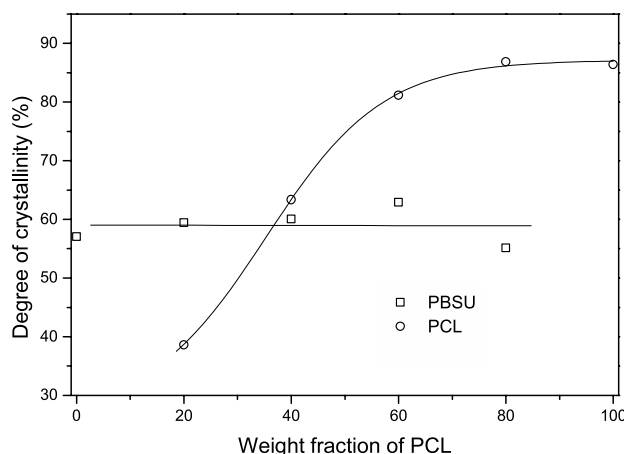


Fig. 5. Variation of degree of crystallinity of PBSU and PCL for the as cast PBSU/PCL blends as a function of blend composition.

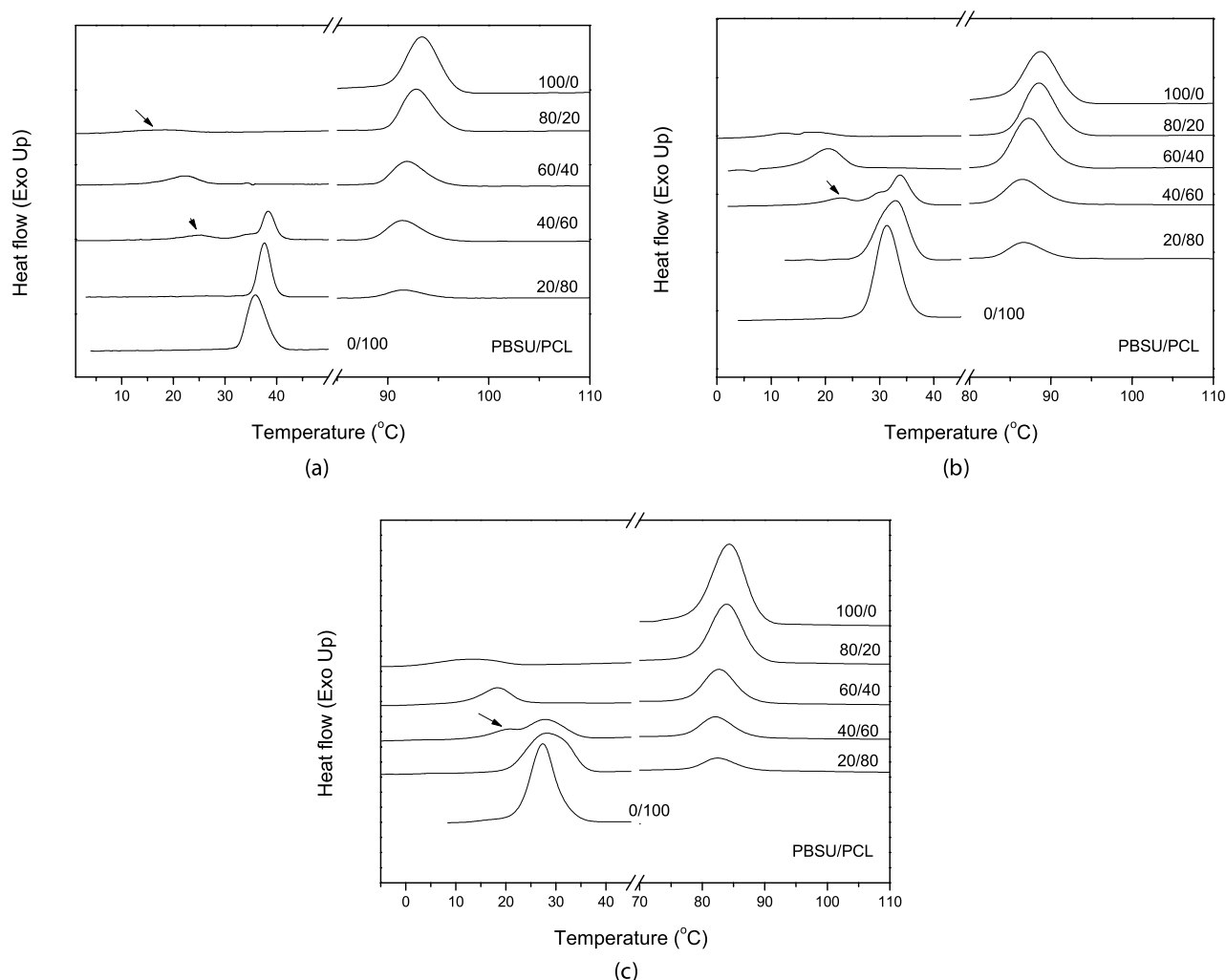


Fig. 6. Nonisothermal crystallization of PBSU/PCL blends from the melt at various cooling rates; (a) 2 °C/min, (b) 5 °C/min, and (c) 10 °C/min.

influence on the crystallization of PCL in the PBSU/PCL blends.

The DSC cooling exotherms from the melt at 2, 5 and 10 °C/min are shown in Fig. 6. Irrespective of the cooling rates used, two crystallization peaks were found during the nonisothermal crystallization for the PBSU/PCL blends, corresponding to the crystallization of PBSU and PCL, respectively. The crystallization peak temperature of PBSU is prior to that of PCL. At a given cooling rate, the crystallization peak temperature of PBSU shifts slightly to the low temperature range with the increase of the PCL content; however, the shift is very limited, and the difference between the crystallization peak temperature of neat PBSU and that of 20/80 blend is no more than 3 °C. But in the case of PCL, it is a little complicated. At a given cooling rate, the crystallization peak temperature of PCL first increases with the addition of the PBSU content for the PCL-rich blends. But for the PBSU-rich blends, the crystallization peak temperature of PCL decreases with the increase of the PBSU content. One particular phenomenon must be emphasized on the crystallization of PCL for 40/60

blend. Despite the cooling rate used, the crystallization exotherm of PCL for 40/60 blend splits into two peaks with the higher one being the main peak while the lower one a shoulder. The reason why 40/60 blend shows two separate crystallization peaks is still unknown at present. The higher crystallization peak temperature is comparable to those of 80/20 blend and neat PBSU, while the lower one is comparable to those of the PBSU-rich blends, i.e. 60/40 and 80/20 blends. It seems that 60/40 is a critical blend composition which has a significant influence on the crystallization peak temperature of PCL in the PBSU/PCL blends. The difference between the crystallization peak temperatures of the PCL-rich blends and those of the PBSU-rich blends is more than 10 °C, indicating that the content of PBSU in the blends plays an important role on the crystallization of PCL.

For comparison, the crystallization peak temperatures of the PBSU/PCL blends, taken from the curves of Fig. 6, are plotted in Fig. 7 as a function of blend composition. Fig. 7 clearly shows the variation of the crystallization peak temperatures against blend composition for both PCL and

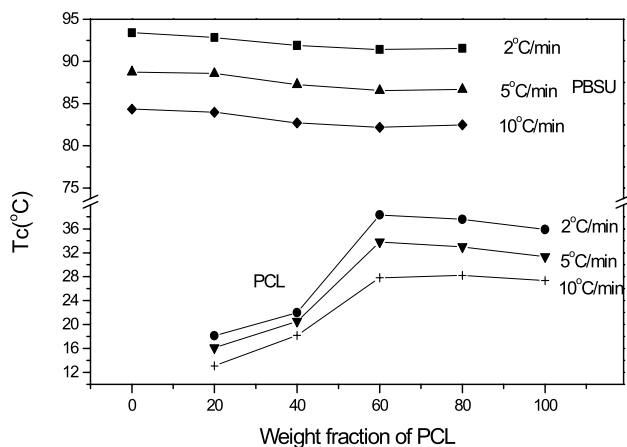


Fig. 7. Variation of crystallization peak temperatures of PBSU and PCL for the PBSU/PCL blends cooled from the melt at various cooling rates as a function of blend composition. For 40/60 blend, the value of the crystallization peak temperature used here is the higher one.

PBSU. It is seen that for a given blend composition, the crystallization peak temperatures of PCL and PBSU shift to the lower temperature range with the increase of the cooling rate. At a given cooling rate, the crystallization peak

temperature of PBSU shifts slightly to the low temperature range with the increase of the PCL content, while that of PCL first increase with the increase of PBSU for the PCL-rich blends and then decreases with the increase of the PBSU for the PBSU-rich blends.

The subsequent melting behavior of PBSU/PCL blends was also studied by DSC at a heating rate of 20 °C/min after the completion of the nonisothermal crystallization at various cooling rates and was shown in Fig. 8. Two separate melting endotherms can be found for all the blends despite the cooling rate used, corresponding to the melting of the crystals of PBSU at higher temperature and that for PCL at lower temperature, respectively. Double melting endotherms or one main melting endotherm with a shoulder on the left side of the main melting peak were found for PBSU, and the ratio of the areas of the two melting peaks was influenced by the cooling rate used and the blend composition. Based on the previous studies [8,12], the lower melting peak is ascribed to be the melting of the PBSU crystals formed previously during the cooling process from the melt, while the higher one arises from the melting–recrystallization of the lower one. At a given cooling rate

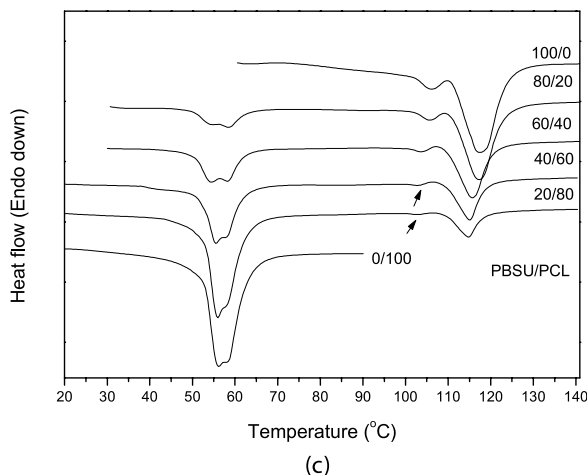
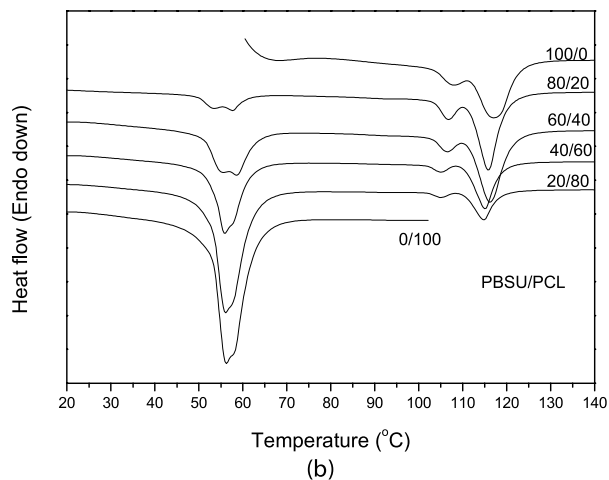
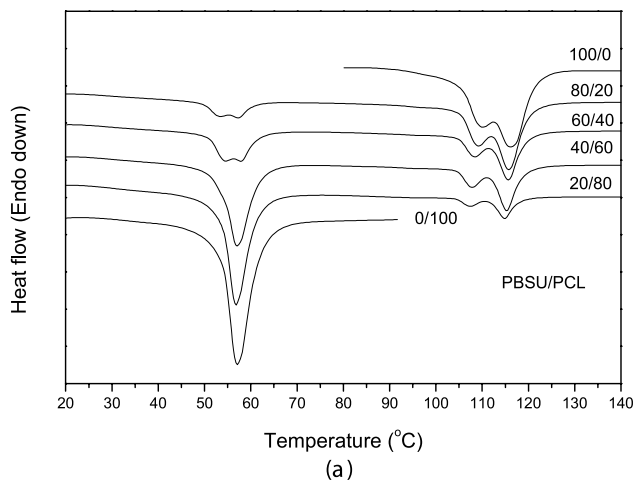


Fig. 8. Subsequent melting behavior of PBSU/PCL blends at a heating rate of 20 °C/min after nonisothermal crystallization at various cooling rates; (a) 2 °C/min, (b) 5 °C/min, and (c) 10 °C/min.

used, the ratio of the area of the lower melting peak to that of the higher one decreases with the increase of the PCL content, indicating that the crystallization of PBSU from the melt is hindered by the presence of PCL and is influenced by the PCL content. For a given blend composition, the ratio of the area of the lower melting peak to that of the higher one decreases with the increase of the cooling rate used, indicating that the crystallization of PBSU from the melt is suppressed at a fast cooling rate. This result is reasonable since less crystallization time is available for PBSU to crystallize at a fast cooling rate. So in such cases the melting–recrystallization will be more pronounced upon heating to the melt after the completion of the nonisothermal crystallization from the melt.

In the case of the melting of PCL, only one well-defined melting peak can be observed for the PCL-rich blends (0/100, 20/80 and 40/60 blends) at the cooling rates of 2 and 5 °C/min used, while a main melting peak with a small shoulder on the right side of the main melting peak can be observed at a fast cooling rate of 10 °C/min used. For the PBSU-rich blends (60/40 and 80/20 blends), two melting peaks can be found for PCL despite the cooling rates used. The double melting behavior of PCL may also arise from the melting–recrystallization mechanism. Generally speaking, the double melting endotherms or one main melting endotherm with a shoulder for PBSU and PCL are apt to appear when the fast cooling rate was used. On the other hand, the blend composition also plays an important role on the melting behavior of the two components. It is easy for the appearance of the double melting behavior and the occurrence of the melting–recrystallization when the content of the other component was higher in the blends. In order to get a better understanding of the origin of the subsequent melting behavior of PBSU/PCL blends, it is necessary to investigate it in more details by taking into account of the effect of the blend composition, the cooling rates used and the heating rates used. This may be the subject of the following research of the PBSU/PCL blends.

4. Conclusions

The miscibility, crystallization and subsequent melting behavior of PBSU/PCL blends were investigated in this work. PBSU was found to be immiscible with PCL as evidenced by the composition independent glass transition temperature and the biphasic melt. On heating from the amorphous state for the melt-quenched samples, the cold crystallization of PCL is prior to that of PBSU due to the lower T_g of PCL compared with that of PBSU. The cold crystallization peak temperature of PCL was almost independent of the blend composition, indicating that the addition of PBSU did not have an obvious influence on the cold crystallization of PCL. On the other hand, the cold crystallization peak temperature of PBSU was found to shift to the low temperature range in the blends compared with

that of neat PBSU, indicating that the cold crystallization of PBSU was enhanced by the addition of PCL due to the possible positive effect of the previously formed PCL crystals on the nucleation of the crystallization of PBSU in the blends. The crystallization and subsequent melting behavior of PBSU/PCL blends were studied as the functions of the cooling rates and the blend compositions. Both the crystallization peak temperatures of PBSU and PCL shifted to the low temperature range with the increase of the cooling rate for a given blend composition. At a given cooling rate, the crystallization peak temperature of PBSU in the blends decreased slightly with the increase of PCL, indicating that the addition of PCL did not have any apparent influence on the crystallization of PBSU. PBSU and PCL were immiscible, so PBSU may probably only crystallize in the domains of the PBSU melt while PCL was just in the melt, which separated from the PBSU melt and did not influence the crystallization of PBSU. This kind of behavior was also consistent with the OM observation. However, on the other hand, the crystallization of PCL in the blends first increased and then decreased with the increase of PBSU. The detailed crystallization mechanism of PCL was still unknown. The presence of the previously formed PBSU crystals was expected to have two opposite effects on the crystallization of PCL. On the one hand, the crystallization of PCL was enhanced by the presence of the previously formed PBSU crystals due to the possible positive effect on the nucleation of the crystallization of PCL. However, on the other hand, the presence of the PBSU crystals may have a negative effect on the crystal growth of PCL freely as in the case of neat PCL due to the surrounding confinement by the PBSU crystals. Therefore, the crystallization behavior of PCL was expected to result from the competition between the opposite effects. The subsequent melting behavior of PBSU/PCL blends were influenced apparently by the blend composition and the cooling rate used. Double melting peaks or one main melting peak with a shoulder were found for both PBSU and PCL after the complete crystallization cooled from the melt, and were ascribed to the melting–recrystallization mechanism.

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