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Melting behaviour of poly(butylene succinate) in miscible blends with poly(ethylene oxide)

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Abstract

The melting behavior of poly(butylene succinate) (PBSU) in miscible blends with poly(ethylene oxide) (PEO), which is a newly found polymer blends of two crystalline polymers by our group, has been investigated by conventional differential scanning calorimetry (DSC). It was found that PBSU showed double melting behavior after isothermal crystallization from the melt under certain crystallization conditions, which was explained by the model of melting, recrystallization and remelting. The influence of the blend composition, crystallization temperature and scanning rate on the melting behavior of PBSU has been studied extensively. With increasing any of the PEO composition, crystallization temperature and scanning rate, the recrystallization of PBSU was inhibited. Furthermore, temperature modulated differential scanning calorimetry (TMDSC) was also employed in this work to investigate the melting behavior of PBSU in PBSU/PEO blends due to its advantage in the separation of exotherms (including crystallization and recrystallization) from reversible meltings (including the melting of the crystals originally existed prior to the DSC scan and the melting of the crystals formed through the recrystallization during the DSC scan). The TMDSC experiments gave a direct evidence of this melting, recrystallization and remelting model to explain the multiple melting behavior of PBSU in PBSU/PEO blends.

Keywords: Multiple melting behavior; Poly(butylene succinate)/poly(ethylene oxide) blends; Temperature modulated differential scanning calorimetry (TMDSC)

1. Introduction

Poly(butylene succinate) (PBSU) is one of the interesting biodegradable synthetic polymers. The crystal structure, crystallization and melting behavior of PBSU have been reported in the literatures [1–3]. PBSU was found to be miscible with poly(vinylidene fluoride) and poly(vinylidene chloride-co-vinyl chloride) in our previous work [4,5]. Recently, we have studied the miscibility and crystallization behavior in blends of PBSU and poly(ethylene oxide) (PEO) by differential scanning calorimetry (DSC) and polarizing optical microscopy [6]. It was found that PBSU was miscible with PEO as shown by the existence of single composition dependent glass transition temperature over the entire composition range. In addition, the polymer–polymer interaction parameter, obtained from the melting depression of the high-T_m component PBSU using the Flory–Huggins equation, was composition dependent, and its value was always negative. These results indicated that PBSU/PEO blends were thermodynamically miscible in the melt.

Double or multiple melting behavior is often found on many isothermally crystallized semi-crystalline polymers upon heating in DSC. However, the origin of the multiple melting is still not very clear. Liu et al. [7] once reviewed the origin and ascribed it to a variety of mechanisms [8–12]: (1) melting, recrystallization and remelting during the DSC heating process, (2) the presence of more than one crystal modifications (polymorphism), (3) variation in morphology (such as lamellar thickness, distribution, perfection or stability), (4) physical aging or/and relaxation of the rigid amorphous fraction, (5) different molecular weight species and so on. Actually, it should be noted that the multiple melting behavior of polymers originates from different reasons depending on the polymer and the crystallization condition.

The melting behavior of PBSU was first reported by Yoo et al. by DSC and wide angle X-ray analysis [3]. The PBSU

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crystallized between 80 and 100 °C showed two endotherms, one endotherm just prior to the high exotherm corresponding to the melting process of the original crystallites, and the other higher endotherm corresponding to the melting process of the recrystallized ones.

However, to our knowledge, no analysis has been carried out so far on the multiple melting behavior of PBSU in the blends. In addition, the multiple melting behavior of semicrystalline polymers is usually studied by conventional DSC. Recently, temperature modulated differential scanning calorimetry (TMDSC) has become available as a new thermal analysis technique, which applies a sinusoidal temperature oscillation (modulation) on a linear heating/cooling conventional DSC and makes the total heat flow (such as that from conventional DSC) to be separated into the heat capacity-related (reversible) and kinetic (non-reversible) components. Thus, the endothermic signals can be detected in both reversible and non-reversible scans, whereas the crystallization exotherms only contribute to the non-reversible signal. This makes TMDSC a very powerful technique for the separation of exotherms (including crystallization and recrystallization) from glass transitions, reversible melting, or other heat capacity related events [13–16].

In our present work, we studied the complex endothermic melting behavior of isothermally melt-crystallized PBSU in PBSU/PEO blends by combining the conventional DSC with TMDSC. The influence of the blend composition, crystallization temperature and scanning rate on the melting behavior of PBSU was studied extensively. The TMDSC experiments gave the direct evidence of the model of melting, recrystallization and remelting to explain the melting behavior of PBSU in PBSU/PEO blends.

2. Experimental

PBSU ($M_w = 140,000$) was supplied by Showa High Polymer Co., Ltd and PEO ($M_w = 100,000$) was purchased from Scientific Polymer Products, Inc. (Ontario, NY). PBSU/PEO blends were prepared with mutual solvent chloroform. The solution of both polymers (0.01 g/ml) was cast on a petri dish at room temperature. The solvent was allowed to evaporate in a controlled air stream for 1 day and the resulting films were further dried in vacuum at 50 °C for 3 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.

A TA 2910 TMDSC was used for both conventional DSC and TMDSC analysis. All scans were run under a nitrogen gas purge to minimize thermo-oxidative degradation. The samples were first melted at 150 °C for 3 min to destroy any thermal history, cooled quickly to the crystallization temperature (T_c), and then maintained at the T_c until the crystallization was completely finished. For the DSC measurements, the heating rate (if not otherwise specified) was 20 °C/min. For the TMDSC measurements, the heating was operated at 2 °C/min with the oscillation amplitude of 0.5 °C, and the oscillation period of 40 s throughout the investigation.

3. Results and discussion

According to the model of melting, recrystallization and remelting, the multiple melting curves observed by DSC are the superposition of three contributions, an endotherm associated with the melting of the original crystals formed before the DSC scan, an exotherm corresponding to recrystallization following the initial melting, and an endotherm associated with the melting of crystals formed by recrystallization [3,17]. Our experimental results suggest that the melting behavior of PBSU in PBSU/PEO blends is most convincingly explained on the basis of this model.

3.1. Influence of crystallization temperature

Crystallization temperature has a significant effect on the melting behavior of PBSU in PBSU/PEO blends. As an example, shown in Fig. 1, the melting endotherms of PBSU/PEO 20/80 blend are isothermally crystallized at different temperatures from the melt for 120 min at a constant heating rate of 20 °C/min. The DSC curves exhibited two endothermic peaks (labeled as T_{m1} and T_{m2} in the order of temperature from low to high) for $T_c \leq 90$ °C; in the case of $T_c \geq 95$ °C, only one melting peak was observed. On increasing the T_c, the T_{m1} shifts to higher temperatures, and finally merges into the T_{m2}. With the increase of the T_c, the T_{m2} almost remains constant at ca. 114 °C. The magnitude of the T_{m1} relative to that of the T_{m2} becomes larger with increasing the T_c. This phenomenon may be explained as follows. The T_{m1} represents the melting of the original crystals formed before the DSC scan, and the T_{m2} is associated with the melting of crystals formed by the recrystallization [3,17]. The degree of undercooling, given

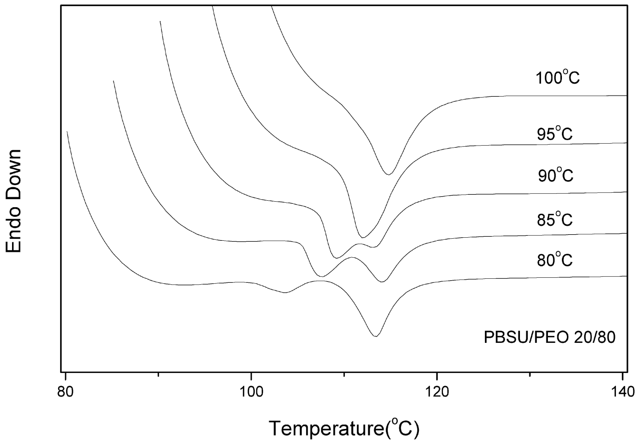


Fig. 1. DSC traces of PBSU/PEO 20/80 blend isothermally melt crystallized at different temperatures for 120 min.

by ($T_m^0 - T_m$) with T_m^0 being the equilibrium melting point temperature and T_m the observed melting point temperature, is the dominant factor for a polymer to undergo recrystallization [18,19]. The larger the degree of undercooling, the greater the tendency towards recrystallization. Therefore, a lower driving force towards recrystallization is found for the crystals formed at a higher T_c because of the higher T_m. Consequently, in the case of PBSU/PEO 20/80 blend, only one endotherm is observed for $T_c \geq 95$ °C due to the weaker tendency towards recrystallization, whereas two melting endotherms are observed for $T_c \leq 90$ °C and the magnitude of the T_{m2} becomes larger for the lower T_c because of the stronger tendency towards recrystallization. In brief, the recrystallization of PBSU in PBSU/PEO blends was inhibited by the increase of the crystallization temperature.

3.2. Influence of blend composition

The influence of the blend composition on the melting behavior of PBSU in PBSU/PEO blends was also investigated by DSC. Figs. 2 and 3 show the melting endotherms of PBSU/PEO blends, which were crystallized at 90 °C for 30 min and at 100 °C for 120 min, respectively. For $T_c = 90$ °C, two melting endotherms are observed for all samples. With increasing the PEO composition, the lower melting endothermic peak T_{m1} increases, while the higher melting endothermic peak T_{m2} is almost unchanged except that a small decrease in PBSU/PEO 20/80 blend is found. Furthermore, the shape of the two melting endotherms is found to vary with the blend composition, too. With increasing the PEO composition, the T_{m2} located at ca. 114 °C gradually diminishes and the T_{m1} increases. In the case of PBSU/PEO 20/80 blend, the T_{m1} becomes dominant. For $T_c = 100$ °C, PBSU does not exhibit double melting behavior, and blending does not exert any strong influence on the shape of the melting endotherms. This is consistent with the dependence of melting behavior of PBSU on the T_c shown in the previous section.

PBSU/PEO blends crystallized at 90 °C for 30 min exhibit double melting behavior, and the influence of the blend composition on the double melting endotherms may be explained as follows. At first glance, it seems strange that the T_{m1} increases with the increase of PEO. It seems more reasonable that the T_{m1} decreases with the increase of PEO due to the diluent factor. However, it should be noted that the supercooling, given by ($T_m^0 - T_c$), is not the same for all the PBSU/PEO blends though they all crystallized at the same $T_c = 90$ °C. As introduced in our previous work, the equilibrium melting point of PBSU decreases with the increase of PEO [6]. So the supercooling of PBSU/PEO blends decreases with the increase of PEO. It is reasonable that the crystals formed at lower supercooling have a higher T_m. On the other hand, the increase of the T_{m1} with the increase of PEO can also be explained by the increase of the normalized crystallinity of PBSU, which was calculated from the melting endotherms and normalized with respect to the composition of each component in the blend. The normalized crystallinity of PBSU increases from ca. 40% for neat PBSU to ca. 56% for PBSU/PEO 20/80 blend with increasing the PEO composition. In a word, the increase of T_{m1} hinders the recrystallization of PBSU upon blending with PEO. This kind of hindrance becomes stronger with the increase of PEO in the blends.

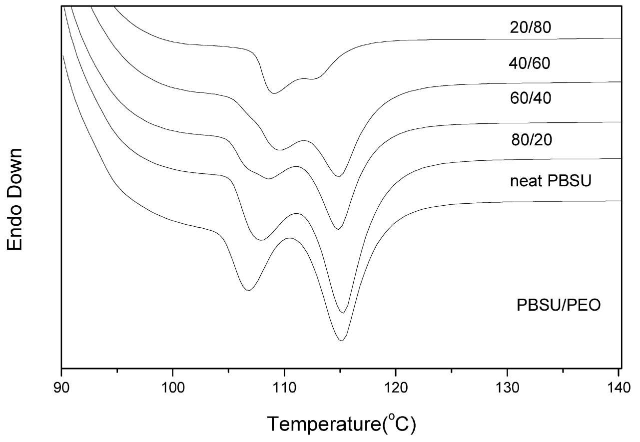


Fig. 2. DSC traces of PBSU/PEO blends isothermally melt crystallized at 90 °C for 30 min.

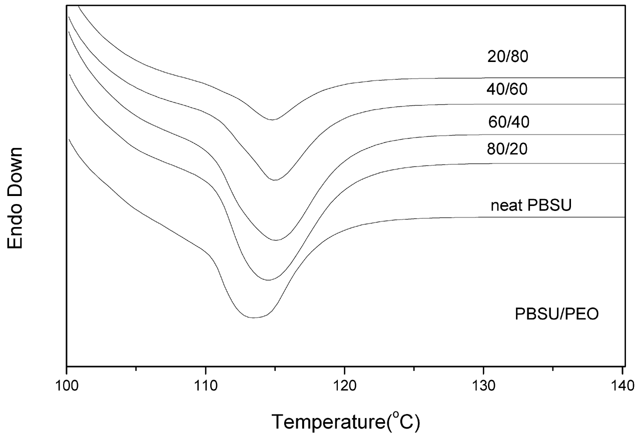


Fig. 3. DSC traces of PBSU/PEO blends isothermally melt crystallized at 100 °C for 120 min.

3.3. Influence of scanning rate

The scanning rate dependence on the multiple melting behavior is often regarded as the evidence of the melting-recrystallization model. Fig. 4 shows the scanning rate dependence of the melting behavior of PBSU/PEO 60/40 blend crystallized isothermally at 90 °C for 10 min. With increasing the scanning rate, the T_{m1} increases and the T_{m2} decreases. Furthermore, the T_{m2} decreases in size relative to the T_{m1}. This is because less time is available for the recrystallization due to the increased DSC heating rate. In brief, with increasing the scanning rate, the recrystallization of PBSU in PBSU/PEO blends is inhibited.

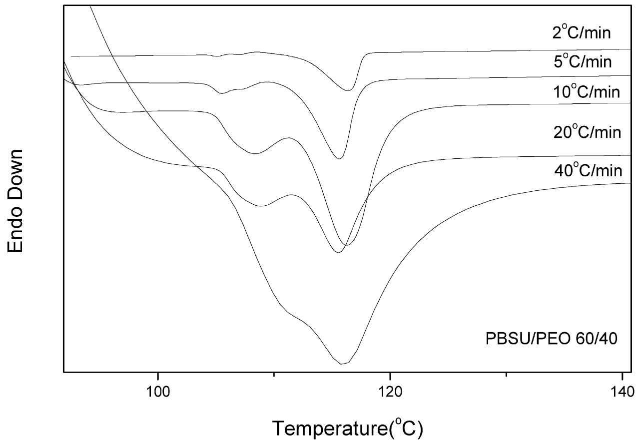
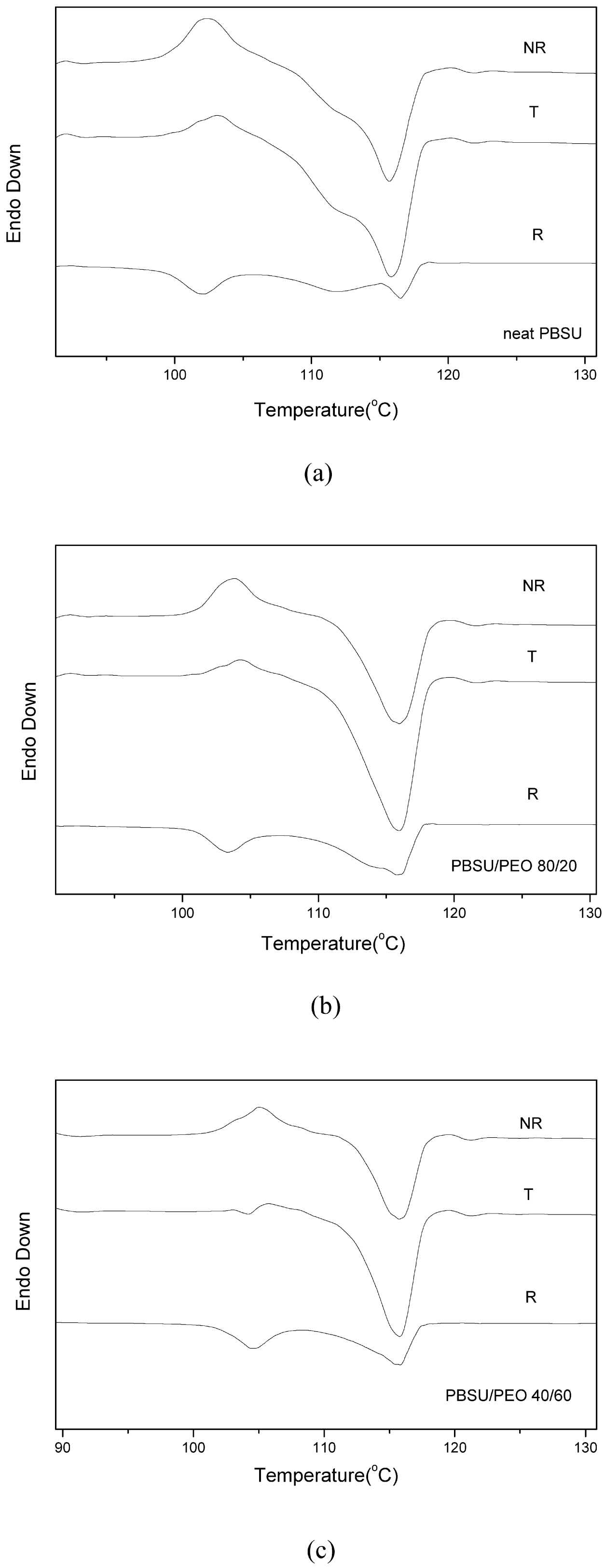


Fig. 4. DSC traces of PBSU/PEO 60/40 blend isothermally melt crystallized at 90 °C for 10 min at different scanning rates.

3.4. Study of the melting behavior of PBSU in PBSU/PEO blends by TMDSC

The above discussions are based on the assumption that simultaneous melting and recrystallization processes occur during the heating scan as the melting-recrystallization model suggests. However, due to the superposition of the recrystallization exotherm and the melting endothermic processes, the exotherm is hardly detected by standard DSC. Therefore, TMDSC was used in this work to characterize the melting and recrystallization of PBSU to give the direct proof of this model. TMDSC is able to distinguish the endothermic heat flow of melting from the exothermic heat flow of recrystallization by examining the behavior of the reversible and non-reversible heat flows, while the total heat flow gives only the sum.

Fig. 5 shows the TMDSC curves of neat PBSU, and PBSU/PEO 80/20 and PBSU/PEO 40/60 blends crystallized at 85 °C for 10 min. The total heat flow (middle curve) can be separated into the well-defined non-reversible heat flow (top curve) and the reversible heat flow (bottom curve). In Fig. 5(a), the total heat flow shows the exotherm just prior to the melting endotherm at ca. 115 °C for neat PBSU. Similar result is also found for PBSU/PEO 80/20 blend as shown in Fig. 5(b). In both cases, the lower melting endotherm T_{m1}, which should be located just prior to the exotherms according to the melting and recrystallization model, is not found. In the case of PBSU/PEO 40/60 blend, though the T_{m1} can be found, the magnitude is very small (Fig. 5(c)). Furthermore, the position of the exothermic peak of PBSU is seen to shift to higher temperature with the increase of the PEO content. This is because of the low scanning rate 2 °C/min used in these cases, where the samples had sufficient time to recrystallize. As a result of the superposition of the recrystallization exotherm and the lower melting endotherm, the lower endotherm T_{m1} is hardly detected by conventional DSC. But the reversing heat flow curves do show the endotherms corresponding to the melting and remelting very clearly. It can also be observed that in all



(a)

(b)

(c)

Fig. 5. TMDSC curves of PBSU/PEO blends crystallized at 85 °C for 10 min: (a) neat PBSU, (b) PBSU/PEO 80/20 blend, (c) PBSU/PEO 40/60 blend. The three curves from the top to the bottom in each figure are non-reversible heat flow (NR), total heat flow (T) and reversible heat flow (R), respectively.

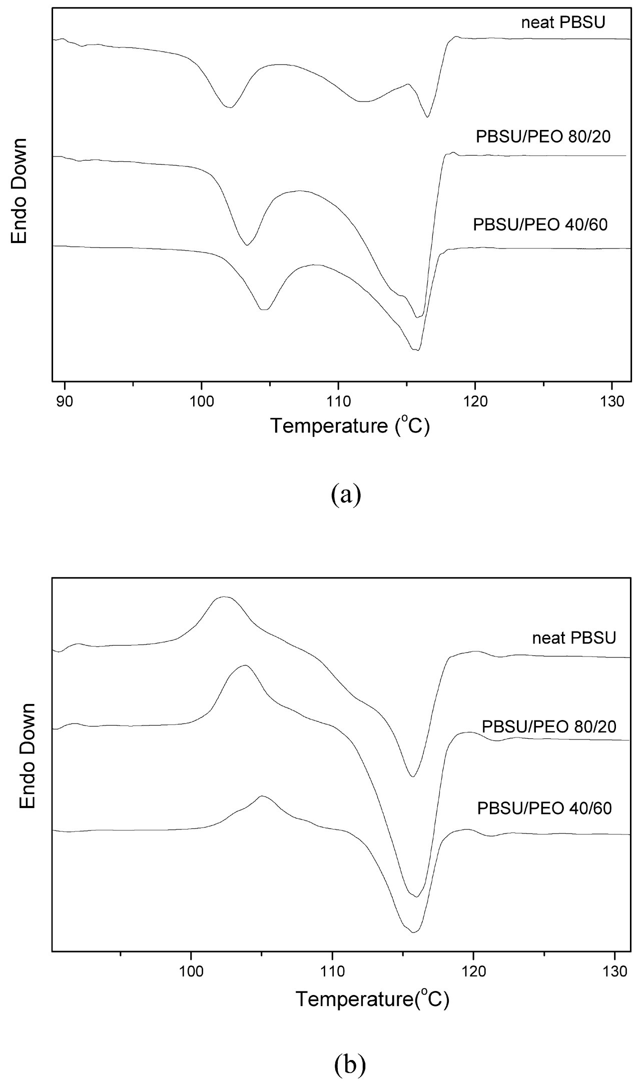


Fig. 6. Comparison of the TMDSC curves of PBSU/PEO blends crystallized at 85 °C for 10 min: (a) reversible curves, (b) non-reversible curves.

cases the recrystallization starts immediately after melting of the initial crystals at lower temperature by comparing the lower melting endotherms observed in the reversible heat flow curves with the exothermic peaks observed in the non-reversible curves.

In the reversible heat flow curves, with the increase of PEO the lower melting endotherm of PBSU shifts to high temperature and the high melting endotherm shifts to lower temperature as in the conventional DSC experiments (Fig. 6(a)). In addition, the recrystallization exothermic peaks observed in the non-reversible heat flow curves increases with the increase of PEO as shown in Fig. 6(b). This shows again the dependence of the melting behavior of PBSU on the blend composition in PBSU/PEO blends, and the reasons have been shown in the previous section.

In a word, there is no doubt that TMDSC offers the direct evidence for the melting and recrystallization mechanism for the melting behavior of PBSU in PBSU/PEO blends.

4. Conclusions

The melting behavior of PBSU in miscible blends with PEO has been studied extensively by conventional DSC and TMDSC and explained by the model of melting, recrystallization and remelting. Based on the thermal analysis, it can be concluded that the melting behavior of PBSU was influenced strongly by several experimental conditions, such as the blend composition, crystallization temperature, and scanning rate. With increasing any of the above variants, the recrystallization of PBSU was restricted. Furthermore, the TMDSC experiments gave the direct evidence of the melting-recrystallization model.

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