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DSC and TMDSC study of melting behaviour of poly(butylene succinate) and poly(ethylene succinate)

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Abstract

The subsequent melting behaviour of poly(butylene succinate) (PBSU) and poly(ethylene succinate) (PES) was investigated using DSC and temperature modulated DSC (TMDSC) after they finished nonisothermal crystallization from the melt. PBSU exhibited two melting endotherms in the DSC traces upon heating to the melt, which was ascribed to the melting and recrystallization mechanism. However, one melting endotherm with one shoulder and one crystallization exotherm just prior to the melting endotherm were found for PES. The crystallization exotherm was ascribed to the recrystallization of the melt of the crystallites with low thermal stability, and the shoulder was considered to be the melting endotherm of the crystallites with high thermal stability. The final melting endotherm was ascribed to the melting of the crystallites formed through the reorganization of the crystallites with high thermal stability during the DSC heating process. TMDSC experiments gave the direct evidences to support the proposed models to explain the melting behaviour of PBSU and PES crystallized nonisothermally from the melt.
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1. Introduction

Biodegradable polymers have received considerable attention due to their potential applications in the fields related to human life such as environmental protection and the maintenance of physical health in the last two decades. Poly(butylene succinate) (PBSU) and poly(ethylene succinate) (PES) are just two of them. The chemical structures of PBSU and PES are $(-OCH_2CH_2CH_2CH_2O_2CCH_2CH_2CO-)_n$ and $(-OCH_2CH_2O_2CCH_2CH_2CO-)_n$, respectively.

The crystal structure, crystallization and melting behaviour of PBSU have been reported in the literature [1–3]. PBSU was found to be miscible with poly(vinylidene fluoride), poly(vinylidene chloride-co-vinyl chloride) and poly(ethylene oxide) (PEO) [4–7]. The miscibility and nonisothermal crystallization of PBSU/poly(hydroxybutyrate) (PHB) blends were also reported [8]. It was found that PBSU showed no miscibility with PHB for almost all the blend composition studied.

The crystal structure, crystallization, morphology and melting behaviour of PES have been reported in the literature [9–14]. The crystallization and morphology of PES in miscible blends of two crystalline polymers, such as PES/PHB and PES/PEO blends [15–17], were also reported recently. The crystallization kinetics and subsequent melting behaviour of PES from the amorphous state were studied by DSC and temperature modulated DSC (TMDSC) [18].

Double or multiple melting endotherms are often found in semicrystalline polymers crystallized isothermally from the melt at selective crystallization temperature [3,7,13,14, 19]. The possible origin of the double or multiple melting endotherms may be listed as follows: (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 [20]. On the other hand, double or multiple melting endotherms are also occasionally found in the polymers crystallized nonisothermally from the melt at various constant cooling rates [8,21]. However, much less attention has been directed to the study of the origin of the double or multiple melting behaviour of polymers crystallized nonisothermally from the melt till now. Furthermore, semicrystalline polymers are usually processed nonisothermally from the melt from the viewpoint of practical application. Therefore, the subsequent melting behaviour of PBSU and PES was investigated in this communication using conventional DSC and TMDSC after they finished the nonisothermal crystallization in order to get a better understanding of the origin of the melting behaviour of polymers crystallized nonisothermally.

2. Experimental

PBSU ($M_w = 140,000$) was supplied by Showa High Polymer Co., Ltd, and PES ($M_w = 10,000$) used in this study was purchased from Scientific Polymer Products, Inc. (Ontario, NY). A TA 2910 TMDSC was used for both conventional DSC and TMDSC analysis. The PBSU samples were first melted at 150 °C for 3 min to destroy any thermal history and then cooled at various constant cooling rates. In the case of PES, the melt temperature was chosen as 130 °C. After the completion of the nonisothermal crystallization, the samples were heated to the melt again to study the melting behaviour of PBSU and PES at a heating rate of 20 °C/min (if not otherwise specified). 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

3.1. Melting behaviour of PBSU by DSC and TMDSC

The DSC traces of the melting behaviour of PBSU and PES are shown in Figs. 1 and 2, respectively. Fig. 1(a) shows the subsequent melting behaviour of PBSU crystallized nonisothermally from the melt at the cooling rate ranging from 1 to 10 °C/min with conventional DSC. The heating rate was 20 °C/min. PBSU shows double melting endotherms for all the samples crystallized nonisothermally from the melt. The low melting endotherm decreases from 109.9 to 103.3 °C when the cooling rate increases from 1 to 10 °C/min. However, the high melting endotherm seems unchanged with the cooling rate and locates at around 116 °C. The magnitude of the area of the low melting
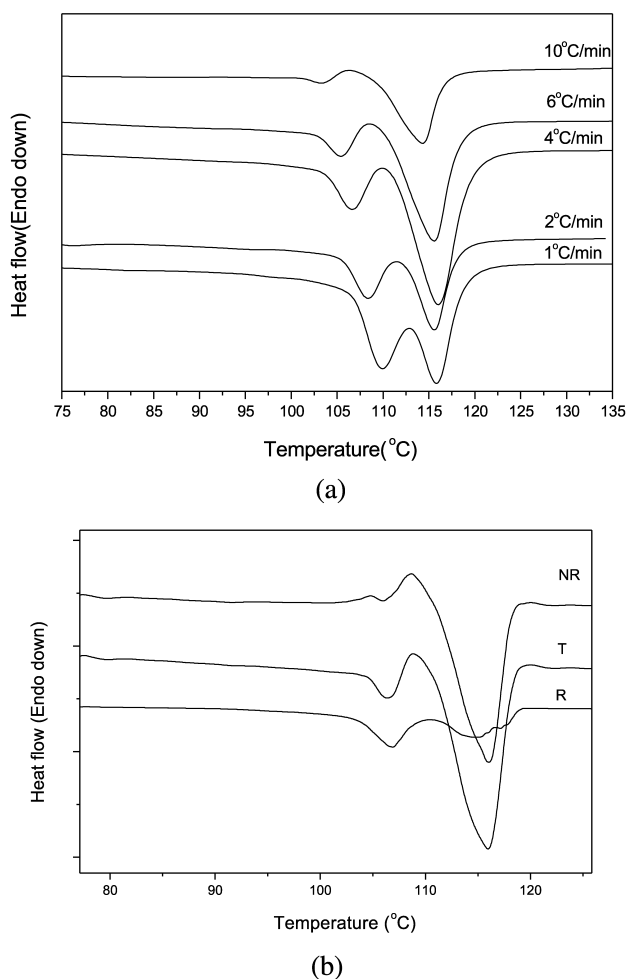

Fig. 1. DSC traces of the melting behaviour of PBSU after the nonisothermal crystallization; (a) conventional DSC and (b) TMDSC. In the conventional DSC traces, the cooling rates are shown in the figure; in the TMDSC traces, the three curves from the top to the bottom are nonreversible heat flow (NR), total heat flow (T) and reversible heat flow (R), respectively.

endotherm increases and that of the high melting endotherm decreases by decreasing the cooling rate. Furthermore, one small crystallization exotherm can be found between the low melting endotherm and the high one in the DSC traces when the cooling rate is faster than 6 °C/min.

Yasuniwa et al. also found that PBSU showed double melting endotherms upon crystallizing nonisothermally from the melt at a constant cooling rate, which was ascribed to the recrystallization and melting mechanism [21]. Im et al. also reported the multiple melting behaviour of PBSU crystallized isothermally from the melt by using DSC and wide angle X-ray diffraction (WAXD), who found that there was no crystal modification change through the WAXD measurement for PBSU crystallized at different temperatures [3]. Therefore, it can be concluded that the multiple melting behaviour of PBSU formed thermally does not originate from the different crystal modification. In this work, the double melting endotherms behaviour of PBSU can be explained reasonably too by the melting and
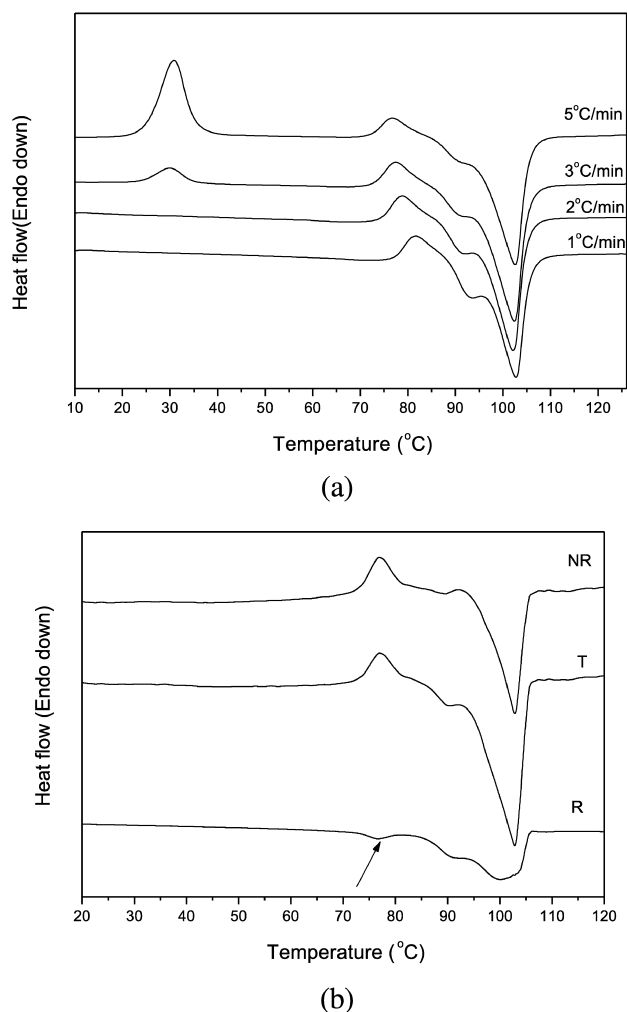
Fig. 2. DSC traces of the melting behaviour of PES after the nonisothermal crystallization; (a) conventional DSC and (b) TMDSC. In the conventional DSC traces, the cooling rates are shown in the figure; in the TMDSC traces, the three curves from the top to the bottom are nonreversible heat flow (NR), total heat flow (T) and reversible heat flow (R), respectively.

recrystallization model. Furthermore, we will provide a direct evidence to support the melting and recrystallization model through the study by TMDSC, which will be shown in Section 3.1.

TMDSC is a relatively 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 (nonreversible) components. Thus, the endothermic signals can be detected in both reversible and nonreversible scans, whereas the crystallization exotherms only contribute to the nonreversible 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 [7,18,22–24]. We studied the melting behaviour of PBSU in miscible blends with PEO

[7] and that of PES from the amorphous state [18] using TMDSC in previous works. Yuan et al. also studied the melting behaviour of syndiotactic polystyrene with TMDSC [24]. All the related research indicated that TMDSC was a suitable candidate to be used to study the complex melting behaviour of polymers.

Fig. 1(b) shows the TMDSC traces of PBSU crystallized nonisothermally from the melt at a cooling rate of 2 °C/min. The nonisothermal crystallization process studied by TMDSC was the same as that by conventional DSC, except that the heating rate of 2 °C/min was used with the oscillation amplitude of 0.5 °C and the oscillation period of 40 s throughout the investigation. The total heat flow (middle curve) can be separated into the well-defined nonreversible heat flow (top curve) and the reversible heat flow (bottom curve). Unlike that in Fig. 1(a) where no crystallization exotherm appears at a heating rate of 20 °C/min in the conventional DSC trace, one crystallization exotherm appears between the two melting endotherms in the total curve of TMDSC trace since the time was long enough for the melting and recrystallization of the crystallites of the low melting endotherm with low thermal stability at a heating rate of 2 °C/min. In the nonreversible curve, the crystallization exotherm becomes more apparent while the low melting endotherm disappears. However, in the reversibe curve only the two melting endotherms can be observed, and the low melting endotherm becomes dominant in this case. However, it is opposite in the total curve of TMDSC trace and in the conventional DSC where the high melting endotherm is dominant. All the facts mentioned above confirmed that the double melting behaviour of PBSU crystallized nonisothermally from the melt at a constant cooling rate originates in the melting and recrystallization of the crystallites of the low melting endotherm with low thermal stability. The high melting endotherm corresponds to the melting of the crystallites with high thermal stability formed through the recrystallization of the melt of the crystallites of the low melting endotherms. This is similar to the double melting behaviour of PBSU crystallized isothermally at a given crystallization temperature from the melt in our previous work [7].

3.2. Melting behaviour of PES by DSC and TMDSC

The subsequent melting behaviour of PES was also investigated in this work after PES finished nonisothermal crystallization from the melt at a constant cooling rate. Fig. 2(a) shows the subsequent melting behaviour of PES crystallized nonisothermally from the melt at the cooling rates ranging from 1 to 5 °C/min. The subsequent melting behaviour of PES crystallized nonisothermally from the melt is more complex than that of PBSU. The cold crystallization from the amorphous phase can be found when the cooling rate was faster than 3 °C/min due to the low crystallizability of PES, which must have a contribution to the melting behaviour upon heating to the melt in DSC

traces. For simplicity, we only studied the subsequent melting behaviour of PES nonisothermally crystallized from the melt at a cooling rate slower than 2 °C/min. In this case, the cold crystallization from the amorphous phase did not appear. One crystallization exotherm at around 81.7 °C is found just prior to the final melting endotherm at around 102.7 °C with a shoulder at around 93.5 °C in the DSC trace upon heating to the melt after PES crystallized nonisothermally from the melt at a cooling rate of 1 °C/min. By increasing the cooling rate to 2 °C/min, the crystallization exotherm is found at around 78.8 °C just prior to the final melting endotherm at around 102.2 °C with a shoulder at around 91.8 °C. This trend is similar to the melting behaviour of PBSU. The shoulder, similar to the low melting endotherm of PBSU, decreases by increasing the cooling rate, while the final melting endotherm, similar to the high melting endotherm of PBSU, seems unchanged with the cooling rate. The crystallization exotherm is found to decrease by increasing the cooling rate. Before proposing a model to explain the complex melting behaviour of PES, it must be pointed out that the crystal form of PES did not change with the temperature during heating to the melt through the synchrotron WAXD study of PES [25]. In other words, any new crystal modification did not occur on heating to the melt for PES, indicating that the complex melting behaviour of PES did not result from the existence of different crystal modification. Therefore, based on the previous studies on the melting behaviour of PES, which was crystallized isothermally from the melt at a given crystallization temperature [13,25] and was crystallized nonisothermally from the amorphous state at a constant heating rate [18], we propose that there are two kinds of PES crystallites with different thermal stabilities which were formed during the cooling crystallization process from the melt at a constant cooling rate. These two kinds of PES crystallites have the same crystal structure but have different thermal stabilities due to the difference in the crystal size and crystal thickness, so they have different melting point temperatures. The crystallites with low thermal stability melt first and then recrystallized upon heating to the melt. The crystallization exotherm found in the DSC traces corresponds to the recrystallization of the melt of the crystallites with low thermal stability. The crystallites with high thermal stability corresponds to the shoulder prior to the final melting endotherm in the DSC traces upon heating to the melt, while the final melting endotherm corresponds to the melting of the crystallites formed through the reorganization of the crystallites with high thermal stability during the DSC heating scan. According to this proposed model, we should observe three melting endotherms and two crystallization exotherms in the DSC scan. But from Fig. 2(a) obtained by conventional DSC, we can only find one crystallization exotherm and one melting endotherm with one shoulder, and we cannot find the melting endotherm corresponding to the melting of the crystallites with low thermal stability.

In order to verify the model proposed to explain the complex melting behaviour of PES crystallized nonisothermally from the melt at a constant cooling rate, we performed the TMDSC experiments. Fig. 2(b) shows the TMDSC traces of PES crystallized from the melt at a cooling rate of 2 °C/min. The total heat flow (middle curve) can be separated into the well-defined nonreversible heat flow (top curve) and the reversible heat flow (bottom curve). The total curve in Fig. 2(b) is similar to that of the conventional DSC trace, showing one crystallization exotherm and one melting endotherm with a shoulder prior to it. In the reversible curve, we can still find the final melting endotherm with a shoulder, similar to the results found in the conventional DSC trace and the total curve in the TMDSC trace. However, in the reversible curve, we do also find a new melting endotherm located at low temperature, corresponding to the position of the crystallization exotherm found in the total and nonreversible curves, which corresponds to the melting of the crystallites with low thermal stability proposed in our model. In the nonreversible curve, the crystallization exotherm is still found at the close position as found in the conventional DSC, which corresponds to the recrystallization of the crystallites with low thermal stability and locates between the newly found melting endotherm at low temperature in the reversible curve and the shoulder. However, the second crystallization exotherm, corresponding to the reorganization of the crystallites with high thermal stability, namely the shoulder, is still difficult to be perceptible between the shoulder and the final melting endotherm in the nonreversible curve. The difficulty of the observation of the second recrystallization exotherm between the shoulder and the final melting endotherm may be related to the very closeness of the two melting endotherms. However, the TMDSC results do provide us a direct evidence to support the proposed model to describe the complex melting behaviour of PES.

4. Conclusions

The subsequent melting behaviour of PBSU and PES was investigated using DSC and TMDSC after they finished the nonisothermal crystallization from the melt. The double melting behaviour of PBSU was ascribed to the melting and recrystallization mechanism. It was more complicated in the case of the melting behaviour of PES. One melting endotherm with one shoulder and one crystallization exotherm just prior to the melting endotherm were found in the DSC traces upon heating to the melt. The crystallization exotherm was ascribed to the recrystallization of the melt of the crystallites with low thermal stability. The shoulder was considered to be the melting endotherm of the crystallites with high thermal stability, while the final melting endotherm was ascribed to the melting of the crystallites formed through the reorganization of the crystallites with high thermal stability during the DSC

heating process. The TMDSC experiments gave the direct evidences to support the proposed models of this work.

Acknowledgements

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