

Poly(hydroxybutyrate)/poly(butylene succinate) blends: miscibility and nonisothermal crystallization

Zhaobin Qiu*, Takayuki Ikehara, Toshio Nishi

Department of Applied Physics, School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received 2 September 2002; received in revised form 27 December 2002; accepted 13 February 2003

Abstract

Four blends of poly(hydroxybutyrate) (PHB) and poly(butylene succinate) (PBSU), both biodegradable semicrystalline polyesters, were prepared with the ratio of PHB/PBSU ranging from 80/20 to 20/80 by co-dissolving the two polyesters in N,N-dimethylformamide and casting the mixture. Differential scanning calorimetry (DSC) and optical microscopy (OM) were used to probe the miscibility of PHB/PBSU blends. Experimental results indicated that PHB showed some limited miscibility with PBSU for PHB/PBSU 20/80 blend as evidenced by the small change in the glass transition temperature and the depression of the equilibrium melting point temperature of the high melting point component PHB. However, PHB showed immiscibility with PBSU for the other three blends as shown by the existence of unchanged composition independent glass transition temperature and the biphasic melt. Nonisothermal crystallization of PHB/PBSU blends was investigated by DSC using various cooling rates from 2.5 to 10 °C/min. During the nonisothermal crystallization, despite the cooling rates used two crystallization peak temperatures were found for PHB/PBSU 40/60 and 60/40 blends, corresponding to the crystallization of PHB and PBSU, respectively, whereas only one crystallization peak temperature was observed for PHB/PBSU 80/20 and 20/80 blends. However, it was found that after the nonisothermal crystallization the crystals of PHB and PBSU actually co-existed in PHB/PBSU 80/20 and 20/80 blends from the two melting endotherms observed in the subsequent DSC melting traces, corresponding to the melting of PHB and PBSU crystals, respectively. The subsequent melting behavior was also studied after the nonisothermal crystallization. In some cases, double melting behavior was found for both PHB and PBSU, which was influenced by the cooling rates used and the blend composition.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(hydroxybutyrate)/poly(butylene succinate) blends; Miscibility; Crystallization

1. Introduction

Poly(hydroxybutyrate) (PHB) is a biodegradable thermoplastic polymer, which has attracted much attention as an environmentally degradable resin. However, practical application of PHB has often been limited by its brittleness and narrow processing window. Therefore, blending of PHB with other polymers has been often reported in the literature. Miscible blends have been prepared by mixing PHB with poly(vinyl acetate), poly(epichlorohydrin), poly(vinyl phenol), poly(vinylidene fluoride), and poly(ethylene oxide) [1–5]. On the other hand, PHB was known to be immiscible with poly(ϵ -caprolactone), poly(cyclohexyl methacrylate), poly(hydroxyoctanoate), high molecular weight poly(L-lactide) and poly(methylene oxide) [6–10]. In our previous work, the miscibility and crystallization behavior of PHB/

poly(vinylidene chloride-co-acrylonitrile) (P(VDC-AN)) blends were investigated by differential scanning calorimetry (DSC) and optical microscopy (OM) [11]. It was concluded that PHB/P(VDC-AN) blends were completely miscible in all proportions from a thermodynamic viewpoint and the miscibility in these blends was ascribed to the specific molecular interaction involving the carbonyl groups of PHB. Recently Ha et al. reviewed the miscibility, properties and biodegradability of blends containing either PHB or poly(3-hydroxybutyrate-co-hydroxyvalerate) [12].

Poly(butylene succinate) is one of the biodegradable synthetic polyesters. The crystal structure, crystallization and melting behavior have been reported in the literatures [13–15]. PBSU was found to be miscible with poly(vinylidene fluoride), poly(vinylidene chloride-co-vinyl chloride) and poly(ethylene oxide) in our previous works [16–18].

However, to the best of our knowledge, no attention has been paid to the blending of PHB and PBSU. Both of the

* Corresponding author.

E-mail address: zbqiu99@yahoo.com (Z. Qiu).

components are crystalline and biodegradable. Therefore, 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. In the present paper, the results of an investigation concerning the miscibility, nonisothermal crystallization and subsequent melting behavior of PHB/PBSU blends were reported, and miscibility and nonisothermal crystallization in PHB/PBSU blends are discussed.

2. Experimental

PBSU ($M_w = 140,000$) was supplied by Showa High Polymer Co., Ltd, and PHB ($M_w = 500,000$) samples used in this study were purchased from Scientific Polymer Products, Inc. (Ontario, NY). PHB/PBSU blends were prepared with mutual solvent *N,N*-dimethylformamide (DMF) at an elevated temperature. 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 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 PHB.

The glass transition temperature (T_g) and melting point temperature (T_m) of the melt-quenched PHB/PBSU 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 200 °C for 2 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 various cooling rate of 2, 5, and 10 °C/min to 20 °C. The subsequent melting behavior was then studied at a heating rate of 10 °C/min.

A polarizing microscopy (Olympus BHA-P) with a temperature controller (Linkam LK-600PM) was used to probe the miscibility of PHB/PBSU blends in the melt.

3. Results and discussion

3.1. Study of miscibility of PHB/PBSU blends based on the glass transition temperature by DSC

According to the miscibility between the two components, binary polymer blends can be classified into three types: 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 of the two components is no 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. The difference in the T_g s between PHB (ca. 4 °C) and PBSU (ca. –34 °C) is about 40 °C, so the miscibility of PHB/PBSU blends can be investigated by the determination of T_g s in this study.

DSC measurements were performed to characterize the melt-quenched PHB/PBSU blends. Fig. 1 shows the DSC traces of PHB/PBSU blends. Neat PHB exhibits a glass transition around 4 °C, an exothermic cold crystallization peak around 58 °C, and an endothermic melting peak around 175 °C. Neat PBSU exhibits a glass transition around –34 °C, an exothermic cold crystallization peak around –5 °C, and an endothermic melting peak around 118 °C. With increasing the PBSU content up to 60%, PHB/PBSU blends show one distinct T_g in DSC measurements at about –35 °C, which is close to that of neat PBSU. The T_g of PHB cannot be observed in PHB/PBSU blends since it is masked by the cold crystallization of PBSU in PHB/PBSU blends. The above results lead us to the conclusion that PHB shows no miscibility with PBSU at all with PBSU in the amorphous state for the blends containing PBSU content up to 60% in PHB/PBSU blends. However, for PHB/PBSU 20/80, the T_g of PBSU is a little higher than those of neat PBSU and PBSU blended with higher PHB content. Meanwhile, the T_m of PHB in PHB/PBSU 20/80 blend is also a little lower than those of neat PHB and PHB blended with lower content PBSU. So it is very possible that PHB shows some limited miscibility with PBSU in PHB/PBSU 20/80 blend. This assumption would be investigated further by observing the melt with OM and studying the depression

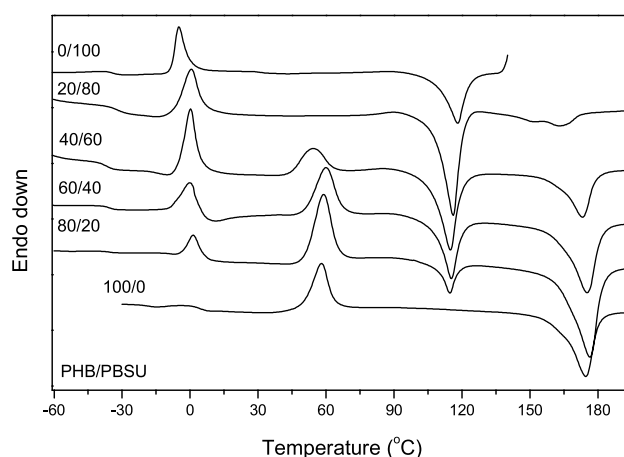


Fig. 1. DSC traces of PHB/PBSU blends after melt quenching at a heating rate of 20 °C/min.

in the equilibrium melting point T_m^0 of high melting point component PHB by DSC in the following sections.

3.2. Optical microscopy study

Optical microscopy (OM) was also used to probe the miscibility of PHB/PBSU blends. Provided that the refractive indices of the two components are not the same, it is possible to infer whether the melt is single-phased or biphasic. If PHB is miscible with PBSU, the single-phased melt should be observed. Otherwise, if PHB is immiscible with PBSU, the biphasic melt should be observed. PHB/PBSU blends samples were first melted at 200 °C and then were observed by OM. For almost all of the compositions studied, clearly defined biphasic separation was observed, indicating that PHB was not miscible with PBSU in the melt. For PHB/PBSU 80/20 and 60/40 blends, PHB appeared as the continuous phase with PBSU being the dispersed phase. With still increasing PBSU, PBSU became the continuous phase with PHB being dispersed phase. A phase inversion occurred. As an example, the phase separation occurred in the melt of PHB/PBSU 40/60 blend observed by OM is shown in Fig. 2. Droplets of PHB, with the size ranges from several to tens of micrometers, were dispersed in the matrix of PBSU. However, no clear optical evidence of phase separation in the melt has been found for PHB/PBSU 20/80 blend. This indicated that PHB showed some miscibility with PBSU to some extent for this composition at least on the level of the observation scale.

3.3. Further study of the limited miscibility between PHB and PBSU for PHB/PBSU 20/80 based on the depression of the T_m^0 of high T_m component PHB

The depression of the T_m in crystalline polymer blend can provide very important information on its miscibility. A completely immiscible blend usually does not show the depression of T_m at all, while it depresses significantly for a

miscible blend or a little for a partially miscible blend. However, the T_m of a polymer is affected not only by the thermodynamic factors but also by the morphological factors. Therefore, the equilibrium melting point T_m^0 should be used to separate the morphological effect from the thermodynamic effect in discussing the melting point depression as described by the Flory–Huggins theory [19,20].

Hoffman and Weeks proposed a relationship between the apparent melting point T_m and the isothermal crystallization temperature T_c

$$T_m = \eta T_c + (1 - \eta) T_m^0 \quad (1)$$

where T_m^0 is the equilibrium melting point, and η may be regarded as a measure of the stability, i.e. the lamellar thickness, of the crystals undergoing the melting process [21]. The higher the value of η , the more unstable the crystals. The T_m^0 can be obtained from the intersection of this line with the $T_m = T_c$ equation.

PHB/PBSU blends are binary blends of two crystalline polymers, with the T_m of PHB higher than that of PBSU. Therefore, the T_m^0 of the high T_m component PHB was studied for neat PHB and PHB blended with 80% PBSU in order to get some evidence of the miscibility between PHB and PBSU. In this paper, since the isothermal crystallization of PHB at higher temperatures above the T_m of PBSU was very time consuming, the crystallization temperature used to calculate the T_m^0 of PHB in PHB/PBSU 20/80 blend was from 80 to 102.5 °C, where PBSU was also able to crystallize. Actually, within the range of crystallization temperatures PBSU crystallized first and then PHB crystallized in the presence of PBSU crystals. It was certain that the presence of PBSU had some effect on the crystallization of PHB and the subsequent melting behavior of PHB. However, it is expected that the T_m^0 of PHB should be the same whether PHB crystallized in the presence of the PBSU crystals or not. Fig. 3(a) shows the melting behavior of PHB in PHB/PBSU 20/80 blend after complete isothermal crystallization at various crystallization temperatures. Two melting endotherms were observed for all the investigated crystallization temperatures. The lower melting peak temperature at ca. 160 °C shifted to high temperature with the crystallization temperature, while the higher melting peak at ca. 170 °C was almost unchanged. Furthermore, the lower melting temperature peak increased in magnitude while the high temperature endotherm decreased. Such phenomenon was often found for the melting behavior of PHB in the blends [11,22], and could be explained by the mechanism of melting, recrystallization and remelting of PHB crystals. The lower melting endotherm is the melting of the crystals formed at the isothermal crystallization temperature which are present prior to the heating scan in DSC, and the higher one is the melting of the crystals formed by the recrystallization during the heating process. Hence, the lower melting endotherms were used for the analysis with the Hoffman–Weeks equation. Fig. 3(b)

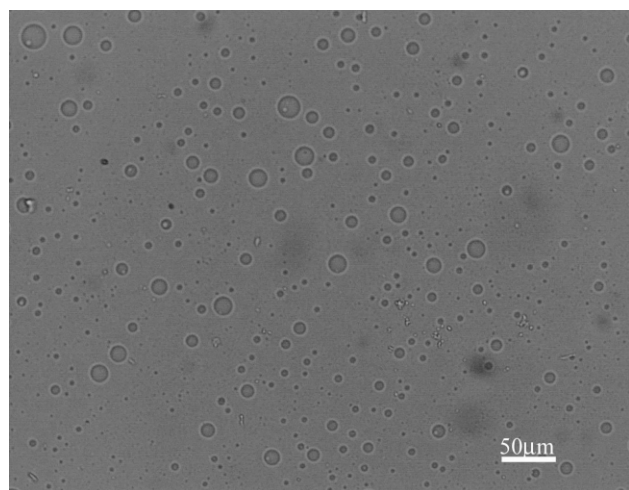


Fig. 2. Polarizing micrograph of PHB/PBSU 40/60 in the melt.

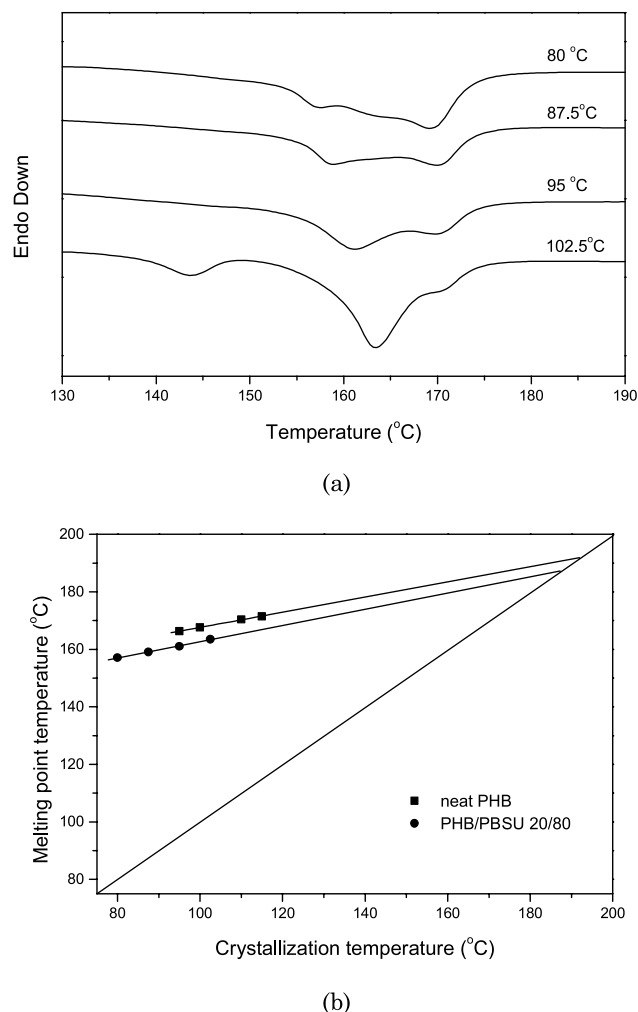


Fig. 3. (a) Melting behavior of PHB/PBSU20/80 blend at various crystallization temperatures, (b) Hoffman–Weeks plots of PHB/PBSU20/80 blend and neat PHB.

shows the Hoffman–Weeks plot for PHB/PBSU 20/80 blend, from which the T_m^0 of PHB was determined to be 187.2 °C. The T_m^0 of neat PHB was also determined to be 191.8 °C by the same method and was included in Fig. 3(b), which was ca. 5 °C higher than the value of PHB/PBSU 20/80 blend. Furthermore, the value of the slope of the Hoffman–Weeks plot η of neat PHB is 0.264, which is lower than the value of 0.282 for PHB/PBSU 20/80 blend. All the results indicate that PHB may show miscibility with PBSU to some extent from the depression of the T_m^0 of the high T_m component PHB.

3.4. Nonisothermal crystallization and subsequent melting behavior

Nonisothermal crystallization and subsequent melting behavior of PHB/PBSU blends were also studied by DSC in this paper. As introduced in Section 2, PHB/PBSU blends were cooled from the melt to 20 °C at various cooling rates

of 2, 5, and 10 °C/min. The subsequent melting behavior was then investigated at a heating rate of 10 °C/min.

The DSC cooling exotherms at 2, 5 and 10 °C/min are shown in Fig. 4. Despite the cooling rates used, during the nonisothermal crystallization two crystallization peak

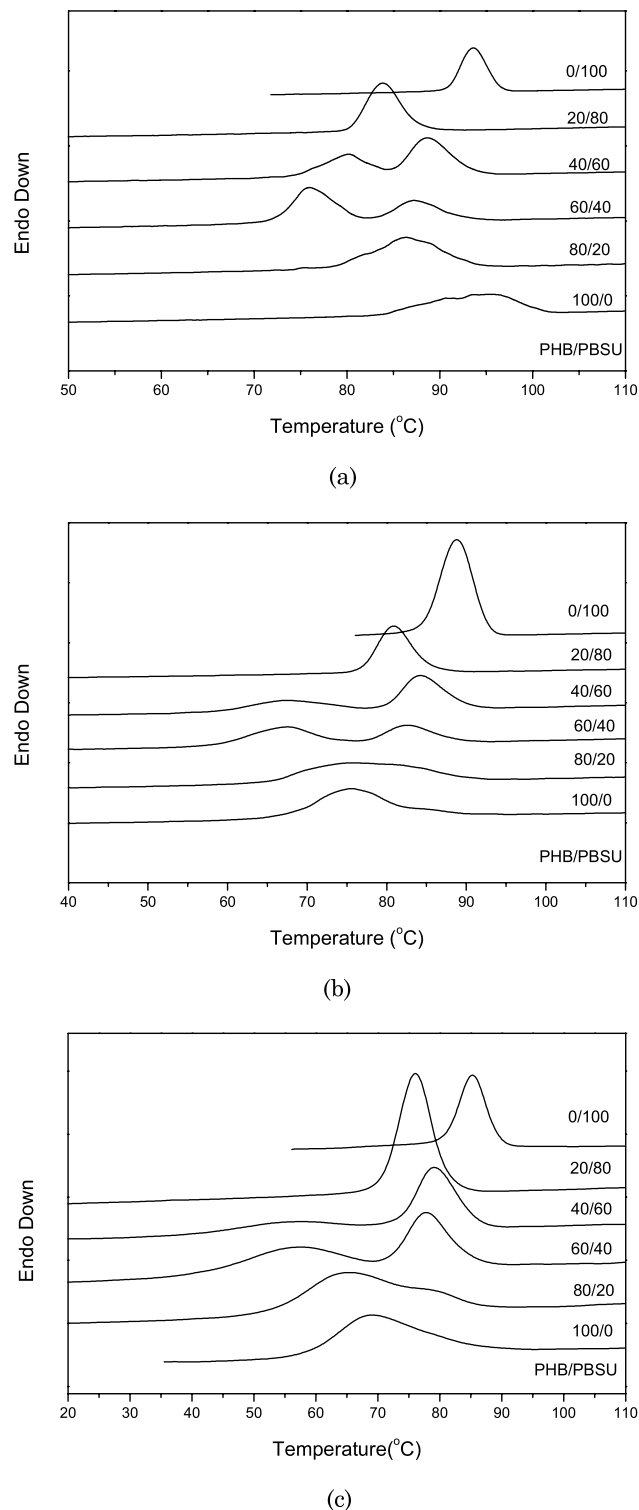


Fig. 4. Nonisothermal crystallization of PHB/PBSU blends from the melt at various cooling rates: (a) 2 °C/min, (b) 5 °C/min, and (c) 10 °C/min.

temperatures were found for PHB/PBSU 40/60 and 60/40 blends, corresponding to the crystallization of PHB and PBSU, respectively, whereas only one crystallization peak temperature (or with one shoulder) was observed for PHB/PBSU 80/20 and 20/80 blends.

The crystallization peak temperatures of the PHB/PBSU blends, taken from the curves of Fig. 4, are plotted in Fig. 5 as a function of composition. Fig. 5 shows the variation of the crystallization peak temperatures against composition for both PHB and PBSU. It is seen that for a given blend composition, the crystallization peak temperatures of PHB and PBSU shift to the lower temperature with the increase in the cooling rates. It is reasonable since less time is available to crystallize with increasing the cooling rate. It should be noted again that the crystallization peak temperature (T_c) of PBSU in PHB/PBSU 20/80 blend is lower than those of neat PBSU, PHB/PBSU 40/60, and 60/40 blends. This is also an additional evidence that PHB shows some limited miscibility with PBSU for PHB/PBSU 20/80 blend. On the other hand, the T_c of PHB decreased also with increasing PBSU composition. But the decrease in the T_c of PHB is not due to the diluent effect from the miscibility between PHB and PBSU. The decrease in T_c may be considered to occur from the physical restriction to the growth of PHB by the PBSU domains [23]. Such a decrease in T_c of PHB was also found in PHB/poly(methylene oxide) (POM) blends, where PHB showed no miscibility with POM at all, but the T_c of PHB shifted to 44 °C for PHB/POM 20/80 from 95 °C for neat PHB on cooling from the melt at 10 °C/min [10].

However, it was found that the crystals of PHB and PBSU actually coexisted in PHB/PBSU 80/20 and 20/80 blends because two melting endotherms, corresponding to the melting of PHB and PBSU crystals, respectively, were observed in the subsequent DSC melting traces after complete nonisothermal crystallization (Fig. 6). For PHB/PBSU 80/20 blend, on cooling from the melt, PHB crystallized and exhibited as the main crystallization peak; while PBSU crystallized too, the crystallization of PBSU was masked by that of PHB and could not appear as a separate crystallization peak. Similarly, PBSU crystallized

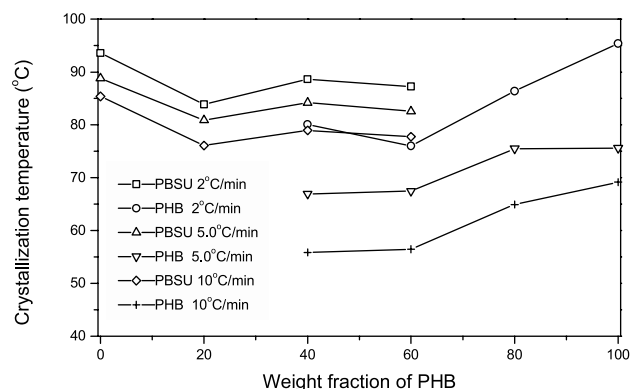


Fig. 5. Variation of the crystallization peak temperatures of PHB/PBSU blends vs. PHB content for various cooling rates.

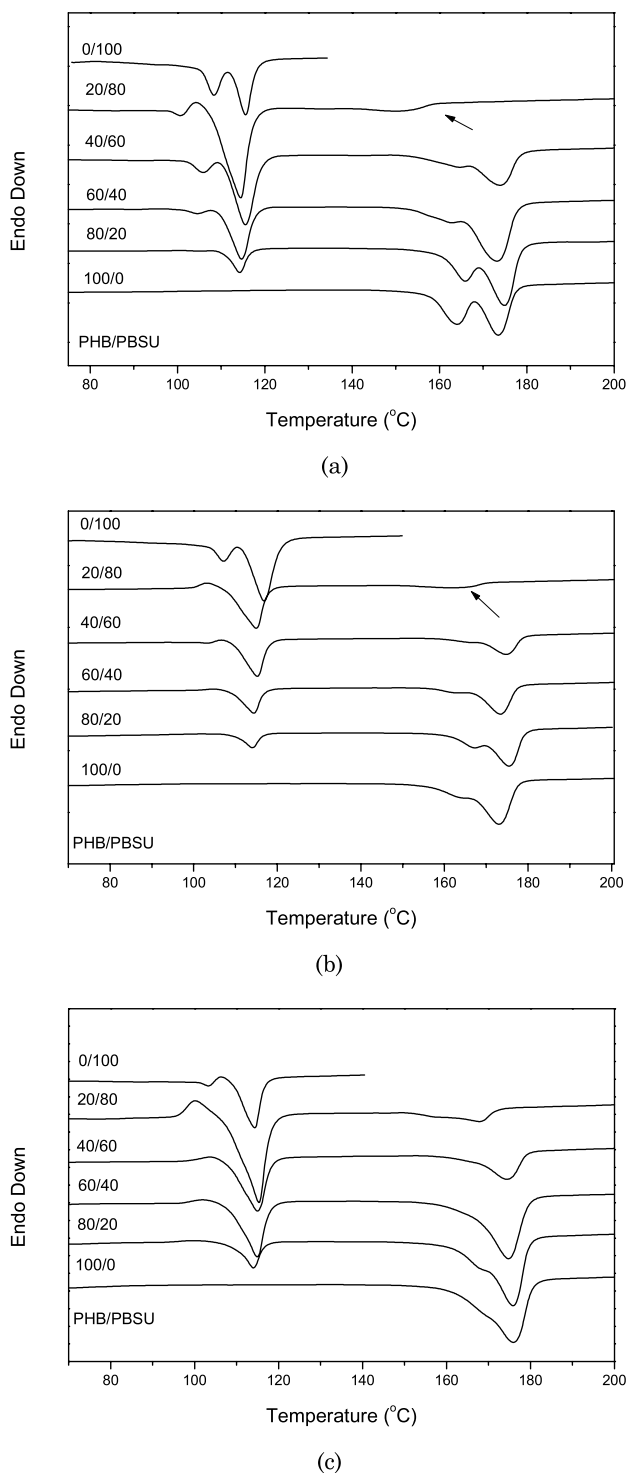


Fig. 6. Subsequent melting behavior of PHB/PBSU blends at the heating rate of 10 °C/min after nonisothermal crystallization at various cooling rates: (a) 2 °C/min, (b) 5 °C/min, and (c) 10 °C/min.

and exhibited as the main crystallization peak on cooling from the melt for PHB/PBSU 20/80 blend, while the crystallization of PHB was masked with that of PBSU and could not appear as a separate crystallization peak. It should be noted that the crystallization of PBSU was prior to that of PHB on cooling from the melt for PHB/PBSU blends from

Figs. 4 and 5, which was consistent with the observation by POM. All these results showed that PBSU was apt to crystallize than PHB in PHB/PBSU blends.

The subsequent melting behavior of PHB/PBSU blends was also investigated by DSC at a heating rate of 10 °C/min after complete nonisothermal crystallization at various cooling rates and was shown in Fig. 6. In some cases, double melting endotherms or one main melting endotherm with a shoulder was found for both PHB and PBSU, which was influenced by the cooling rates used and the blend composition. Generally speaking, the double melting endotherms or one main melting endotherm with a shoulder for both PHB and PBSU was apt to appear when the lower cooling rate was used. On the other hand, the blend composition also played an important role on the melting behavior of the two components. It was difficult for one component to show the double melting endotherm if the content of the other component was higher. The details of the subsequent melting behavior of PHB/PBSU blends are still underway by taking account of the effect of the blend composition, the cooling rates and the heating rates.

4. Conclusion

The miscibility of PHB/PBSU blends was investigated by DSC and OM. PHB was found to show some limited miscibility with PBSU for PHB/PBSU 20/80 blend from the change in the glass transition temperature, the depression of the equilibrium melting point temperature of high melting point component PHB, and the decrease in the crystallization peak temperature of PBSU. However, PHB showed immiscibility with PBSU for the blends with PBSU content greater than 40% as shown by the existence of unchanged composition independent glass transition temperature and the biphasic melt observed by OM. During the nonisothermal crystallization, two crystallization peak temperatures were found for PHB/PBSU 40/60 and 60/40 blends, corresponding to the crystallization of PHB and PBSU, respectively, whereas only one crystallization peak temperature was observed for PHB/PBSU 80/20 and 20/80 blends. However, the crystals of PHB and PBSU actually co-existed in PHB/PBSU 80/20 and 20/80 blends since two melting endotherms were observed in the subsequent DSC

melting traces, corresponding to the melting of PHB and PBSU crystals, respectively.

Acknowledgements

Part of this work was supported by Grant-in-Aid for Scientific Research on Priority Areas (A) 'Dynamic Control of Strongly Correlated Soft Materials' (No. 413/13031012) from the Ministry of Education, Science, Sports, Culture, and Technology, Japan. Z. Qiu thanks the Japan Society for the Promotion of Science for providing the fellowship and the grant-in-aid to do this research at the University of Tokyo. The authors thank the reviewer for valuable suggestions.

References

- [1] Greco P, Martuscelli E. *Polymer* 1989;30:1475.
- [2] Finelli L, Sarti B, Scandola M. *J Macromol Sci, Pure Appl Chem* 1997;A34:13.
- [3] Irujo P, Irujo JJ, FernandezBerridi MJ. *Macromolecules* 1996;29:5605.
- [4] Avella M, Martuscelli E. *Polymer* 1988;29:1731.
- [5] Marand H, Collins M. *ACS Polym Prepr* 1990;31:552.
- [6] Lisuardi A, Schoenberg M, Gada R, Gross A, McCarthy SP. *Polym Mater Sci Engng* 1992;67:298.
- [7] Lotti N, Pizzoli M, Ceccorulli G, Scandola M. *Polymer* 1993;34:4935.
- [8] Dufresne A, Vincendon M. *Macromolecules* 2000;33:2998.
- [9] Blumm E, Owem AJ. *Polymer* 1995;36:4077.
- [10] Avella M, Martuscelli E, Orsello G, Raimo M, Pascucci B. *Polymer* 1997;38:6135.
- [11] Lee JC, Nakajima K, Ikehara T, Nishi T. *J Polym Sci Polym Phys* 1997;35:2645.
- [12] Ha CS, Cho WJ. *Prog Polym Sci* 2002;27:759.
- [13] Chatani Y, Hasegawa R, Tadokoro H. *Polym Prepr Jpn* 1971;20:420.
- [14] Miyata T, Masuko T. *Polymer* 1998;39:1399.
- [15] Yoo ES, Im SS. *J Polym Sci Polym Phys* 1999;37:1357.
- [16] Lee JC, Tazawa H, Ikehara T, Nishi T. *Polym J* 1998;30:327.
- [17] Lee JC, Tazawa H, Ikehara T, Nishi T. *Polym J* 1998;30:780.
- [18] Qiu ZB, Ikehara T, Nishi T.
- [19] Flory PJ. *Principles of polymer chemistry*. Ithaca, NY: Cornell University Press; 1953.
- [20] Nishi T, Wang TT. *Macromolecules* 1975;8:909.
- [21] Hoffman JD, Weeks JJ. *J Chem Phys* 1965;42:4301.
- [22] Hay JN, Sharma L. *Polymer* 2000;41:5749.
- [23] Kong Y, Hay JN. *Polymer* 2002;43:1805.