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Poly(butylene succinate)/poly(vinyl phenol) blends. Part 1. Miscibility and crystallization

Zhaobin Qiu[a,b,*], Motonori Komura[b], Takayuki Ikehara[b,c], Toshio Nishi[a,b*]

[a] *Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo 152-8552, Japan*

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

[c] *Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*

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Abstract

Miscibility has been investigated in blends of poly(butylene succinate) (PBSU) and poly(vinyl phenol) (PVPh) by differential scanning calorimetry in this work. PBSU is miscible with PVPh 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 PBSU using the Nishi–Wang equation, is composition dependent, and its value is always negative. This indicates that PBSU/PVPh blends are thermodynamically miscible in the melt. Preliminary morphology study of PBSU/PVPh blends was also studied by optical microscopy (OM). OM experiments show the spherulites of PBSU become larger with the PVPh content, indicative of a decrease in the nucleation density, and the coarseness of PBSU spherulites increases too with increasing the PVPh content in the blends.

Keywords: Poly(butylene succinate)/poly(vinyl phenol) blends; Miscibility; Morphology

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1. Introduction

Much more attention has been directed to the biodegradable polymers in the last two decades because of their potential applications in the fields related to environmental protection and the maintenance of physical health. Biodegradable polymers 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) is just one of them. The chemical structure of PBSU is $(-OCH_2CH_2CH_2CH_2O_2CCH_2CH_2CO-)_n$.

The crystal structure, crystallization and melting behaviour of PBSU have been reported in the literature [1–8]. Two crystal modifications have been found for PBSU. Chatani et al. reported an α-form with monoclinic crystal structure [1]. Ihn et al. reported similar values of the crystal parameters through a single crystal study using electron diffraction [2]. Recently, Ichikawa et al. found another new crystal modification β-form which was induced by strain and was able to transform reversibly back into the conventional crystal modification α-form after the removal of the strain [3,4]. Yoo et al. investigated the multiple melting behaviour of isothermally crystallized PBSU from the melt using differential scanning calorimetry (DSC) and wide angle X-ray diffraction [5]. Miyata et al. reported the crystallization behaviour of PBSU in terms of the cooling rate and supercooling using DSC and optical microscopy (OM) [6]. Gan et al. reported that there was a regime transition between III and II at around 96 °C [7]. The ratio of the nucleation rate constant K_g^{III} to K_g^{III} was influenced significantly by the values chosen for the calculation, which varied between 1.3 and 2.3. The nonisothermal crystallization kinetics and subsequent melting behaviour of PBSU was also studied in our recent work [8]. The Ozawa method was found to fail to describe the nonisothermal crystallization process of PBSU.

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* Corresponding authors. Address: Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo 152-8552, Japan. Tel./fax: +81-3-5734-3507.

E-mail addresses: zbqiu99@yahoo.com (Z. Qiu), tnishi@polymer.titech.ac.jp (T. Nishi).

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Copolymerization and polymer blending are often performed in order to improve the physical properties and extend the application fields of PBSU. Park et al. synthesized poly(butylenes succinate-co-butylene 2-methyl succinate) random copolymers and studied their crystallization behaviour and morphology using DSC, OM and small angle X-ray scattering [9]. Gan et al. studied the crystallization, morphology and melting behaviour of poly(butylenes succinate-co-14 mol% ethylene suucinate) and poly(butylenes succinate-co-15 mol% hexamethylene succinate) copolymers [7,10].

PBSU was found to be miscible with poly(vinylidene fluoride) and poly(vinylidene chloride-co-vinyl chloride) in our previous work [11,12]. Recently, we have studied the miscibility, crystallization and melting behaviour of PBSU blended with poly(ethylene oxide) (PEO) [13,14]. 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. The double melting behaviour of isothermally crystallized PBSU blended with PEO was ascribed to the melting and recrystallization model. The miscibility and nonisothermal crystallization in PBSU/poly(hydroxybutyrate) (PHB) blends were also reported in our recent work [15]. It was found that PBSU showed no miscibility with PHB for almost all the blend composition studied, except that PBSU showed limited miscibility to some extent with PHB for PHB/PBSU 20/80 blend. We also studied the miscibility and crystallization behaviour of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and PBSU blends and found that they were immiscible at all [16].

Poly(4-vinyl phenol) (PVPh) is an amorphous polymer with high glass transition temperature. PVPh is miscible with various polymers such as poly(ethylene oxide) [17,18], PHB [19], poly(hydroxyvalerate) [20] and poly(L-lactide) [21]. The miscibility of polymer blends containing PVPh usually arises from the hydrogen bonding interaction between the hydroxyl group of PVPh and other groups of the partners, such as the carbonyl group.

It is very likely that PBSU and PVPh can form a miscible polymer blend since the carbonyl group of PBSU may form the hydrogen bonding with the hydroxy group of PVPh. Thus the application field of PBSU can be extended. However, to the best of our knowledge PBSU/PVPh blends have not been reported so far in the literature. It is interesting to investigate the miscibility of PBSU/PVPh blends and the nature of specific interaction involved. In this work, we studied the miscibility, crystallization and morphology of PBSU/PVPh blends for the first time by DSC and OM. It is found that PBSU forms miscible blend with PVPh over the entire composition range as shown by the single composition dependent glass transition temperature. The preliminary morphological study of PBSU/PVPh blends was also investigated by OM in this paper. The detailed morphological study as a function of blend composition and the crystallization temperature by OM as well as the specific interaction involved in the PBSU/PVPh blends by Fourier transform infrared spectroscopy (FTIR) are still underway and will be reported in a separate paper.

2. Experimental

PBSU ($M_w = 140000$) was supplied by Showa High Polymer Co., Ltd, and PVPh ($M_w = 20000$) samples used in this study were purchased from Aldrich Company. PBSU/PVPh blends were prepared with mutual solvent *N*,*N*-dimethylformamide. 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 PBSU.

The glass transition temperature (T_g) and the melting point (T_m) of the melt-quenched PBSU/PVPh 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 3 min to destroy any thermal history and subsequently quenched into liquid nitrogen. The crystallization exothermic peak temperature (T_{cp}) was obtained from the DSC cooling exotherm from the crystal-free melt at a cooling rate of 10 °C/min.

The isothermal crystallization of PBSU/PVPh blends from the melt was also examined by DSC. The sample was melted at 200 °C for 3 min, cooled quickly to the crystallization temperature (T_c), and then maintained at the T_c until the crystallization was completed. After complete crystallization, the sample was heated to 150 °C at a rate of 20 °C/min to measure the T_m of PBSU.

The spherulitic morphology was observed under crossed polars with a polarizing microscope (Olympus BHA-P) equipped with a first order retardation plate and a temperature controller (Linkam LK-600PM). The sample was first melt at 200 °C for 3 min to destroy any thermal history and then quenched to the T_c at a cooling rate of 100 °C/min.

3. Results and discussion

3.1. Miscibility study based on the glass transition temperature analysis

A single composition dependent T_g is the most widely and conventionally used criterion for the miscibility of a polymer blend. The miscibility of PBSU/PVPh blends was first studied by measuring the glass transition temperature of the melt-quenched samples with DSC. Shown in Fig. 1 are the DSC traces of the quenched samples of neat PBSU, neat PVPh and the blends. PBSU is a semicrystalline polyester with a T_g of -33 °C, a cold crystallization temperature of -5 °C and a T_m of 118 °C. PVPh is an amorphous polymer with a high T_g of 175 °C. PBSU/PVPh blends exhibit a single composition dependent T_g between the T_g of neat PBSU and that of neat PVPh, indicating that PBSU and PVPh are miscible over the entire composition range. The cold crystallization temperature of PBSU shifts to high temperature range in the blends compared with that of neat PBSU, indicating that the crystallization of PBSU is retarded due to the presence of PVPh. The presence of high T_g component PVPh in the PBSU/PVPh blends increases the T_g of the blends, resulting in the decrease of the mobility of PBSU. Therefore, the crystallization of PBSU is hindered by the presence of PVPh. The cold crystallization temperature of PBSU cannot be detected in the blends containing PVPh above 40 weight percent due to the high T_g of the blends. The T_m of PBSU is also found to shift to low temperature range upon the addition of PVPh in the PBSU/PVPh blends. The T_m of PBSU decreases with the PVPh content. With the PVPh content above 40 weight percent in the blends, the T_m of PBSU cannot be detected, which is similar to the trend of the cold crystallization temperature.

Fig. 2 summarizes the composition dependence of T_g of the PBSU/PVPh blends. Meanwhile, the composition dependence of the cold crystallization temperature of PBSU and that of the T_m of PBSU are also shown in Fig. 2. From Fig. 2, it can be concluded more apparently that PBSU shows miscibility with PVPh from the composition dependence of T_g of the blends, the depression of the T_m of PBSU and the increase of the cold crystallization temperature of PBSU with increase in the PVPh content.

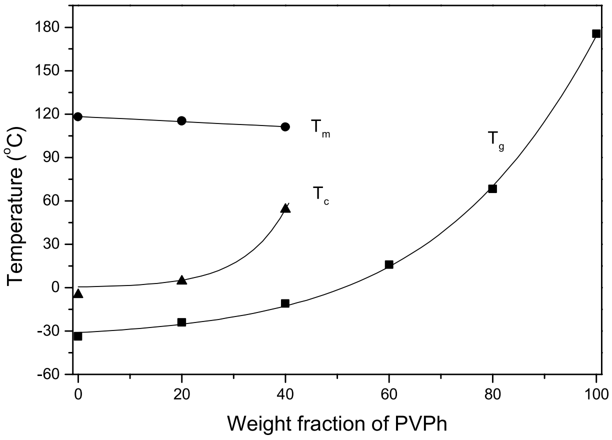


Fig. 2. Phase behaviour of PBSU/PVPh blends as a fuction of PVPh weight fraction.

The melting behaviour of neat and blended PBSU was also studied by DSC for the as cast samples. The melting endotherm of PBSU cannot be detected in the PBSU/PVPh blends with the PVPh content above 40 weight percent for the melt-quenched samples. However, for the as cast samples, the melting endotherms of PBSU for each of the PBSU/PVPh blends has been found. This is because the thermal history is different in these two cases. PBSU in as cast samples has a larger mobility to crystallize than that in melt-quench samples. Neat PBSU shows a single well defined endotherm located at ca. 120 °C. In the PBSU/PVPh blends, two melting endotherms are found for the melting behaviour of PBSU. In some cases, three melting endotherms are found. The multiple melting endotherms are often found for the as cast polyester blend samples and are attributed to the melting and recrystallization model [22]. In the case of PBSU/PVPh blends, the multiple melting endotherms are also expected to arise from the melting and recrystallization model. Roughly speaking, the high temperature melting endotherm shifts to low temperature range with the increase in the PVPh content. The magnitude of the low temperature melting endotherm at ca. 80 °C increases with the PVPh content, while the magnitude of the high melting endotherm at above 100 °C decreases and becomes a shoulder for the PBSU/PVPh blends with PVPh content above 60 weight percent (Fig. 3).

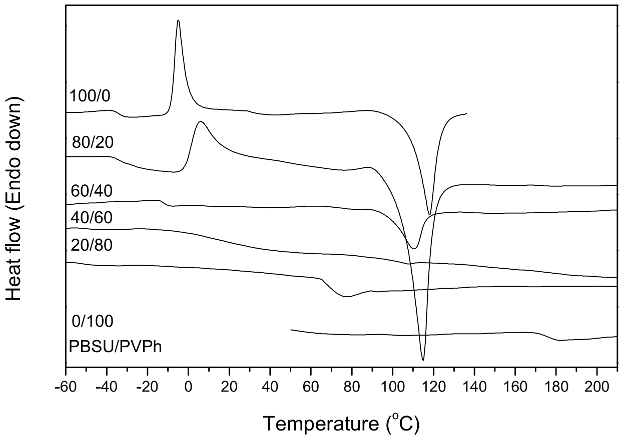


Fig. 1. DSC traces of PBSU/PVPh blends for the melt-quenched samples at a heating rate of 20 °C/min.

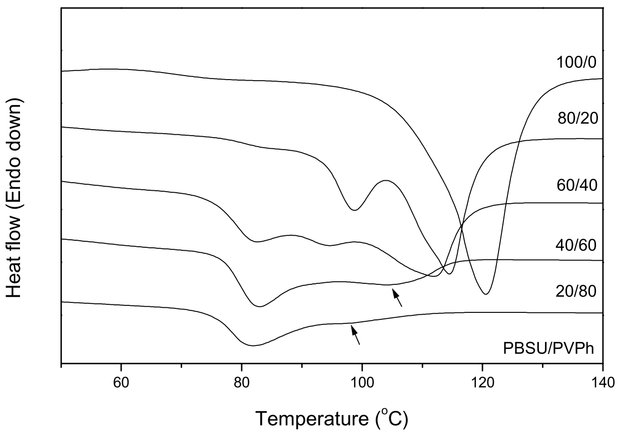


Fig. 3. Melting traces of PBSU/PVPh blends for the as cast samples at a heating rate of 20 °C/min.

The crystallization behaviour of PBSU/PVPh blends was also studied in this work at a cooling rate of 10 °C/min after the samples were held at 200 °C for 3 min to destroy any thermal history. The DSC traces obtained during the nonisothermal crystallization process are shown in Fig. 4. No crystallization of PBSU can be detected with the PVPh content above the 60 weight percent. The crystallization temperature of PBSU shifts to 69 °C for 60/40 blend from 84 °C for neat PBSU. The crystallization temperature of PBSU is 75 °C for 80/20 blend. The high T_g and the low mobility of PBSU/PVPh blends prevent PBSU from crystallizing from the melt for the samples with high PVPh content. The decrease of the crystallization temperature of PBSU with the PVPh content is also another evidence of the miscibility between PBSU and PVPh.

3.2. The depression in the equilibrium melting point of PBSU of PBSU/PVPh blends

The depression of the melting point of a crystalline polymer blended with an amorphous polymer provides important information about its miscibility and its associated polymer–polymer interaction parameter. An immiscible or partially miscible blend typically does not show the depression of the melting point, which is depressed significantly with increasing the content of the amorphous polymer for a miscible blend, especially one containing specific interaction between the components. However, the melting point of a polymer is affected not only by the thermodynamic factors but also by the morphological factors such as crystalline lamellar thickness. Therefore, the equilibrium melting point 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 [23,24].

Hoffman and Weeks [25] have shown a relationship between the apparent melting point T_m and the isothermal crystallization temperature T_c

$$T_m = \eta T_c + (1 - T_c) T_m^o \tag{1}$$

where T_m^o 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. The equilibrium melting point can be obtained from the intersection of this line with the $T_m = T_c$ equation.

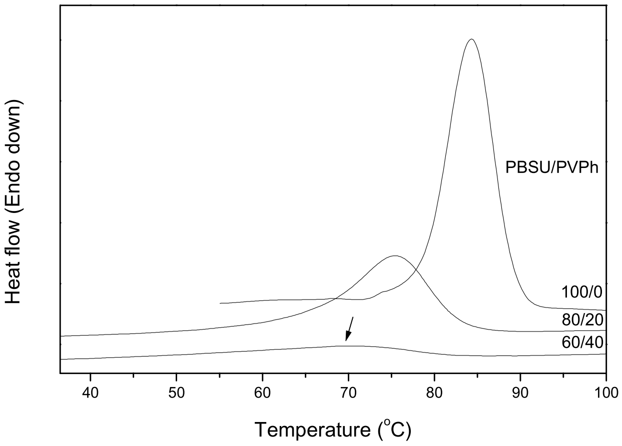


Fig. 4. Nonisothermal crystallization of PBSU/PVPh blends from the melt at a cooling rate of 10 °C/min.

The melting behaviour of PBSU/PVPh blends was studied in this work with DSC using the process introduced in Section 2. As an example, Fig. 5(a) shows the melting behaviour of 80/20 blend after finishing isothermal crystallization at various crystallization temperatures. Two endothermic melting peaks or one main endothermic melting peak with one shoulder are observed for the melting behaviour of PBSU. The lower endothermic melting peak shifts to high temperature range with the crystallization temperature, while the higher one is almost unchanged. Furthermore, the ratio of the area of the lower melting peak to that of the higher melting peak increases with the crystallization temperature. The lower temperature melting peak becomes dominant with the higher one being a shoulder at high crystallization temperature. This fact can be explained by the mechanism of melting, recrystallization and remelting of PBSU crystals [5,14]. The lower endothermic peak 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. Similar results are also found in our previous work on PBSU/PEO blends which were explained by the melting and recrystallization model through conventional and modulated temperature DSC studies [14]. Hence, the lower melting peaks are used for the analysis with the Hoffman–Weeks equation. Fig. 5(b) shows the Hoffman–Weeks plot for80/20, from which the equilibrium melting point T_m^o was determined to be 132.9 °C. The equilibrium melting point temperature T_m^o for neat PBSU and 60/40 were obtained by the same method. The equilibrium melting points T_m^os of neat and blended PBSU are shown in Fig. 5(c) as a function of PVPh weight fraction, from which it is found that the equilibrium melting point of PBSU decreases with increasing the PVPh content.

The equilibrium melting point data obtained in this study were analyzed by the Nishi–Wang equation [24] based on the Flory–Huggins theory [23]. The melting point depression is given by Eq. (2),

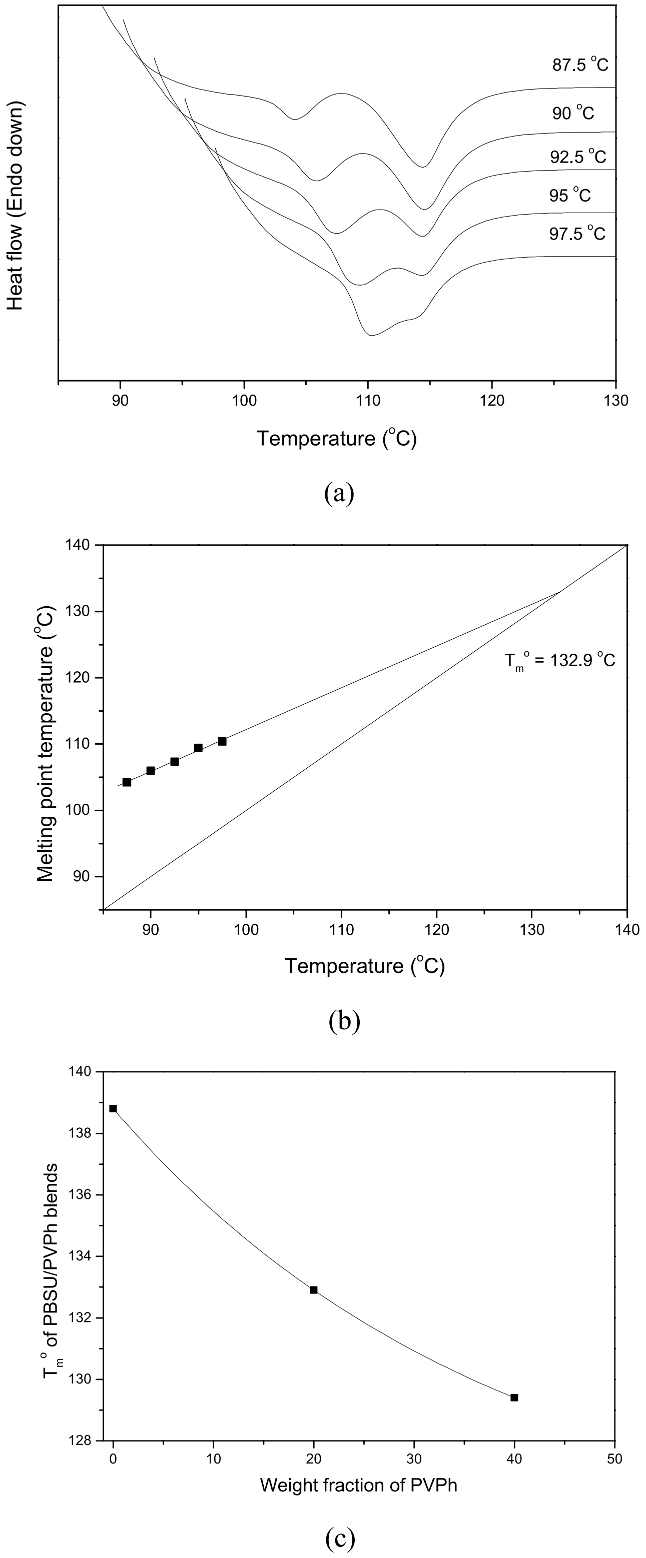
$$\frac{1}{T_m^o(b)} - \frac{1}{T_m^o(p)} = -\frac{RV_2}{\Delta H^o V_1}\left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)\phi_1 + \chi_{12}\phi_1^2\right] \tag{2}$$

where $T_m^o(p)$ and $T_m^o(b)$ are the equilibrium melting point of the pure crystallizable component and of the blend, respectively. ΔH^o is the heat of fusion of the perfectly crystallizable polymer per mole of the repeat unit, V is the molar volume of the repeating units of the polymers, m and ϕ are degree of polymerization and the volume fraction of the component in the blend, respectively. Subscripts 1 and 2 refer to the amorphous and crystalline polymer, respectively. R is the universal gas constant, and χ_{12} is the polymer–polymer interaction parameter. When both m_1 and m_2 are large, for high molecular weight polymers, these related terms in Eq. (2) can be neglected. The interaction parameter χ_{12} can be written as

$$-\frac{\Delta H^o V_1}{RV_2}\left(\frac{1}{T_m^o(b)}-\frac{1}{T_m^o(p)}\right)=\beta=\chi_{12}\phi_1^2 \qquad (3)$$

For PBSU/PVPh blends, PBSU is the crystalline polymer while PVPh acts as an amorphous diluent. Eq. (3) can therefore be applied to get the polymer–polymer interaction parameter χ_{12} of the PBSU/PVPh blends.

In order to calculate the left-hand side term of Eq. (3), the following parameters were used: $V_1 = 100\ \text{cm}^3/\text{mol}$ [26], $V_2 = 145.9\ \text{cm}^3/\text{mol}$, and $\Delta H^o = 34435$ J/mol [6]. The plot of the left-hand side of Eq. (3) versus ϕ_1^2 is shown in Fig. 6. The fact that the line dose not pass through the origin according to the prediction of the Eq. (3) indicates the polymer–polymer interaction parameter χ_{12} is composition dependent. The values of χ_{12} obtained from the broken lines in Fig. 6 were negative for all investigated compositions, indicating that PBSU and PVPh are thermodynamically miscible in the melt. We estimated the values of χ_{12} for the 80/20 and 60/40 blends to be -2.57 and -1.03, respectively, from the slopes of the broken lines, which were greatly lower than the value of -0.295 for poly(vinylidene fluoride) (PVF_2)/poly(methyl methacrylate) (PMMA) blends [24], indicating that the polymer–polymer interaction in PBSU/PVPh blends was much stronger than that in PVF_2/PMMA blends due to the possible formation of inter-hydrogen bonding between the carbonyl group of PBSU and the hydroxyl group of PVPh.



(a)

(b)

(c)

Fig. 5. (a) Melting behaviour of 80/20 blend isothermally crystallized at various crystallization temperature from the melt, (b) Hoffman–Weeks plot of 80/20 blend for the estimation of the equilibrium melting point, and (c) variation of the equilibrium melting of PBSU/PVPh blends as a function of PVPh weight fraction.

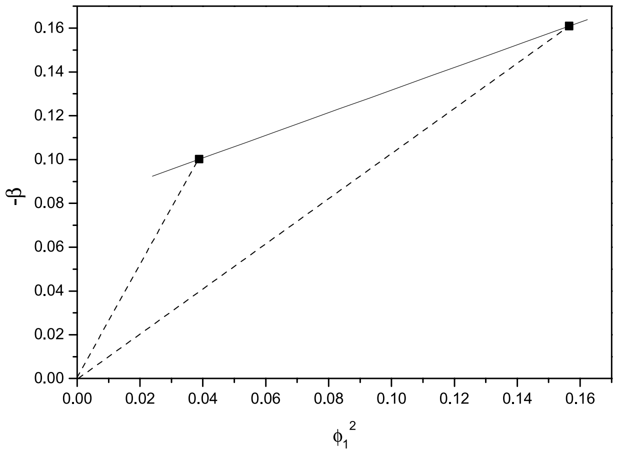


Fig. 6. Nishi–Wang plot for the calculation of the polymer–polymer interaction parameter of PBSU/PVPh blends.

The miscibility of PBSU/PVPh blend is expected to arise from the formation of inter-hydrogen bonding between the carbonyl group of PBSU and the hydroxyl group of PVPh. The specific interaction involved in the PBSU/PVPh blends studied by FTIR is still underway and will be reported in a separate paper.

3.3. Preliminary study on the morphology of PBSU/PVPh blends

The preliminary morphology of PBSU/PVPh blends was also studied by OM in this work. As introduced in the experimental section, the samples were first annealed at 200 °C for 3 min to destroy any thermal history and quenched to crystallization temperature at a cooling rate of 100 °C/min. PBSU can only crystallize in the PBSU-rich blends, namely with PBSU content above 60 weight percent. In this paper we only report the preliminary morphology study of the neat and blended PBSU crystallized at 85 °C. The detailed morphology studies of PBSU/PVPh blends as a function of blend composition and the crystallization temperature are still underway and will be reported in a separate paper.

Fig. 7 shows the spherulitic morphology of the neat and blended PBSU crystallized at 85 °C. It is seen that the spherulites of PBSU become larger with the PVPh content, indicative of a decrease in the nucleation density. The spherulites of neat PBSU are very compact. In the case of the PBSU/PVPh blends, the PBSU spherulites become coarse compared with those of neat PBSU. For 80/20 blend, the bundles of lamellae are fewer but thicker than those for neat PBSU, and assume a feather-like pattern finally. In addition, this kind of difference is more apparent in 60/40 blend, indicating that the coarseness of PBSU spherulites increases with increasing the PVPh content in the blends. The fact that PBSU spherulites are space-filling indicates that PVPh is rejected in the crystallization process as a noncrystallizable component and resides primarily in the interlamellar and interfibrillar domains of the PBSU spherulites [27,28].

4. Conclusions

PBSU and PVPh are completely miscible in an amorphous phase over the entire composition range as shown by the single composition dependent glass transition temperature. The negative and composition dependent polymer–polymer interaction parameter was calculated from the equilibrium melting depression of PBSU using the Nishi–Wang equation. This indicates that PBSU/PVPh blends are thermodynamically miscible in the melt. The miscibility of PBSU/PVPh blends is expected to arise from the formation of the hydrogen bonding between the carbonyl group of PBSU and the hydroxyl group of PVPh. OM experiments show the spherulites of PBSU become

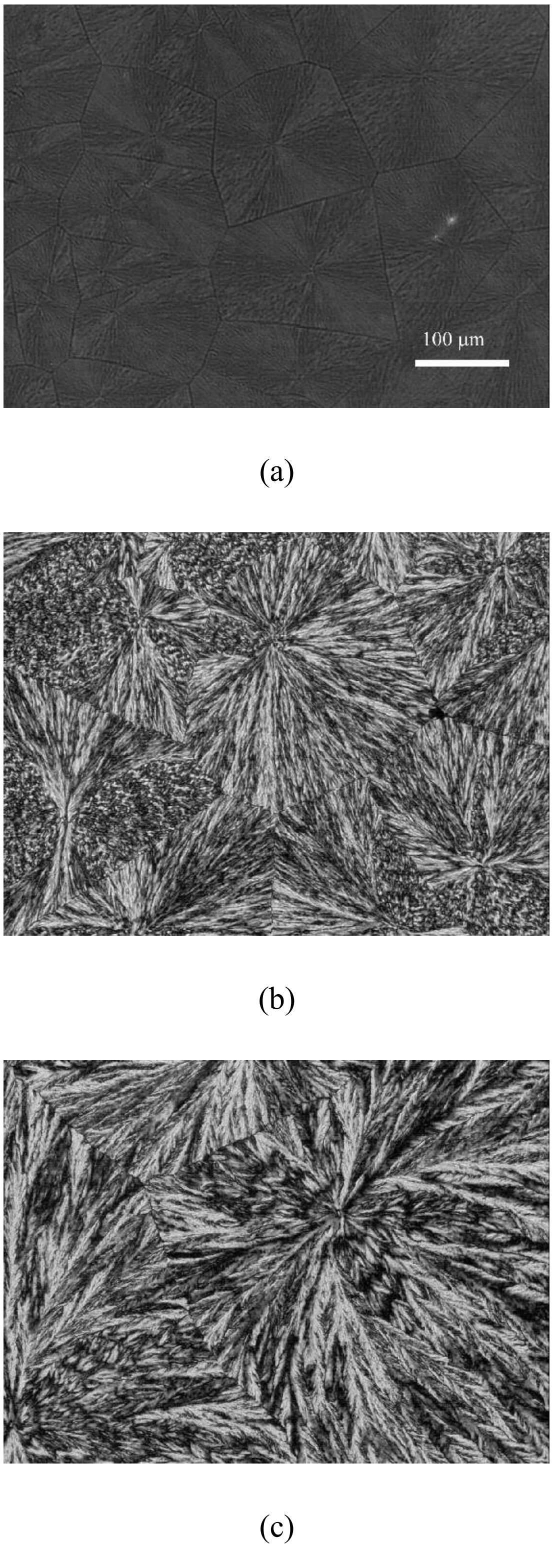


Fig. 7. Optical micrographs (same magnification with bar = 100 μm) of the spherulitic morphology of PBSU crystallized at 85 °C in the PBSU/PVPh blends; (a) neat PBSU, (b) 80/20, and (c) 60/40.

larger with the PVPh content, indicative of a decrease in the nucleation density, and the coarseness of PBSU spherulites increases too with increasing the PVPh content in the blends.

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