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MISCIBILITY EVALUATION OF SPS/APS BLEND INVESTIGATED FROM CRYSTALLIZATION DYNAMICS

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Abstract

The miscibility of crystalline syndiotactic polystyrene (SPS)/non-crystalline atactic polystyrene (APS) blend was estimated by the crystallization dynamics method, which evaluated the nucleation rate, the crystal growth rate and the surface free energy parameter. The melting temperature depression suggested that SPS/APS blends were the miscible system but not in molecular level. The relationship between the blend content and the chemical potential difference evaluated at a constant crystal growth rate showed a good linear relationship. These facts suggested that SPS/APS blends contained the concentration fluctuation with the size between few nm to less than 80 nm.

Keywords: atactic polystyrene, blend, crystallization dynamics, DSC, miscibility, syndiotactic polystyrene

Introduction

Generally, polymer blend is scarcely miscible because the entropic contribution to the mixing Gibbs energy is too low to mix each other. The specific intermolecular interaction is necessary to establish the miscible polymer blends. Interaction parameter is evaluated from the melting temperature depression [1, 2] and the glass transition temperature deviation [3–5] based on Flory–Huggins lattice theory [6, 7]. However, analysis of interaction parameter is able to evaluate only for the thermodynamic miscible blend. Therefore we have proposed the 'crystallization dynamics method' [8, 9] which evaluated the mixing state of polymer blends including crystalline polymer, not only for the miscible blends but also the partially miscible and the immiscible blends. As the crystallization process takes place in the homogeneous mixed state, the nucleation rate (N) and the crystal growth rate (G) depend on both the crystallization temperature (T_c) and the blend content (ϕ) in the miscible blend. On the other hand, as the crystallization process occurs in the crystalline component rich phase, the N and G scarcely depend on the blend content ϕ in the case of partially miscible and immiscible blends. After the crystallization, the surface free energy of crystallite also de-

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pends on ϕ for the miscible blends and the surface free energy is free from ϕ for the partially miscible and immiscible blends.

The mixing state of syndiotactic polystyrene (SPS)/atactic polystyrene (APS) blend is reported as the miscible system investigating by the temperature modulated differential scanning calorimetry [10] and the thermal mechanical analysis [11] under the non-isothermal condition. In the literatures [10, 11], SPS/APS blend is the miscible because the crystallization temperature cooling from the molten state depends on the blend content. Woo [12] reports a small negative interaction parameter from the Flory–Huggins approach for SPS/APS blends under the isothermal crystallization condition. However, the data on the literatures [10–12] showed some deviation from the linear relationship estimated from thermodynamic assumption. In this study, the mixing state of SPS/APS blend was investigated under the non-isothermal and isothermal conditions and was examined by the 'crystallization dynamics method'.

Experimental

Materials

Syndiotactic polystyrene (SPS; M_w=4.0·10^5, M_w/M_n=2.3, T_g=97°C) and atactic polystyrene (APS; M_w=1.6·10^5, M_w/M_n=1.3, T_g=90°C) were used. The tacticity of SPS was 98% evaluated by ^{1}H-NMR. The blends were prepared in *o*-dichlorobenzene solution at 130°C and the blend solution was pored into the excess amount of methanol. The precipitated powder was dried in vacuum for 24 h, subsequently heated to 150°C. The dry powder was pressed at 290°C using a hot press and quenched into ice water. The obtained blend films were dried under vacuum at room temperature for 24 h. The obtained film samples were completely amorphous by the X-ray diffraction method. The blend content (ϕ_{APS}) was indicated by the mass fraction of APS.

Differential scanning calorimetry (DSC)

DSC measurements were carried out by a Seiko differential scanning calorimetry (DSC200) connected with a Seiko thermal analysis system SSC5200H. The temperature and heat flow scales were calibrated using standard samples.

The non-isothermal crystallization was carried out at 5°C min^{-1} under dry nitrogen gas flow. The samples were heated to 300°C and maintained for 5 min, the samples were quenched to room temperature by taking out from DSC cell. The quenched samples were heated from room temperature to 300°C and were cooled from 300°C after maintaining samples at 300°C for 5 min.

For the isothermal crystallization, the sample was cooled to the pre-determined isothermal crystallization temperature at 5°C min^{-1} after maintaining samples at 300°C for 5 min and the crystallization exothermic heat was monitored until the crystallization was completed. After crystallization, the sample was heated from the isothermal crystallization temperature to 300°C at 5°C min^{-1} to evaluate the melting temperature.

Results and discussion

Non-isothermal crystallization

Figure 1 (A) showed the heating DSC curves of SPS/APS blends from the glassy state. The glass transition temperature (T_g) of SPS and APS are closed each other, it is difficult to evaluate the effect of blend on T_g. However the cold-crystallization temperature (T_{cc}) depended slightly on the blend content ϕ_{APS}, T_{cc} increased with ϕ_{APS}. Figure 1 (B) showed the cooling DSC curves of SPS/APS blends from the molten state. The start temperature of crystallization exothermic peak (T_c) depended slightly on ϕ_{APS}, T_c decreased with ϕ_{APS}. The non-isothermal crystallization results suggested that the crystallization of SPS was retarded by blending with APS. However, the non-isothermal measurement had only qualitative analysis of the effect of ϕ_{APS} on the crystallization rate of SPS.

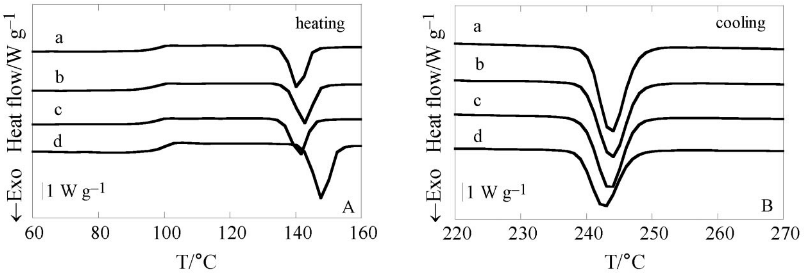

Fig. 1 A – DSC heating curve of SPS/APS blends from the glassy state and B – DSC cooling curves from the molten state. Scanning rate is 5 K $\min^{-1}$

The crystallization enthalpy normalized by SPS content was 16.5 kJ g^{-1} for heating and 29.2 kJ g^{-1} for cooling, respectively. The crystallinity of SPS scarcely influenced by blending with APS. In the case of poly(ethylenoxide) (PEO)/poly(methylmethacrylate) (PMMA) blend [14], which is the miscible blend in molecular level, the crystallinity of PEO decreases with the increase of PMMA content because PMMA molecules is excluded from the crystal growth surface to the inter-lamellar region with proceeding the crystallization and the excluded PMMA inhibits the crystallization of PEO. The non-isothermal crystallization results indicated that SPS/APS blends were the miscible but the concentration fluctuation seemed to be existed in the blend system from the viewpoint of the crystallinity.

Isothermal crystallization

From the isothermal crystallization experiments, two characteristic times were evaluated. The time, required to start the crystallization exotherm from the time at which the isothermal condition was established, was used as a nucleation time (t_N). The time, required to form a half of crystal from the start time of the crystallization exotherm, was used as a crystal growth time ($t_{1/2}$). The reciprocal of t_N and $t_{1/2}$ were employed as the nucleation rate ($N=t_N^{-1}$) and the crystal growth rate ($G=t_{1/2}^{-1}$), respectively.

The melting temperature depression by blend was described by the following Nishi–Wang equation [2, 15] using the melting temperature of pure polymer (T_m^*).

$$\frac{T_m}{T_m^*}=1+B\left(\frac{V_2}{\Delta H_2}\right)\phi^2 \tag{1}$$

$$B=\frac{RT}{V_1}\chi_{12} \tag{2}$$

Here, the subscript 1 and 2 indicated SPS and APS, respectively. ΔH, V and χ_{12} indicated the molar melting enthalpy, the molar volume and the interaction parameter, respectively.

The melting temperature depression of SPS/APS blend described by Eq. (1) was shown in Fig. 2. The non-linear relationship between T_m/T_m^* and ϕ^2 was observed in Fig. 2. For the miscible blend such as poly(vinylidene fluoride)/PMMA [2, 15], the linear relationship between T_m/T_m^* and ϕ^2 is reported. The melting temperature depression shown in Fig. 2 suggested that SPS/APS blend was the miscible but the non-linear relationship indicated that SPS/APS blend was not the thermodynamic miscible state, in other word, SPS/APS blend mixed each other but not in molecular level. From data shown in Fig. 2, the tentative interaction parameter (χ_{12}) was evaluated by the assumption of linear relationship between T_m/T_m^* and ϕ^2 using Eq. (1). To evaluate χ_{12}, $V_{(APS)}$ 99 cm^3 mol^{-1} [12], $V_{(SPS)}$ 121 cm^3 mol^{-1} [17], $\Delta H_{(SPS)}$ 10 kJ mol^{-1} [18], and T; $T^0_{m(SPS)}$ 292.82°C were used. The χ_{12} values evaluated for $\phi^2<0.05$ and $0.05<\phi^2$ were -0.24 and -0.08, respectively. The latter value was almost the same with the previous report [12] in which the data had non-linear relationship between T_m/T_m^* and ϕ^2.

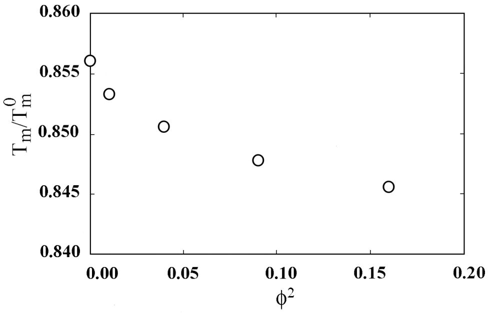

Fig. 2 Melting temperature depression of SPS/APS

Figure 3 shows the temperature dependency of nucleation rate (A) and crystal growth rate (B) for SPS/APS blends with various ϕ_{APS}. ΔT was the temperature difference between the melting temperature obtained by heating immediately after the isothermal crystallization and the isothermal crystallization temperature ($\Delta T=T_m-T_c$). With increasing ϕ_{APS} not only the melting temperature decreased but also the crystallization temperature decreased. At a given ΔT, both N and G decreased with the increase of ϕ_{APS} with some discrepancy in N. In order to evaluate the effect of ϕ_{APS} on G, the value of ΔT at a given G value (0.0018 s^{-1}) was obtained for each blend.

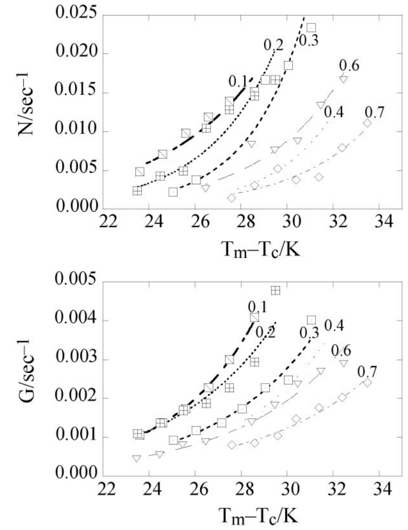

Fig. 3 A – Temperature dependency of nucleation rate and B – crystal growth rate for SPS/APS blend with various ϕ_{APS}

The ΔT values thus obtained were normalized by the equilibrium melting temperature (T_m^0) which was estimated by Hoffman–Weeks plot [19]. $\Delta T/T_m^0$ was plotted *vs.* ϕ_{APS} in Fig. 4. The linear relationship between $\Delta T/T_m^0$ and ϕ_{APS} was obtained for the ϕ_{APS} region up to 0.6. $\Delta T/T_m^0$ corresponded to the chemical potential difference ($\Delta\mu$) between SPS molecule in the molten state and the crystalline state as described by the following equation

$$\frac{\Delta T}{T_m^0}=\frac{\Delta\mu}{\Delta h_m} \qquad (3)$$

where Δh_m is the enthalpy of melting per molecule. Essentially, $\Delta\mu$ is the driving force of crystallization from the molten state.

In the crystallization of polymer, the diffusion process is the rate-determining stage. If the molecular diffusion through the super-cooled liquid state is considered by the reptation model [16], the diffusion distance is estimated as same as the radius gyration of SPS molecule. The calculated value of the radius gyration of SPS molecule was about 80 nm. As the melting temperature depression of SPS/APS blends shown in Fig. 2 was hardly described by Eq. (1), SPS/APS blends were not the thermodynamic miscible state and contained the concentration fluctuation. However, the linear relationship between $\Delta T/T_m^0$ and ϕ_{APS} suggested that the order of concentration fluctuation was less than the diffusion distance, 80 nm.

The slope of linear relationship shown in Fig. 4 corresponded to the energy increment required to disturb the diffusion of SPS molecule, which was similar to the interaction parameter to evaluate in the diffusion distance scale. The slope values of the miscible PVDF/PMMA blend in the molecular level and of the immiscible

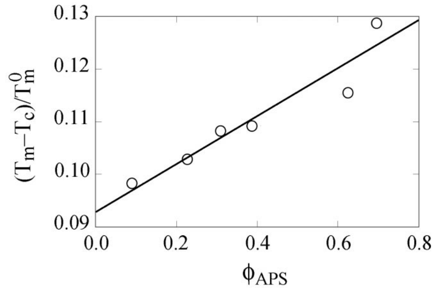

Fig. 4 Relationship between the blend content and the degree of supercooling normalized by the equilibrium melting temperature

PVDF/PtBMA were 0.281 and almost 0, respectively [20]. On the other hand, the slope of SPS/APS was 0.031, which suggested that interaction between SPS and APS was probably week.

Surface free energy

According to the classical Turnbull–Fisher theory [21], the temperature dependence of nucleation rate (N) is written by the following equation

$$N=N_0\exp\left[-\frac{E_D}{RT}-\frac{kT_m^2}{T_c(\Delta T)^2}\right] \tag{4}$$

$$k=\frac{8\pi\sigma_e\sigma_u^2}{R\Delta H_m^2} \tag{5}$$

$$\Delta T=T_m-T_c$$

where N_0, E_D, ΔH_m, σ_e, σ_u indicated a pre-exponential constant, an activation energy for diffusion through interface between liquid and nuclear, a heat of melting, a surface free energy of fold surface and a surface free energy of side surface of nuclear, respectively.

According to the Lauritzen–Hoffman theory [22], a lateral growth of polymer crystal is determined by the relationship between a nucleation rate of surface nuclear and a lateral growth rate of surface nuclear. The temperature dependence of crystal growth rate (G) is written by the following equation

$$G=G^0\exp\left[-\frac{\Delta E}{RT_c}-\frac{KT_m}{T_c\Delta T}\right] \tag{6}$$

$$K=\frac{nb\sigma_e\sigma_u}{R\Delta H_m} \tag{7}$$

Here, n and b indicate a constant depending the crystal growth ‘Regime’ and a thickness of molecule, respectively.

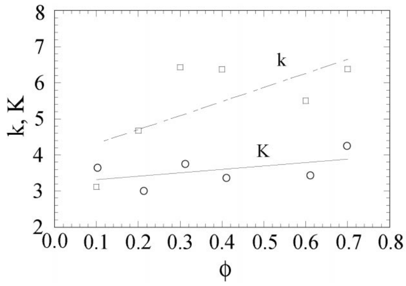

Fig. 5 Relationship between the blend content and the surface free energy parameters evaluated from the nucleation rate and the crystal growth rate

The surface free energy parameters *k* and *K* were obtained from the slope of plots, $\log N+\Delta E/(2.303RT)$ *vs.* $1/[T_c(\Delta T)^2]$ and $\log G+\Delta E/2.303RT$ *vs.* $1/(T_c\Delta T)$, respectively. Both plots showed a good linear relationship, and the values of *k* and *K* were evaluated from each slope concerning to *N* and *G*, respectively. The obtained surface free energy parameters *k* and *K* were plotted *vs.* ϕ_{APS} in Fig. 5. The surface energy parameter *K* evaluated from *G* showed a good linear relationship as same as the relationship shown in Fig. 4. However, the parameter *k* evaluated from *N* showed a relationship having a positive slope with same extent of scattering. These results were influenced by the existence of concentration fluctuation. The nucleation process was essentially in the intramolecular process, the space range of nucleation was considered in the size of few nm, whereas the crystal growth process was the diffusion process with the space range of 80 nm. As mentioned above, SPS/APS blends were the miscible system having a concentration fluctuation. The size of concentration fluctuation was estimated between few nm to less than 80 nm.

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