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MISCIBILITY EVALUATION OF NYLON 66/NYLON 6 BLENDS INVESTIGATED BY CRYSTALLIZATION DYNAMICS

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The crystallization dynamics of Nylon 66/Nylon 6 blends, the crystalline/crystalline polymer blends, was analyzed by DSC under isothermal conditions. The crystal growth rate (G) and the nucleation rate (N) depended on both the degree of supercooling (ΔT) and the blend mass fraction (ϕ). The $\Delta T/T_m^0$ values obtained at the fixed G, which corresponded to the chemical potential difference of molecules between liquid and crystal states, and the surface free energy parameters evaluated from G and N depended on ϕ for blends. The results suggested that Nylon 66/Nylon 6 blends with $\phi_{N66}\geq 0.80$ or $\phi_{N66}\leq 0.15$ are miscible.

Keywords: *crystallization dynamics, DSC, miscibility, nylon 66/Nylon 6 blend*

Introduction

Generally, polymer blend is scarcely miscible because the entropic contribution to the mixing Gibbs energy is too low to mix each other. Miscibility of polymers depends on polymer-polymer interactions such as hydrogen bonding, ion-dipole and dipole-dipole interactions. Several crystalline/crystalline polymer blends are reported, including Nylon 66/Nylon 48 [1], PHB/PBSU [2], PBSU/PEO [3], PEO/PHP [4], PEEK/PEK [5], PEO/PHB blends [4, 6]. Polyamide blends are essentially immiscible, because of a week attractive interaction between different polyamide [7].

Nylon 66/Nylon 6 (N66/N6) blends, the crystalline/crystalline polymer blends, are commercially available. They show improved printability, clarity, barrier and dimensional stability compared to the pure polymers [8]. Hensen's solubility parameter was a practical extension of the Hildebrand parameter method applied to polar and hydrogen bonding systems. The solubility parameter (δ) for Nylon 66 and Nylon 6 are 22.87 and 24.25 (J mL^{-1})$^{1/2}$ [9], respectively, which is close to each other. The intermolecular interaction parameter (χ) between two polymers is given by David and Sincock [10].

$$\chi=\frac{V_\mathrm{r}}{RT}(\delta_\mathrm{i}-\delta_\mathrm{j})^2 \qquad (1)$$

where T, R and V_r are temperature, gas constant, and molar volume of repeat unit, respectively. The subscripts i and j indicate blend components. Therefore, the χ value for N66/N6 blend should be small. Many studies for N66/N6 blends were reported extensively by Matsuda *et al*., including structure studies [11], phase behavior [12], crystallization and melting of Nylon 66/Nylon 6 blends [13]. Pseudo super-miscibility of Nylon 66/Nylon 6 blends exhibiting a single T_g and a single T_m is reported by Khanna *et al*. [14].

We have proposed the method evaluating a compatibility of crystalline/amorphous or crystalline/crystalline polymer blends by analyzing crystallization dynamics under isothermal condition using DSC [15, 16]. This method has been used successfully for the evaluation of the mixed state of PVDF/PMMA [15, 16], sPS/aPS [17], Nylon 66/Nylon 48 [1]. By this method, the interaction and miscibility can be estimated by investigating the blend fraction (ϕ) dependence of the crystal growth rate (G) and the surface energy of crystal. In a miscible blend, the crystallization of a crystalline component is influenced by another component because of intermolecular interactions between both polymers; that is to say, the crystal growth rate (G) of the blends depends on the blend fraction (ϕ). On the other hand, the crystallization of a crystalline component is free from another crystalline component because the crystalline component crystallizes in own phase for the immiscible blend. In this way, interaction and miscibility can be estimated by investigation of dependence of G. In this study, miscibility of N66/N6 blends was evaluated from the viewpoint of crystallization dynamics, including the nucleation rates, crystal growth rates, chemical potential difference and surface free energy.

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Experimental

Samples

Nylon 66 and Nylon 6 used in this study were purchased from Anshan Dragon-Smar Plastic Ltd, China. The limiting viscosity of Nylon 66 and Nylon 6 is $[\eta]$=101.7 and 164.2 mL g^{-1}, respectively (measured in 90% formic acid at 25°C using solutions of the polymer, 0.01 g mL^{-1}). Both materials were used as received without further purification. Nylon 66 and Nylon 6 were dissolved in *m*-cresol at room temperature, and the solutions were poured into excess methanol. The precipitated powder was filtered, washed, and dried at room temperature in vacuum for 4 days and then at 100°C in a vacuum oven for 8 h. The blend sample were heated to 283°C, and were quenched to 0°C. The obtained blend samples were further dried, and used for DSC measurement. The blend fraction (ϕ) is expressed in the mass fraction of Nylon 66 (ϕ_{N66}=0.1 indicates the blend of composition Nylon 66/Nylon 6=0.1/0.9), the mass fraction of Nylon 6 (ϕ_{N6}=0.9 indicates the blend of composition Nylon 66/Nylon 6=0.1/0.9).

Differential scanning calorimetry (DSC)

DSC measurement was carried out using a Seiko Differential Scanning Calorimeter (DSC 6200) connected to a Seiko thermal analysis system. The scanning velocity and the time resolution of DSC were 5 K min^{-1} and 1.0 sec, respectively. The sample was heated to 283°C and maintained at that temperature for 10 min, cooled to 143°C, and then heated to 283°C again. DSC non-isothermal crystallization exotherms and melting endotherms for various compositions of Nylon 66/Nylon 6 blends were obtained.

The sample was heated to 283°C and maintained at that temperature for 10 min, then cooled to a predetermined crystallization temperature (T_c). The heat of crystallization at T_c was measured until the crystallization was completed. After crystallization, samples were heated to 283°C, and the melting temperature T_m was measured. The T_m value was determined from the DSC endothermic peak. Two characteristic times were evaluated from the exothermic DSC peak: the time from cooling at T_c to the start of the exothermic peak due to crystallization (t_{st}) and the time from t_{st} to when 50% of the crystallization had occurred, denoted t_N and $t_{0.5}$, respectively [15]. The reciprocals of t_N and $t_{0.5}$ were employed as the nucleation rate (N) and the crystal growth rate (G). Temperature variation during crystallization was at most ±0.2°C. Isothermal crystallization was carried out at various T_c values, and runs in which crystallization occurred before arriving at T_c were eliminated.

Results and discussion

Non-isothermal features

Figure 1 (A) showed the DSC non-isothermal crystallization exotherms of Nylon 66/Nylon 6 blends from the molten state. For blends with ϕ_{N66}=0.2, 0.3, 0.4, 0.5, two peaks due to the separate crystallization of

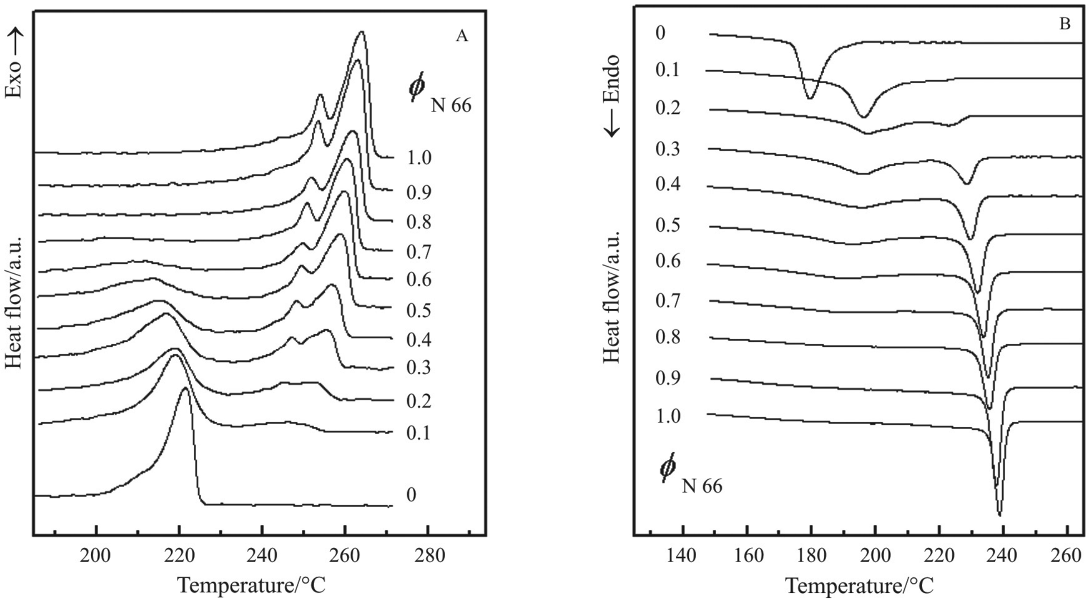

Fig. 1 DSC A – crystallization exotherms and B – melting endotherms for the Nylon 66/Nylon 6 blends with various blend fractions

Nylon 66 and Nylon 6 were observed. As shown in Fig. 1 (A), the temperature of crystallization exothermic peak (T_c) for Nylon 66 decreased with increasing ϕ_{N6}, and the T_c for Nylon 6 increased with increasing ϕ_{N66}. However, the non-isothermal crystallization had only qualitative analysis of the effect of composition on the crystallization of crystalline component.

Figure 1 (B) showed the DSC melting endotherms of Nylon 66/Nylon 6 blends. Two melting peaks were observed for the blends with $\phi_{N66}<0.7$, while the lower-temperature melting peak disappeared when $\phi_{N66}\geq0.7$. As shown in Fig. 1 (B), the melting temperature of Nylon 66 decreased continuously with increasing ϕ_{N6}, however, the melting temperature of Nylon 6 increased with increasing ϕ_{N66}. The reduction of melting temperature in Nylon 66/Nylon 6 blends reported by Matsuda *et al*. [13] is very similar compared to our data here, they mentioned that a considerable reduction of melting temperature of Nylon 66 was brought about by a thermodynamic reason, and a relatively large negative polymer-polymer interaction parameter was calculated.

Treatment of data

According to Hoffman-Lauritzen theory [18], when T_c is close to the melting point, the temperature dependence of the crystallization rate (G) is written as

$$G=G^0\exp-\left(\frac{\Delta E}{RT_c}-\frac{K_g}{RT\Delta T}\right) \tag{2}$$

where G_0, ΔE and R are a constant that is independent of temperature, the activation energy of diffusion and the gas constant, respectively. K_g is a nucleation factor given by

$$K_g=\frac{nbT_m\sigma}{\Delta H_m^2} \tag{3}$$

where n, b and ΔH_m are a constant that depend on regime, stem length and heat of melting, respectively. σ is the average surface free energy and is given as

$$\sigma=\sigma_u^2\sigma_e \tag{4}$$

where σ_u and σ_e indiscate lateral surface energy and fold surface energy, respectively. According to the crystallization theory of Turnbull-Fisher [19], the temperature dependence of G is written also as

$$\log G+\frac{\Delta E}{RT_c}=G^0-\frac{KT_m}{T_c\Delta T} \tag{5}$$

where

$$K=\frac{8\pi\sigma}{R\Delta H_m^2} \tag{6}$$

The temperature dependence of the nucleation rate (N) is given by

$$\log N=N^0-\frac{ST_m^2}{T_c\Delta T^2} \tag{7}$$

$$S=A\left[\frac{2\sigma}{R\Delta H_m^2}-\frac{T\log(v)\sigma_e}{\Delta H_m^2}\right] \tag{8}$$

where N^0 is a constant that is independent of temperature. A and v are a constant depends on both nucleation and crystal growth process, and the volume fraction of amorphous part, respectively. Usually $\sigma_u>>\sigma_e$, Eq. (8) is given by

$$S=\frac{2A\sigma}{R\Delta H_m^2}\quad \text{for } \sigma_u>>\sigma_e \tag{9}$$

S values obtained from the nucleation process and K values obtained from the crystallization process are proportional to surface free energy (σ).

Nucleation and crystal growth rates

Figures 2 and 3 showed the nucleation rate (N) and the crystal growth rate (G) changes with the degree of supercooling ($\Delta T=T_m^0-T_c$) for Nylon 66/Nylon 6 blends with variousϕ. As shown in Figs 2 and 3, N and G of all blend fractions became the faster with increasing ΔT. According to classical crystallization theory, the temperature dependence of the homogeneous crystal nucleation rate and the crystal growth rate from the melt are generally described by the exponential equations [20], in which the first and second terms in the exponential form have the opposite temperature dependence. The crystallization at higher temperature, that is to say, will reduce the nucleation rate and the crystal growth rate. It is well known that N *vs*. ΔT and G *vs*. ΔT plots show a maximum between T_m and T_g, because the diffusion of molecules is restricted due to high viscosity at large ΔT [20]. In this study, however, data at high ΔT were neglected since the crystallization occurred before the isothermal condition. For the blends with $\phi_{N66}\geq0.80$ shown in Figs 2A and 3A, N and G increased with increasing ϕ_{N6} at the same ΔT. For the blends with $\phi_{N66}\leq0.15$ shown in Figs. 2B and 3B, N and G increased with increasing ϕ_{N66} at the same ΔT. All temperature dependence curves of N and G shifted to the small ΔT side with increasing ϕ_{N6} and ϕ_{N66} as shown in Figs 2 and 3. The result that the G values for Nylon 66/Nylon 6 blends were larger than that for pure Nylon 66 or Nylon 6, indicating that the crystallization process of blends was accelerated by another component. An explanation was that the interaction between same Nylons became weak owing to the formation of irregular hydrogen bonding between different Nylons, and lead to faster *G* and *N* for the blends [1].

An obvious feature for the miscible blend is the strong dependence of *G* on ϕ [15, 16]. The crystallization of a crystalline polymer was restricted by mixing of another polymer in a miscible system, because the diffusion process of crystalline molecules to crystal growth surface was obstructed due to the attractive in-

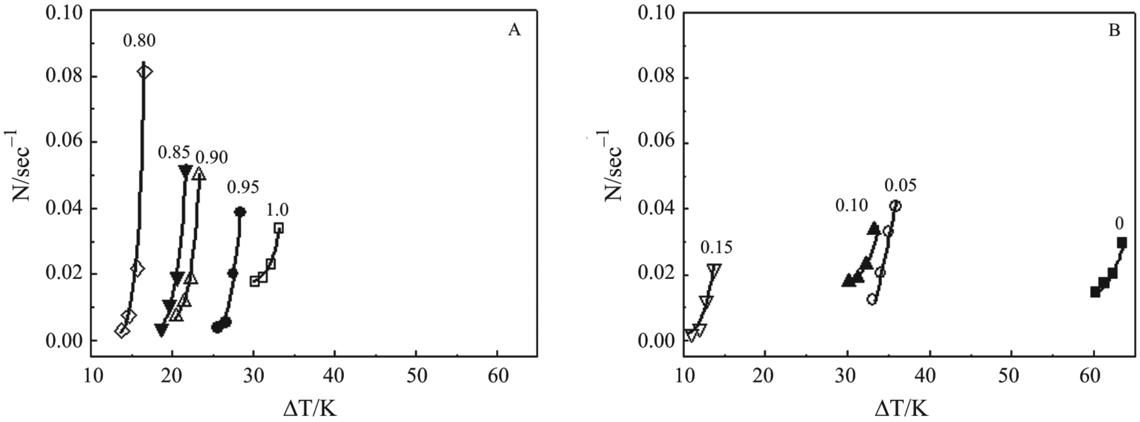

Fig. 2 Nucleation rate (*N*) changes for Nylon 66/Nylon 6 blends with various ϕ_{N66} (the numbers in figures indicate ϕ_{N66}) as a function of supercooling ($\Delta T=T_m^0-T_c$)

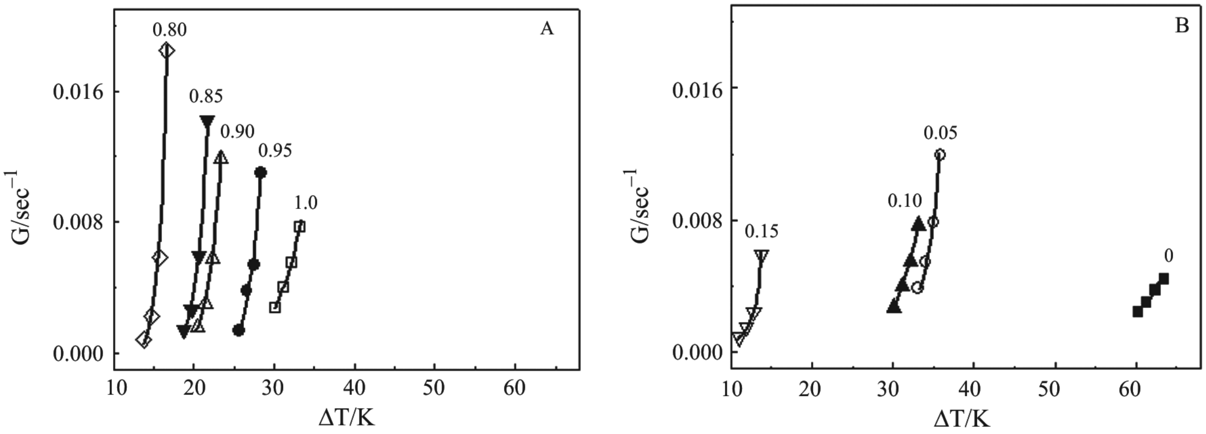

Fig. 3 Crystal growth rate (*G*) changes for Nylon 66/Nylon 6 blends with various ϕ_{N66} (the numbers in figures indicate ϕ_{N66}) as a function of supercooling($\Delta T=T_m^0-T_c$)

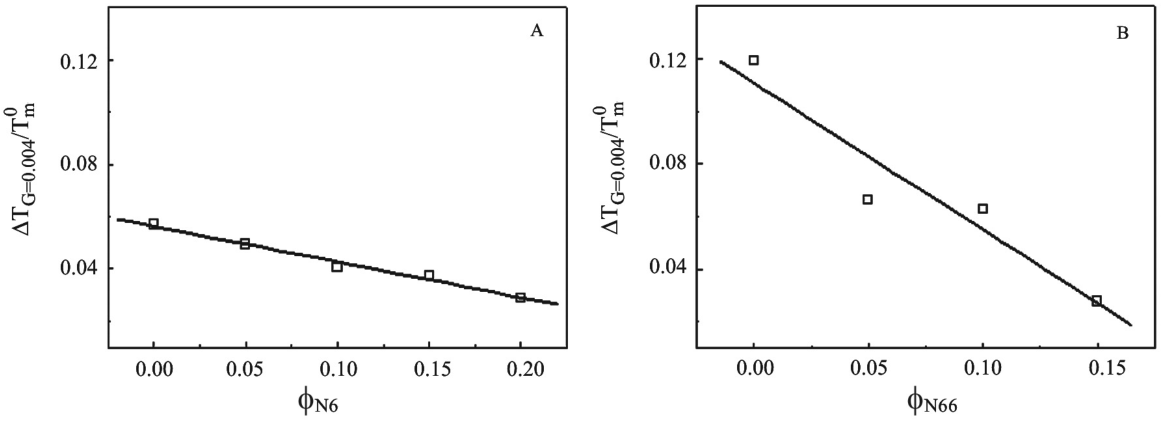

Fig. 4 Relationship between $\Delta T/T_m^0$ and ϕ_{N6} (A), $\Delta T/T_m^0$ and ϕ_{N66} (B) obtained at the fixed *G* (0.004 s^{-1})

teraction between blend components. The chemical potential difference (Δμ) between molecules in the liquid and the crystal states may be expressed by

$$\frac{\Delta\mu}{\Delta H_\mathrm{m}}=\frac{\Delta T}{T_\mathrm{m}^0} \tag{10}$$

where ΔH_m, ΔT, and T_m^0 indicated the melting enthalpy of repeating unit, the degree of supercooling ($\Delta T=T_\mathrm{m}^0-T_\mathrm{c}$) and the equilibrium melting temperature, respectively. The melting temperature (T_m) of Nylon 66, Nylon 6 and their blends were measured after crystallization at various T_c. Equilibrium melting temperature (T_m^0) of Nylon 66, Nylon 6 and their blends was evaluated by applying the Hoffman-Weeks plot [21]. To discuss the dependence of G on φ according to Eq. (10), the ΔT value at which G approached to 0.004 s^{-1} ($\Delta T_{G=0.004}$) was evaluated from the relationship between G and ΔT for each ϕ shown in Fig. 3. The obtained results are plotted *vs*. ϕ_{N6} (A) or ϕ_{N66} (B) in Fig. 4. The $\Delta T_{G=0.004}/T_\mathrm{m}^0$ value decreased with increasing ϕ_{N6} (A) and ϕ_{N66} (B). The reason for decreasing Δμ with the increasing ϕ_{N6} and ϕ_{N66} may be in relation to the different interaction between Nylon 66/Nylon 66, Nylon 6/Nylon 6 or Nylon 66/Nylon 6. Owing to all being crystalline polymer for Nylon 66 and Nylon 6, the interaction between same crystalline polymers is stronger than that between different crystalline polymers. Therefore, Fig. 4 shows the chemical potential difference decreased with increasing ϕ_{N6} (A) and ϕ_{N66} (B). The results that $\Delta T_{G=0.004}/T_\mathrm{m}^0$ depended on ϕ_{Nylon} for blends suggested that Nylon 66/Nylon 6 blends are miscible, and have the different interaction according to the slopes of relationship between Δμ and ϕ.

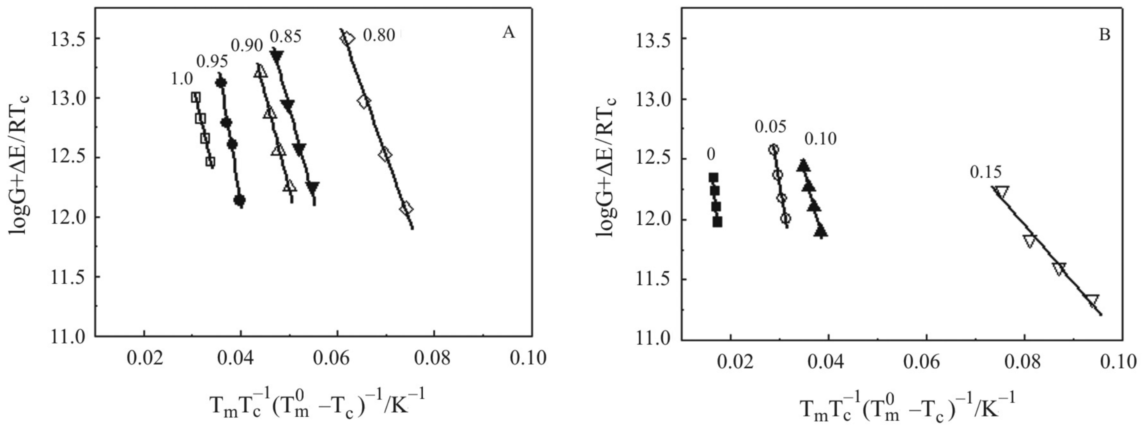

Fig. 5 Relationships described in Eq. (5) to evaluate the surface free energy parameters from G for Nylon 66/Nylon 6 blends with various ϕ_{N66} (the numbers in figures indicate ϕ_{N66})

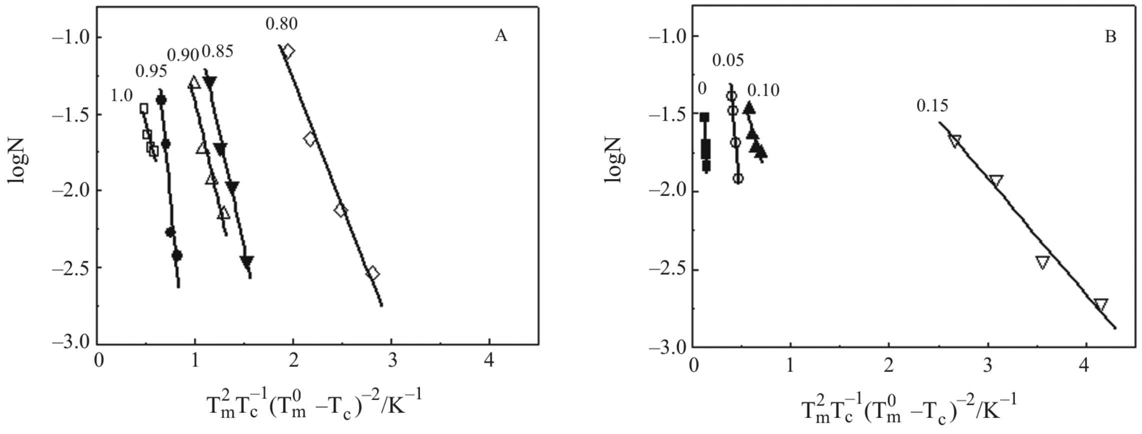

Fig. 6 Relationships described in Eq. (7) to evaluate the surface free energy parameters from N for Nylon 66/Nylon 6 blends with various ϕ_{N66} (the numbers in figures indicate ϕ_{N66})

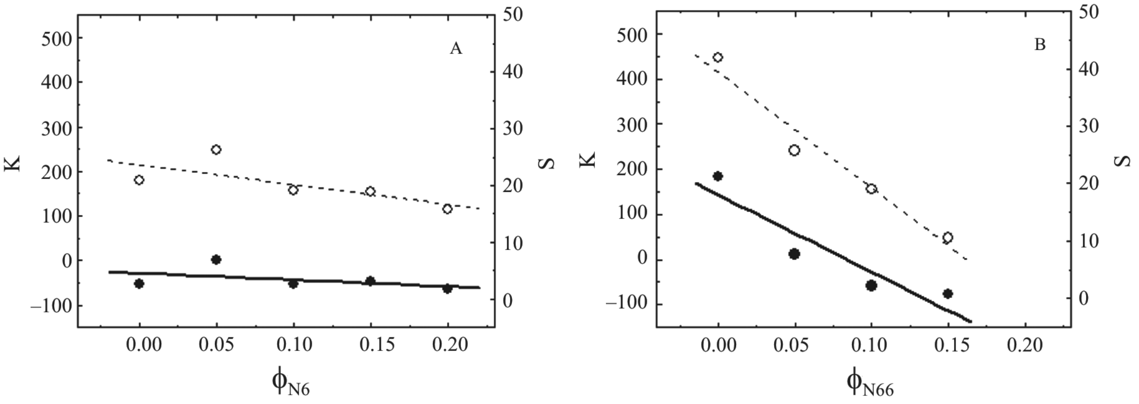

Fig. 7 Relationship between surface free energy parameters (*K* as open circle, *S* as filled circle) *v.s.* A – and B – ϕ_{N6}

Surface free energy

According to Eqs (5) and (7), the slope of the plots of $\log G{+}\Delta ER^{-1}T_c^{-1}$ *vs*. $T_mT_c^{-1}\Delta T^{-1}$ and $\log N$ *vs*. $T_m^2T_c^{-1}\Delta T^{-2}$ are used for evaluation of surface free energy parameter *K* and *S* values from the independence *G* and *N* values, respectively. The relationship between $\log G{+}\Delta ER^{-1}T_c^{-1}$ and $T_mT_c^{-1}\Delta T^{-1}$, $\log N$ and $T_m^2T_c^{-1}\Delta T^{-2}$ for Nylon 66/Nylon 6 blends is shown in Figs 5 and 6, respectively. The values of *K* and *S* were evaluated from each slope of linear relationships shown Figs 5 Fig. 6, respectively. The ϕ dependence of *K* and *S* is shown in Fig. 7. *K* and *S* showed a good agreement at all ϕ. *K* and *S* are proportional to crystal surface free energy (σ) as described in Eqs (6) and (9).

Figure 7 showed the similar tendency of the ϕ dependence with $\Delta T_{G=0.004}/T_m^0$ shown in Fig. 4. These results supported the miscibility of the Nylon 66/Nylon 6 blends. Figure 7 suggested that the σ of Nylon 66 and Nylon 6 decreased with increasing ϕ. The reason for decreasing σ of pure Nylon by mixing may be in relation to the change of the hydrogen bonding interaction between nylons [1].

Conclusions

It is possible to estimate the mixing state of Nylon 66/Nylon 6 blends, crystalline/crystalline polymer, analyzing crystallization dynamics by DSC method. Because the interaction between nylons became weaker owing the formation of the interaction between Nylon 66 and Nylon 6, *N* and *G* for the blends were faster than that for pure Nylon 66 and Nylon 6. The ϕ dependence of *G* showed good agreement with ϕ dependence of estimated from *G* and *N*. According to the strong ϕ dependences of the chemical potential ($\Delta T_{G=0.004}/T_m^0$) and the surface energy parameters (*K* and *S*), the Nylon 66/Nylon 6 blends with $\phi_{N66}\geq 0.80$ or $\phi_{N66}\leq 0.15$ were miscible.

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