

# Miscibility of Nylon 66 and Nylon 48 blend evaluated by crystallization dynamics

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## Abstract

The crystallization dynamics of Nylon 66/Nylon 48 blends, the crystalline/crystalline polymer blend, was analyzed by differential scanning calorimetry (DSC) under isothermal conditions. The equilibrium melting temperature ( $T_m^0$ ), crystal growth rate ( $G$ ) and the nucleation rate ( $N$ ) depended on both the degree of supercooling ( $\Delta T$ ) and the blend fraction ( $\phi$ ). The  $\Delta T/T_m^0$  values obtained at the fixed  $G$ , which corresponded to the chemical potential different between molecules in the liquid and the crystal states, and the surface free energy parameters evaluated from  $G$  and  $N$  depended on  $\phi$  for blends. The results suggested that Nylon 66/Nylon 48 blends are miscible in all blend fractions. The result agrees with the intermolecular interaction parameter ( $\chi$ ) obtained from  $T_m^0$  depression. Infrared spectroscopic and X-ray diffraction data indicated that the hydrogen bond became weak and the crystalline structure became disordered one by blending.

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**Keywords:** DSC; Nylon 66/Nylon 48 blend; Miscibility; Crystallization dynamics; Hydrogen bond

## 1. Introduction

Generally polymers scarcely mix with each other, because the entropy effect on the Gibbs energy change of mixing is considerably low. Miscibility of polymers strongly depends on polymer–polymer interactions such as hydrogen bonding, ion–dipole and dipole–dipole interactions. Miscibility between crystalline and amorphous polymers has been examined, and several pairs are known as miscible blends [1–5], which are results of the specific interaction. On the other hand, a few crystalline/crystalline polymer blends are reported [6–11] including Nylon 6/sulfonated polystyrene ionomers blends [6–8], Nylon 11/poly(vinylidene fluoride) blend [9] and Nylon 6/polyethylene blends [10]. Polyamide blends are essentially immiscible, because of a weak attractive interaction between different polyamides [11].

As Nylon 66 (N66) and Nylon 48 (N48) are isomeric compounds, the N66/N48 blend is expected to form regular hydrogen bonding between the polar amide (NHCO) groups due to the same NHCO/CH<sub>2</sub> ratio and the same distance between amide groups. Hansen's solubility parameter was

a practical extension of the Hildebrand parameter method applied to polar and hydrogen bonding systems. The value of the solubility parameter ( $\delta$ ) for Nylon 66 was found to be 13.6 cal cm<sup>-1</sup> [12]. From the similar chemical structure of N66 and N48, their solubility parameter should also be close. The intermolecular interaction parameter ( $\chi$ ) between two polymers is given by [13]

$$\chi = \frac{V_r}{RT}(\delta_i - \delta_j)^2 \quad (1)$$

where  $T$ ,  $R$  and  $V_r$  are the temperature, the gas constant, and the molar volume of repeat unit, respectively. The subscripts  $i$  and  $j$  indicate blend components. Therefore, the  $\chi$  value for N66/N48 blend should be very small. It is well known that the smaller the  $\chi$  value the larger the compatibility. This predicts that the blend of two polymers is either miscible or partially miscible.

We have proposed the method evaluating a compatibility of crystalline/amorphous polymer blends by analyzing crystallization dynamics under isothermal condition using DSC [14,15]. By this method, the interaction and miscibility can be estimated by investigating the blend fraction ( $\phi$ ) dependence of the crystal growth rate ( $G$ ) and the surface free energy of crystal. In a miscible blend, the crystalliza-

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tion 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 blend depends on the blend fraction ( $\phi$ ). 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  $\phi$  dependence of  $G$ . This method is not, however, reported for evaluating the crystalline/crystalline polymer blends system. In this study, miscibility of N66/N48 blends was evaluated using the crystallization dynamics method.

## 2. Experimental

### 2.1. Samples

Nylon 66 (Scientific Polymer Products) was used in this study. Nylon 48 was prepared using the interface polymerization of chloro-octanedioyl and butanediamine. The relative viscosity of N66 and N48 is  $\eta_{\text{rel}} = 1.79$  and 1.90, respectively (measured at 25 °C in *m*-cresol of a concentration of 0.5%). N66 and N48 were dissolved in *m*-cresol at room temperature. The blend fraction ( $\phi$ ) is expressed in the weight fraction of N66 ( $\phi_{\text{N66}} = 0.4$  indicates the blend of composition N48/N66 = 0.6/0.4), or the weight fraction of N48 ( $\phi_{\text{N48}} = 0.6$  indicates the blend of composition N48/N66 = 0.6/0.4). After precipitating from methanol and drying at 80 °C in a vacuum oven for 48 h, blend samples were pressed at 280 °C and were quenched to ice water. The obtained blend films were further dried under vacuum at room temperature for 48 h. The blend sample cramped in an aluminum vessel was used for DSC measurement.

### 2.2. Isothermal crystallization

Isothermal crystallization was carried out using a Seiko Differential Scanning Calorimeter (DSC200) connected to a Seiko thermal analysis system SSC5200H. The sample was heated to 280 °C and maintained for 5 min, then quenched 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 280 °C, and melting temperature ( $T_m$ ) was measured at 5 K min<sup>-1</sup>.  $T_m$  was defined as the onset temperature of endothermic peak. Two characteristic times were evaluated from the exothermic DSC peak: the time from quenching at  $T_c$  to the start of the exothermic peak due to crystallization ( $t_{\text{st}}$ ) and the time from  $t_{\text{st}}$  to when 50% of the crystallization had occurred, denoted  $t_N$  and  $t_{0.5}$ , respectively [14]. 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  $\pm 0.2$  °C. Isothermal crystallization was carried out at various  $T_c$  values, and runs

in which crystallization occurred before arriving at  $T_c$  were eliminated.

### 2.3. FT-IR and WAXS measurements

The infrared measurements were performed with a JASCO620 FT-IR spectrometer with a wavenumber resolution of 2 cm<sup>-1</sup>, and the accumulation of one spectrum was 64 times. The IR samples were prepared from solvent casting on a glass plate at 100 °C in a desiccator. The obtained blend films were further dried under vacuum at room temperature for 48 h. The sample film sandwiched with thin KBr discs after isothermal crystallization and then quenching to room temperature was used for FT-IR measurement.

The wide angle X-ray scattering (WAXS) was recorded by a Mac Science Model SRA MXP-18 diffractometer operating at 40 kV and 400 mA. The WAXS samples were prepared by isothermal crystallization and then quenching to room temperature.

## 3. Results and discussion

### 3.1. Treatment of data

According to Hoffman–Lauritzen theory [16], when  $T_c$  is close to the melting point, the temperature dependence of the crystallization rate ( $G$ ) is written as

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

where  $G^0$ ,  $\Delta E$  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

$$K_g = \frac{nbT_m\sigma}{\Delta H_m^2} \quad (3)$$

where  $n$ ,  $b$  and  $\Delta H_m$  are a constant that depend on regime, the length of stem and the heat of melting, respectively.  $\sigma$  is the average surface free energy and is given as

$$\sigma = \sigma_u^2 \sigma_e \quad (4)$$

where  $\sigma_u$  and  $\sigma_e$  indicate lateral surface free energy and fold surface free energy, respectively. According to the crystallization theory of Turnbull–Fisher [17], the temperature dependence of  $G$  is written also as

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

where

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

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

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

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

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  $\sigma_u \gg \sigma_e$ , Eq. (6) is given by

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

$S$  values obtained from the nucleation process and  $K$  values obtained from the crystallization process are all proportional to surface free energy ( $\sigma$ ).

### 3.2. Equilibrium melting temperature

As described in Section 2, the melting temperatures ( $T_m$ ) of N66, N48 and their blends were measured after crystallization at various  $T_c$ . Equilibrium melting temperature ( $T_m^0$ ) of N66, N48 and their blends was evaluated by applying the Hoffman–Weeks plot [18]. The relationship between  $T_m^0$  and  $\phi_{N66}$  is shown in Fig. 1. The  $T_m^0$  value of pure N66 and N48 are close as shown in Fig. 1, because of their similar chemical structure. The symmetric  $T_m^0$  change was observed at the minimum  $T_m^0$  for  $\phi_{N66} = 0.5$ .

As shown in Fig. 1,  $T_m^0$  of N66 and N48 decreased with increasing  $\phi$ , that suggested the miscibility of N66/N48 blends. The melting temperature depression of blends is used for calculation of the interaction parameter ( $\chi$ ) for crystalline/amorphous polymer blends [1–5] by applying the equation derived by Nishi and Wang [1]. The interaction parameter ( $\chi$ ) can then be used to study the miscibility of the blend. Shien et al. calculated  $\chi$  values of polypropylene/poly(butene-1) blends, a crystalline/crystalline polymer blend, using the Nishi and Wang's method [19]. The obtained  $\chi$  values are not a constant and depend considerably on the blend fraction. The following Nishi and Wang's equation was used to calculate  $\chi$  of N66/N48 blends in the range of  $\phi_{N66} = 0.5$ –1.0:

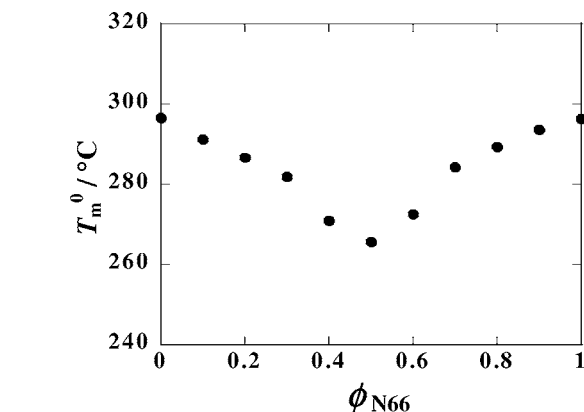


Fig. 1. Equilibrium melting temperature ( $T_m^0$ ) change for Nylon 66/Nylon 48 blend as a function of Nylon 66 weight fraction ( $\phi_{N66}$ ).

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_{u2}}{\Delta H_{u2}V_{u1}} \chi \phi_1^2 \quad (10)$$

where  $T_m$ ,  $T_m^0$ ,  $\phi_i$ ,  $V_{ui}$  and  $\Delta H_{ui}$  are the equilibrium melting temperature of N66 in the blend and in the neat N66, volume fraction, molar volume and molar enthalpy of fusion of component  $i$ , respectively. Subscripts 1 and 2 refer to N48 and N66, respectively. The  $\Delta H_u$  for N66 was taken as  $458 \text{ cal g}^{-1}$  [20].  $V_{u1}$  and  $V_{u2}$  are considered as approximately equal. The calculated value of  $\chi$  was  $-1.93$ , which indicates very strong interactions between Nylon 66 and Nylon 48 existed in N66/N48 blend.

### 3.3. Nucleation and crystal growth rates

Figs. 2 and 3 show the nucleation rate ( $N$ ) and the crystal growth rate ( $G$ ) changes with the degree of supercooling ( $\Delta T = T_m^0 - T_c$ ) for N66/N48 blends with various  $\phi$ . As shown in Figs. 2 and 3,  $N$  and  $G$  of all blend fractions became the faster with increasing  $\Delta T$ . According to classical crystallization theory, the temperature dependence of the homogeneous crystal nucleation rate and the crystal growth

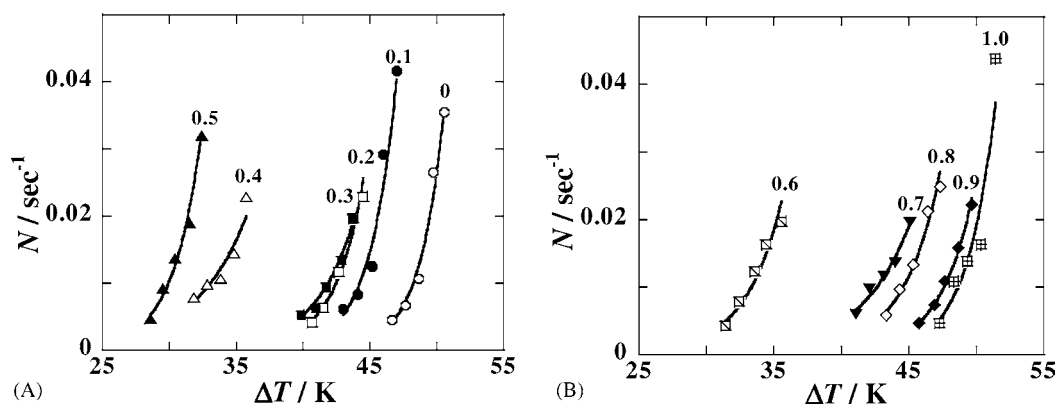


Fig. 2. Nucleation rate ( $N$ ) changes for Nylon 66/Nylon 48 blend with various  $\phi_{N66}$  (the numbers in figures indicate  $\phi_{N66}$ ) as a function of super cooling ( $\Delta T = T_m^0 - T_c$ ).

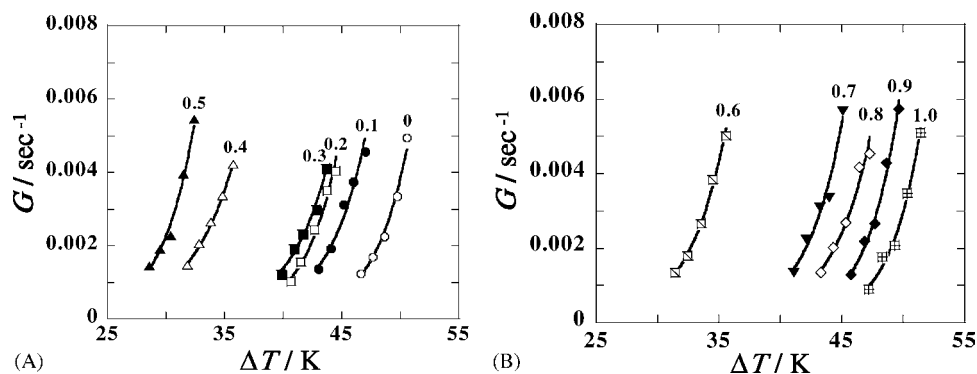


Fig. 3. Crystal growth rate ( $G$ ) changes for Nylon 66/Nylon 48 blend with various  $\phi_{N66}$  (the numbers in figures indicate  $\phi_{N66}$ ) as a function of supercooling ( $\Delta T = T_m^0 - T_c$ ).

rate from the melt are generally described by the exponential equations [21], in which the first and second terms in the exponential have opposing 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  $N$  versus  $\Delta T$  and  $G$  versus  $\Delta T$  plots show a maximum between  $T_m$  and  $T_g$ , because the diffusion of molecules is restricted due to high viscosity at large  $\Delta T$  [21]. In this study, however, data at high  $\Delta T$  were neglected since the crystallization occurred before the isothermal condition. For the blends with  $\phi_{N66} < 0.5$  shown in Figs. 2(A) and 3(A),  $N$  and  $G$  increased with increasing  $\phi_{N66}$  at same  $\Delta T$ . For the blends with  $\phi_{N66} > 0.5$  shown in Figs. 2(B) and 3(B),  $N$  and  $G$  increased with increasing  $\phi_{N48}$  at same  $\Delta T$ . All temperature dependence curves of  $N$  and  $G$  shifted to the small  $\Delta T$  side with increasing  $\phi_{N66}$  and  $\phi_{N48}$  as shown in Figs. 2 and 3.

An obvious feature for the miscible blend is the strong dependence of  $G$  on  $\phi$  [14,15]. The crystallization of a crystalline polymer was restricted by mixing of another polymer in a miscible system because the diffusion process of the crystalline polymer to crystal growth surface was obstructed due to the attractive interaction between blend components. The chemical potential difference ( $\Delta\mu$ ) between molecules in the liquid and the crystal states may be expressed by

$$\frac{\Delta\mu}{\Delta H_m} = \frac{\Delta T}{T_m^0} \quad (11)$$

Here  $\Delta H_m$ ,  $\Delta T$ ,  $T_m^0$  indicated the melting enthalpy of repeating unit, the degree of supercooling ( $\Delta T = T_m^0 - T_c$ ) and the equilibrium melting temperature, respectively. To discuss the dependence of  $G$  on  $\phi$  according to Eq. (11), the  $\Delta T$  value at which  $G$  approached to  $0.003 \text{ s}^{-1}$  ( $\Delta T_{G=0.003}$ ) was evaluated from the relationship between  $G$  and  $\Delta T$  for each  $\phi$  shown in Fig. 3. The obtained results are plotted against  $\phi_{N66}$  in Fig. 4. The  $\Delta T_{G=0.003}/T_m^0$  value increased with increasing  $\phi_{N66}$  and  $\phi_{N48}$ . In other words, Fig. 4 indicates the blend effect on chemical potential difference between molecules in the liquid and crystal states. The results

that  $\Delta T_{G=0.003}/T_m^0$  depended on  $\phi_{Nylon}$  for blends suggested that N66/N48 blends were miscible.

### 3.4. Surface free energy

According to Eqs. (5) and (7) the slope of the plots of  $\log G + \Delta ER^{-1}T_c^{-1}$  versus  $T_m T_c^{-1} \Delta T^{-1}$  and  $\log N$  versus  $T_m^2 T_c^{-1} \Delta T^{-2}$  are used for the evaluation of surface free energy parameter  $K$  and  $S$  values from the independent  $G$  and  $N$  values, respectively. The relationship between  $\log G + \Delta ER^{-1}T_c^{-1}$  and  $T_m T_c^{-1} \Delta T^{-1}$ ,  $\log N$  and  $T_m^2 T_c^{-1} \Delta T^{-2}$  for N66/N48 blends is shown in Fig. 5. The values of  $K$  and  $S$  were evaluated from each slope of linear relationships shown in Fig. 5(A) and (B), respectively. The  $\phi$  dependence of  $K$  and  $S$  is shown in Fig. 6.  $K$  and  $S$  showed a good agreement at all  $\phi$ .  $K$  and  $S$  are proportional to crystal surface free energy ( $\sigma$ ) as described in Eqs. (6) and (9). Fig. 6 showed the similar tendency of the  $\phi$  dependency with  $T_m^0$  shown in Fig. 1 and  $\Delta T_{G=0.003}/T_m^0$  shown in Fig. 4. These results supported the miscibility of N66/N48 blend system. Fig. 6 suggested that the  $\sigma$  of N66 and N48 decreased with increasing  $\phi$ . The reason for decreasing  $\sigma$  of pure Nylon by mixing may be in relation to the change of the hydrogen bonding interaction between nylons.

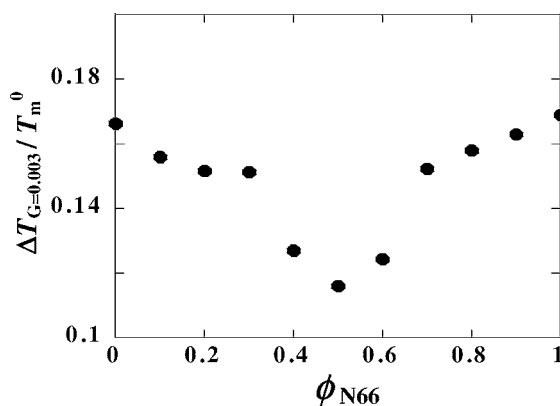


Fig. 4. Relationship between  $\Delta T_{G=0.003}/T_m^0$  and  $\phi_{N66}$  obtained at the fixed  $G$  ( $0.003 \text{ s}^{-1}$ ).

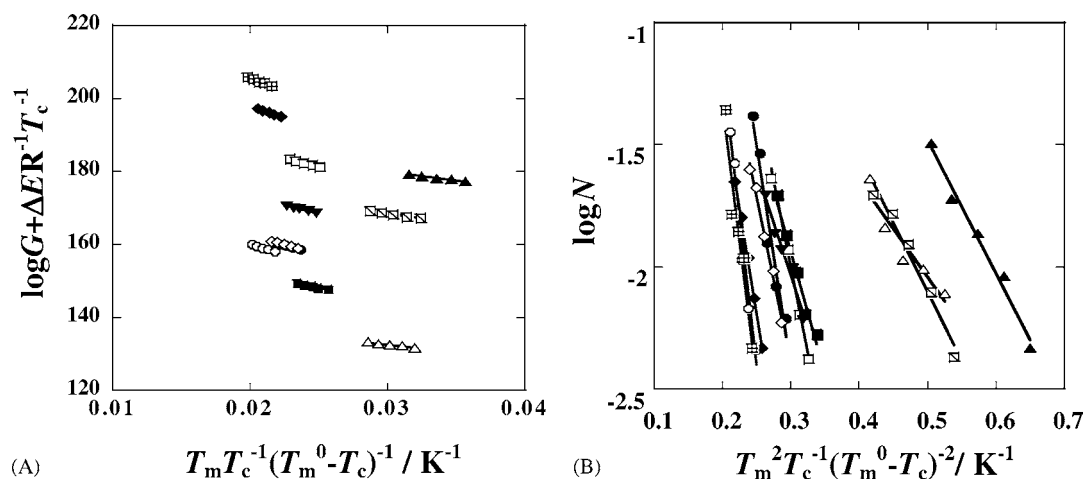


Fig. 5. Relationships described in Eqs. (5) and (7) to evaluate the surface free energy parameters from crystal growth rate (A) and nucleation rate (B) for Nylon 66/Nylon 48 blends with  $\phi_{N66} = 0$  ( $\circ$ ), 0.1 ( $\bullet$ ), 0.2 ( $\square$ ), 0.3 ( $\blacksquare$ ), 0.4 ( $\triangle$ ), 0.5 ( $\blacktriangle$ ), 0.6 ( $\boxplus$ ), 0.7 ( $\blacktriangledown$ ), 0.8 ( $\diamond$ ), 0.9 ( $\blacklozenge$ ) and 1.0 ( $\boxtimes$ ).

### 3.5. IR and WAXS analysis

In general, in a miscible blend due to specific interaction, the mixing obstructs the crystallization process that means the decrease of  $G$  with  $\phi$ . However, the fact that the  $G$  values for N66/N48 blends were larger than that for pure N66 or N48, indicating that the crystallization process of blends was accelerated by another component. It is well known that crystallization of the polymer is basically composed of two processes, the primary nucleation of a new phase from the melt and the three-dimensional growth of lamella including lamella thickening, folding surface smoothing and reorganization into more perfect crystals. But, the crystallization behavior of crystalline/crystalline polymer blends should be quite different from that of crystalline/amorphous blends [22]. Lee et al. [22] reported that for poly(butylene succinate) (PBSU)/poly(vinylidene chloride-co-vinyl chloride) [P(VDC-VC)], crystalline/crystalline polymer blend, the spherulite growth rate of low- $T_m$  component PBSU is much faster than that of high- $T_m$  component P(VDC-VC). In this study, as seen in Fig. 1, the blend with  $\phi_{N66} = 0.5$

showed the minimum  $T_m^0$ . According to their structural formula, intermolecular hydrogen bonding between N66 and N48 forms easily, however the distances between NH and CO containing slight difference (e.g. 0.73 nm for N66 and 0.74 nm for N48) which may lead to weakening the hydrogen bonding between N66 and N48. If the blend crystal with  $\phi_{N66} = 0.5$  was considered as a low- $T_m$  component, N66 and N48 as high- $T_m$  components, the result seen in Figs. 2 and 3 might be explained as the similar effect of Lee et al. [22]. Another explanation was that the interaction between nylons became weak owing to the formation of irregular hydrogen bonding between nylons, and lead to faster  $G$  and  $N$  for the blends.

In order to confirm and understand the nature of the specific interaction between N66 and N48 that lead to thermodynamically miscible blends, spectroscopic examination was applied. In the region between 1700 and 1500  $\text{cm}^{-1}$ , amide groups of the N66 exhibit two characteristic bands. The amide I bands (carbonyl stretch) and amide II bands (NH twist + CN stretch) appear at 1634 and 1541  $\text{cm}^{-1}$ , respectively [23], which are thought to relate to the vibration of  $\text{N-H} \cdots \text{O}=\text{C}$  intermolecular hydrogen bonds. The FT-IR spectra of N66, N48 and their blends are shown in Fig. 7. The peak maximum of both bands for the blends shifted to high wavenumber side, about 3  $\text{cm}^{-1}$  for  $\phi_{N66} = 0.7$  and 0.3 and 5  $\text{cm}^{-1}$  for  $\phi_{N66} = 0.5$ . The shift of amides I and II band of N66/N48 blends to higher wavenumbers indicated the weak hydrogen bonding between nylons for blends. The formation of weak hydrogen bond suggested that N66 and N48 became the disordered state by blending. This was actually one of the reasons why  $G$  for the blends was faster than that for pure N66 and N48.

WAXS results (intensity versus  $2\theta$ ) for N66, N48 and their blends are shown in Fig. 8. All specimens were prepared after isothermal crystallization at low isothermal temperature shown in Fig. 3. Although samples were crystallized for a sufficient time, the blend samples showed the

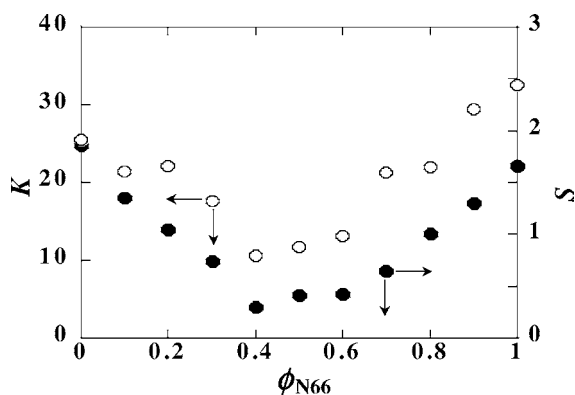


Fig. 6. Relationship between surface free energy parameters ( $K$  as open circle,  $S$  as filled circle) and  $\phi_{N66}$  for Nylon 66/Nylon 48 blend.



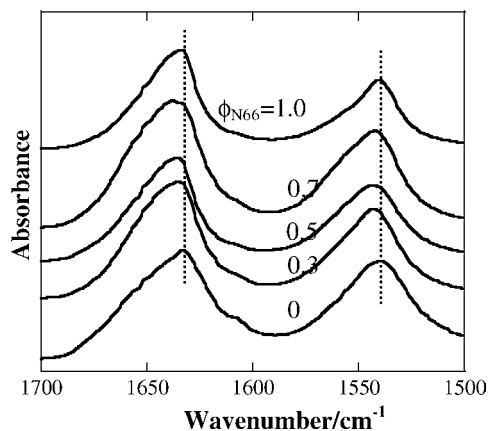


Fig. 7. Infrared spectra for Nylon 66, Nylon 48 and their blends after isothermal crystallization.

lower crystallinity. The two prominent reflections in N66 located at  $20.3$  (100 plane) and  $24.1^\circ$  (010 plane) ( $2\theta$ ) indexed based on a triclinic unit cell [20], in which, the (010) plane corresponded to the hydrogen-bonded sheets [24]. The two main spaces as a function of  $\phi_{N66}$  are quantitatively represented in Fig. 9. The  $d$ -spacing of (010) plane was obviously changed in the blends as compared to pure N66 and N48, especially the blend with  $\phi_{N66} = 0.5$  showed the largest  $d$ -spacing of (010) plane, which indicated that N48 (or N66) molecules were incorporated into the N66 (or N48) crystals and changed the unit cell. In other words, the  $d$ -spacing of (010) plane became larger with increasing  $\phi$ , which indicated to decrease the packing regularity of polymer stems in the hydrogen-bonded sheet.

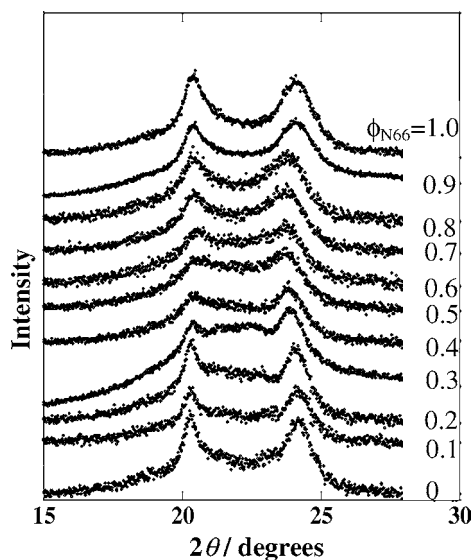


Fig. 8. X-ray diffraction for Nylon 66, Nylon 48 and their blends after isothermal crystallization.

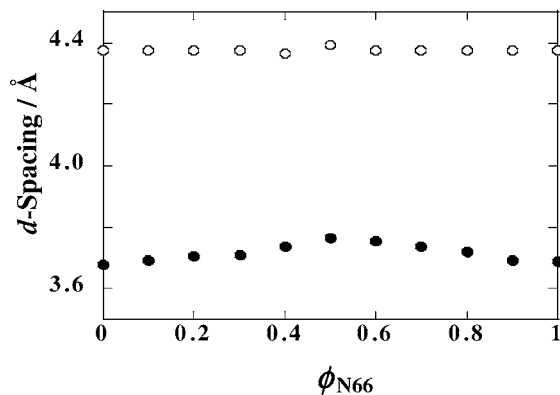


Fig. 9. Changes of  $d$ -spacing of (100) (open circle) and (010) (filled circle) plans as a function of  $\phi_{N66}$ .

#### 4. Conclusions

It is possible to estimate the mixing state of N66/N48 blends, crystalline/crystalline polymer, analyzing crystallization dynamics by DSC method. Because the interaction between nylons became weaker owing the formation of the interaction between N66 and N48,  $N$  and  $G$  for the blends were faster than that for pure N66 and N48. The  $\phi$  dependence of  $G$  showed good agreement with  $\phi$  dependence of  $\sigma$  estimated from  $G$  and  $N$ . According to the strong  $\phi$  dependences of the equilibrium melting temperature ( $T_m^0$ ), the chemical potential ( $\Delta T_{G=0.003}/T_m^0$ ) and the surface energy parameters ( $K$  and  $S$ ), the N66/N48 blend was miscible. The IR and WAXS measurements to the analyzed amides I and II bands together with the calculated  $d$ -spacing for N66, N48 and their blends indicated that the hydrogen bonding became weak and the crystal structure became disordered by blending.

#### References

- [1] T. Nishi, T.T. Wang, *Macromolecules* 8 (1975) 909.
- [2] G.C. Alfonso, T.P. Russell, *Macromolecules* 19 (1986) 1143.
- [3] P.P. Kundu, D.K. Tripathy, S. Banerjee, *Polymer* 37 (1996) 2423.
- [4] P. Xing, L. Dong, Y. An, Z. Feng, M. Avella, E. Mavtuscilli, *Macromolecules* 30 (1997) 3726.
- [5] Y.S. Chun, J. Park, J.B. Sun, W.N. Kim, *J. Polym. Sci., Part B: Polym. Phys.* 38 (2000) 2072.
- [6] A. Moluar, A. Eisenbery, *Macromolecules* 25 (1992) 5774.
- [7] X.Y. Lu, R.D. Weiss, *Macromolecules* 25 (1992) 6185.
- [8] J.K. Wei, Y.K. Dar, *Macromolecules* 26 (1993) 6583.
- [9] Q. Gao, J. Scheibeim, *Macromolecules* 33 (2000) 7564.
- [10] R. Gadekar, A. Kulikarni, *J. Appl. Polym. Sci.* 69 (1998) 161.
- [11] S.K. Yang, Y.J. Chen, X.F. Wu, *Polym. Mater. Sci. Eng.* 13 (1997) 111.
- [12] H. Burrell, *Interchem. Rev.* 14 (1955) 31.
- [13] D.J. David, T.F. Sincock, *Polymer* 33 (1992) 4505.
- [14] H. Sasaki, P.K. Bala, H. Yoshida, *Polymer* 25 (1995) 4805.
- [15] H. Yoshida, G.Z. Zhang, T. Kitamura, T. Kawai, *J. Therm. Anal. Cal.* 64 (2001) 577.
- [16] J.I. Lauritzen, J.D. Hoffman, *J. Appl. Phys.* 44 (1973) 4340.
- [17] D. Turnbull, J.C. Fisher, *J. Chem. Phys.* 17 (1949) 71.

- [18] J.D. Hoffman, J.J. Weeks, J. Res. Natl. Bur. Stand. 66 (1962) 13.
- [19] Y.T. Shien, M.S. Lee, S.A. Chen, J. Polym. Sci., Part B: Polym. Phys. 40 (2000) 638.
- [20] H.W. Starkweather, J.P. Zoller, G.A. Jones, J. Polym. Sci. Polym. Phys. Ed. 22 (1984) 1615.
- [21] N. Okui, J. Mater. Sci. 25 (1990) 1623.
- [22] J.C. Lee, H. Tazawa, T. Ikehara, T. Nishi, Polym. J. 30 (1998) 780.
- [23] G. Dana, W. Howard, J. R. Starkweather, J. Polym. Sci. Polym. Phys. Ed. 23 (1985) 537.
- [24] G.A. Jones, H.W. Starkweather, J. Macromol. Sci.: Phys. B 24 (1985) 131.