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Miscibility and crystallinity control of nylon 6 and poly(*m*-xylene adipamide) blends

Mitsuhiro Shibayama,* Kyoko Uenoyama, Jun-ichi Oura and Shunji Nomura
Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

and Takehiro Iwamoto
Packaging Products R&D Center, Idemitsu Petrochemical Industry Co., Ltd, Kou 841-3, Shirahama-cho, Himeji, 672, Japan
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A methodology to control miscibility and crystallinity of melt blend films of nylon 6 and poly(*m*-xylene adipamide) is discussed based on the results of differential scanning calorimetry. The blend film was partially miscible, i.e. miscible in the amorphous phase, as evidenced by (1) two crystallization temperatures and two melting temperatures that interacted with one other and (2) a negative Flory–Huggins interaction parameter, χ. However, the miscibility was further enhanced by ageing the blend film at 275°C, which was due to amide exchange reaction. This miscibility enhancement was studied as a function of the ageing time, τ.

(Keywords: polymer blends; miscibility; crystallinity)

INTRODUCTION

Numerous efforts have been made to improve the physical properties of the polyamides by blending them with other polymers, such as polyelfin[1–3], other kinds of polyamide[4–9], polyester[10,11] and polystyrene copolymers[12,13]. Among these, polyamide–polyamide blends are of interest not only because of the similarity of the chemical structures but also because of the possibility of amide exchange reaction. The latter is of particular significance in industry for reactive polymer processing.

The blend of nylon 6 (Ny6) with poly(*m*-xylene adipamide) (MXD) is known as one potential candidate having the merits of high gas-barrier properties as well as improved mechanical strength. Takeda and Paul studied the miscibility of Ny6 and MXD by differential thermal calorimetry (D.S.C.), dynamic mechanical measurements, and ^{1}H nuclear magnetic resonance spectroscopy[7]. They observed a miscibility enhancement of the blend via the amide exchange reaction between Ny6 and MXD. The toughness of Ny6/MXD binary blends and ternary blends with a functionalized block copolymer was also studied by dynamic mechanical analysis, where the ability of the blend to crystallize after phase homogenization, owing to the amide exchange reaction, was shown to be important[8].

In the case of polymer blends in which at least one component is a crystalline polymer, partial miscibility is expected at a temperature below their melting temperatures if the Flory–Huggins interaction parameter, χ, is negative. This is due to crystallization-induced phase separation. Here, partial miscibility means that the blend is miscible in the amorphous region. Ny6/MXD blend is a crystalline–crystalline polymer blend in which the crystallization of each component plays an important role in the phase separation behaviour of the blend. Since crystallization kinetics are themselves sophisticated, dependent on the blend composition, blending temperature, cooling rate, and so on, systematic studies by varying these variables are required so as to design desired polymer blends. Furthermore, since the components can react with each other during blending in this particular case, the resultant phase behaviour depends not only on their crystallization kinetics but also on the time and temperature of blending. It is noteworthy that crystallization and the amide exchange reaction have opposite effects on miscibility. The former leads to phase separation and the latter leads to homogenization.

Taking account of these facts, we discuss the methodology of miscibility and crystallinity control of Ny6/MXD blends by varying (1) the ageing time τ of the blend cured at a temperature above the melting temperatures of the components and (2) the blend composition.

EXPERIMENTAL

Samples

Nylon 6 (Ny6; grade no. 1023) and poly(*m*-xylene adipamide) (MXD; grade no. 6007), supplied by Ube Chemical Co. and Mitsubishi Gas Chemical Co.,

* To whom correspondence should be addressed

respectively, were used for blending. The chemical structures of Ny6 and MXD are shown in *Figure 1*. The molecular weights of Ny6 and MXD were 23 x 10^3 and 25 x 10^3, respectively, and chosen to keep the melt viscosities roughly the same at the blending temperature. These polymers were blended in a single-screw extruder for a few tens of seconds at 275°C and extruded as a film about 160 μm thick. The blend compositions, coded with x/y where x and y are percentages of Ny6 and MXD in weight, were 100/0 (pure Ny6), 90/10, 80/20, 70/30, 60/40, 40/60 and 0/100 {pure MXD).

The heat treatments were conducted with a differential scanning calorimeter (DSC3 1 00, Mac Science, Co.}. The samples were prepared by heating the blend film at the rate of 10°C min^{-1} up to 275°C, the temperature being maintained for a given ageing time τ, followed by rapid quenching to liquid nitrogen temperature. These samples were stored in a desiccator to avoid moisture adsorption until use.

Differential scanning calorimetry (D.S.C.)

D.S.C. measurements were conducted with the same calorimeter as above. The heating rate was 10°C min^{-1} and samples of about 5 mg were purged by nitrogen gas during the experiment. In the case of D.S.C. runs on cooling, the cooling rate was roughly controlled to be 10°C min^{-1}.

RESULTS AND DISCUSSION

Cold crystallization and melting behaviour

Figure 2 shows the D.S.C. thermograph of the 60/40 blend quenched to liquid nitrogen temperature from 275°C without ageing ($\tau = 0$ min). The thermogram has two exothermic peaks at $T_{c,Ny6}$ and $T_{c,MXD}$, indicating cold crystallization of Ny6 and MXD, respectively. These peaks are followed by two melting endotherms at $T_{m,Ny6}$ and $T_{m,MXD}$. The small endothermic peak which appeared at 55°C is due to enthalpy relaxation of Ny6.[9] The presence of two cold crystallization peaks indicates that the quenching rate was too fast for the components to complete crystallization during the cooling process and amide exchange reaction did not occur at this stage. Thus crystallization-induced phase separation occurs during the D.S.C. run. These crystals then melt at different temperatures, $T_{m,Ny6}$ and $T_{m,MXD}$.

Figure 3 shows the composition dependence of the cold crystallization. The ageing time τ was Omin for all the samples. This figure clearly indicates that $T_{c,Ny6}$ and $T_{c,MXD}$ are highly dependent on the composition. The composition dependence of $T_{c,Ny6}$ and $T_{c,MXD}$ is shown in *Figure* 4. It is noteworthy that $T_{c,MXD}$ decreases with increasing Ny6 content, whereas $T_{c,Ny6}$ increases with increasing MXD content. The presence of a cold crystallization peak indicates the presence of a crystallizable region which remained amorphous in a sample preparation, probably due to rapid quenching. A cold crystallization takes place when the temperature is raised above the glass transition temperature of the matrix. Since the endothermic peak due to the enthalpy relaxation in *Figure* 3, corresponding to the glass transition temperature, increases gradually with increasing MXD content, the peak shifts of the cold crystallization temperature to the inward direction are quite reasonable.

The time course of the amide exchange reaction can be traced by taking a series of D.S.C. thermograms for samples quenched after different ageing times τ, as

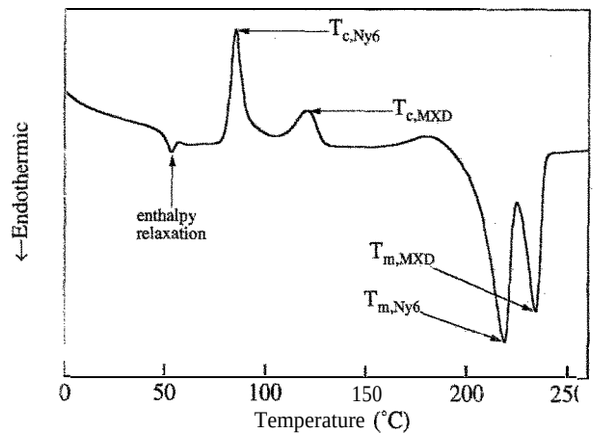

Figure 1 Chemical structures of Ny6 and MXD

Figure 2 D.S.C. thermogram of the 60/40 blend quenched in liquid nitrogen

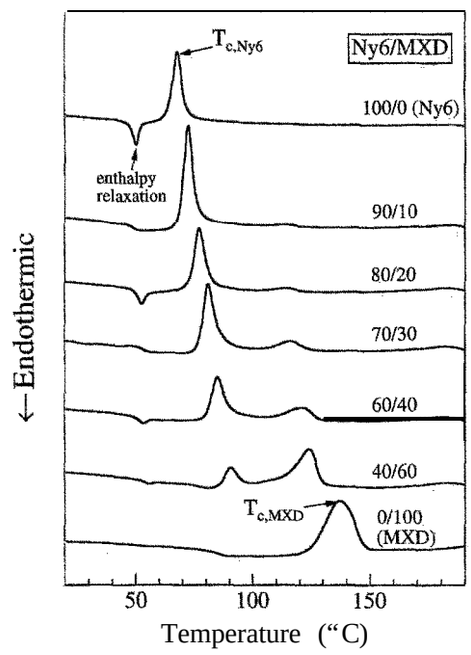

Figure 3 D.S.C. thermograms showing composition dependence of cold crystallization. Ageing time τ was Omin for all the samples

shown in *Figures 5a* and *b*. Knowing that the melting temperatures of Ny6 and MXD, are about 220°C and 235°C respectively, the lower endotherm corresponds to $T_{m,Ny6}$ and the higher to $T_{m,MXD}$. In *Figure 5a*, two endothermic peaks, indicating $T_{m,Ny6}$ and $T_{m,MXD}$, are clearly resolved for $\tau \leq 20$ min. However, for a larger τ ($\tau \geq 60$ min), $T_{m,MXD}$ is merged to $T_{m,Ny6}$. A similar phenomenon is seen in the case of 40/60 blend, where $T_{m,Ny6}$ is merged to $T_{m,MXD}$ as shown in *Figure 5b*. This observation suggests that the crystallinity of Ny6 and MXD can be controlled by annealing time, which leads to miscibility enhancement of the blend due to a lowering of the degree of crystallinity. This phenomenon is accounted for by an amide exchange reaction between Ny6 and MXD, as discussed by Takeda and Paul[7]. It is expected that degradation of both Ny6 and MXD proceeds via two types of hydrolysis, namely acidolysis and aminolysis[7]. Although this may also lead to a significant change in the thermal properties of the blend, these chemical reactions were not discriminated in this study.

Figure 6 shows the τ dependence of the melting temperature, T_m. The dependences of T_m on τ for pure Ny6 and MXD are given by thick lines and are almost independent of τ. However, T_m values for all the blends studied here are decreasing functions with τ, particularly for $T_{m,Ny6}$ of the 40/60 blend and for $T_{m,MXD}$.

The variation of the enthalpy of fusion with τ is shown in *Figure 7*, in which progressive miscibility enhancement in blends is again clearly seen as a decrease in ΔH, particularly in 40/60 and 60/40 blends. Although the monomer molecular weights of Ny6 and MXD are 113.2 and 246.3, respectively, the stoichiometric amide group ratio of the blend is roughly given by Ny6/MXD = 49/51 by taking account of the numbers of amide groups per monomeric unit. Since both 40/60 and 60/40 blends are close to stoichiometric blend, the efficiency of the amide exchange reaction is higher in these than in the other blends. This again indicates that the miscibility of the Ny6/MXD blends is increased by annealing at 275°C and the miscibility enhancement is most effective for the stoichiometric blend. The fact that the decrease in ΔH for the 40/60 blend is larger than that for the 60/40 blend may be explained as follows: the effect of blending on

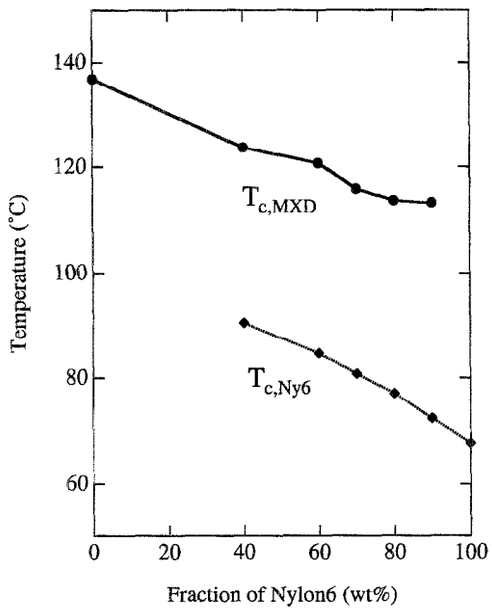

Figure 4 Composition dependence of the cold crystalization temperatures, $T_{c,Ny6}$ and $T_{c,MXD}$

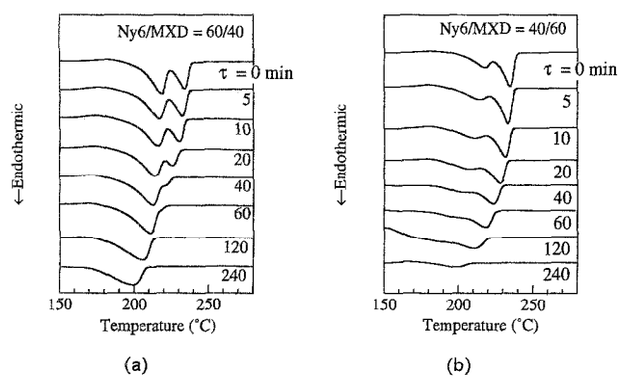

Figure 5 D.S.C. thermograms showing time course of the amide exchange reaction

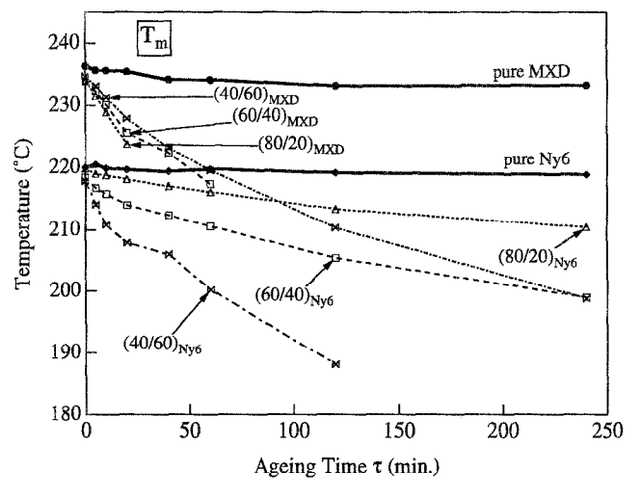

Figure 6 Dependence of melting temperature T_m on ageing time τ. Thick lines show the τ dependence of T_m for pure Ny6 and MXD. The melting temperature of component i for blends are denoted by $(x/y)i$, where x/y are the blend compositions

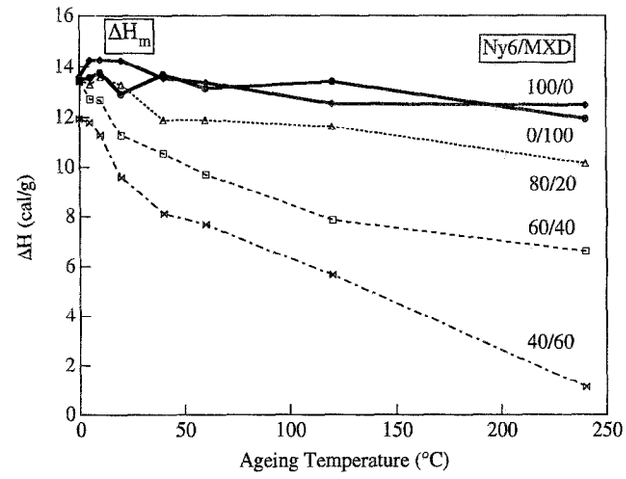

Figure 7 Variation of the enthalpy of fusion with τ

crystallinity is larger in MXD than in Ny6, since the crystallinity of MXD is inherently lower than of Ny6.

Crystallization on cooling

Figure 8 shows single heat treatment cycles traced by D.S.C. for $\tau = 0$ min for as-received Ny6, MXD and Ny6/MXD 60/40 blend (*a*, *b*, and *c*, respectively). The term of 'as-received' means that heat treatment by quenching from 275°C was not conducted for these samples. In *Figure 8*, $T_{m,x}$ and $T^c_{c,x}$ denote the melting temperature and crystallization temperature of x (= Ny6, MXD, and Ny6/MXD), respectively. Several interesting features are disclosed in this figure. (1) The crystalline exotherm of Ny6, $T^c_{c,Ny6}$, is sharper than melting endotherm, $T_{m,Ny6}$, in *Figure 8a* but (2) an opposite trend is seen for MXD in *Figure 8b*. (3) In the case of the 60/40 blend, only one crystallization exotherm is seen, while two endotherms of of Ny6 and MXD are clearly resolved as shown in *Figure 8c*. The result in *Figure 8c* is very different from the heating process of the same sample shown in *Figure 2*. In the case of *Figure 2*, the sample was prepared by quenching and cold crystallization was observed on heating both for Ny6 and MXD. However, the cold crystallization peak located around 70°C is remarkably depressed in *Figure 8*, where the cooling rate (10°C min^{-1}) was slow enough for crystallization of Ny6. Thus a sharp crystallization exotherm of Ny6 was observed. In the case of MXD, on the other hand, the crystallization exotherm is broader than the melting endotherm. When blended, crystal nuclei seem to be absorbed by Ny6. These facts may indicate that the crystallization of MXD is much slower than that of Ny6 and/or MXD needs a larger supercooling for crystallization. This may be the reason why only a single exotherm appeared, located at almost the crystallization temperature of Ny6.

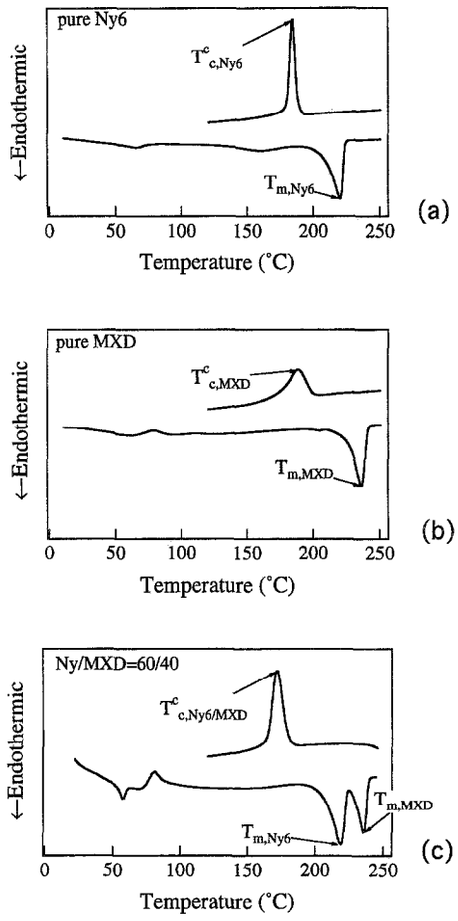

Figure 8 D.S.C. thermograms of single heat treatment cycles for (a) Ny6, (b) MXD and (c) Ny6/MXD 60/40 blends. Ageing time τ was 0 min for all the samples

Figure 9 shows the ageing time τ dependence of the crystallization temperature on cooling, T^c_c. In the case of homopolymers, no noticeable depression of T^c_c is observed. However, a significant depression of T^c_c is observed for the blends, particularly the 60/40 and 40/60 blends. *Figure 10* shows the enthalpy of crystallization exotherm, ΔH^c_c. For Hy6 homopolymer, ΔH^c_c does not show any dependence on, τ whereas ΔH^c_c of the MXD homopolymer has a strange τ dependence, the reason for which is not clear at this stage. Apart from this, significant depression of crystallinity is observed for blend samples after ageing.

The reason why melting point depression and decrease in ΔH due to amide exchange reaction is observed exclusively in blends, while each component of the blends also has amide groups, is an interesting problem. This question can be answered by remembering the fact that amide exchange reaction in either Ny6 or MXD homopolymer simply leads to a formation of the same (Ny6) or a similar homopolymer (MXD). Thus it can be considered that amide exchange reaction does occur in homopolymers as well, but the reaction cannot be detected by thermal analysis. Although this is an interesting and important question, it should be studied from the viewpoint of chemical reaction of polymers and is beyond of the context of this study.

Melting point depression

Miscibility enhancement of Ny6/MXD blends with τ can be evaluated by using the data of melting point depression. Although the melting point depression of MXD should be evaluated because of $T_{m,MXD} > T_{m,Ny6}$, samples having small fractions of MXD were not available due to the difficulty of sample preparation. Thus, an evaluation of the melting point depression of Ny6 is conducted. The melting point depression from T°_m

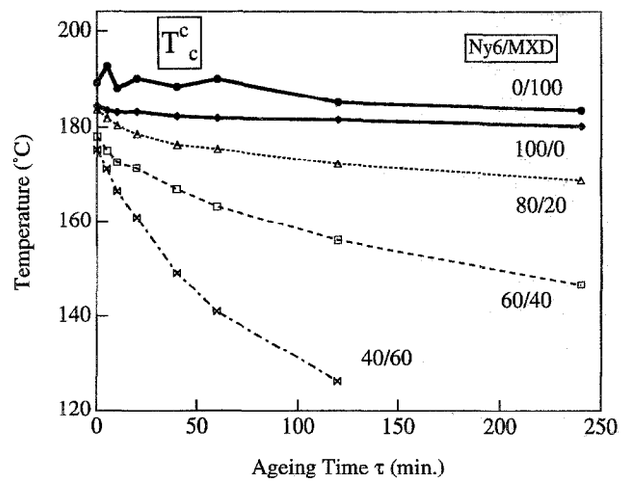

Figure 9 Dependence of the crystallization temperature on cooling T^c_c on ageing time τ

to T_m is related to the interaction parameter B of the blend as follows[15]

$$\left(\frac{1}{T_{m,Ny6}}-\frac{1}{T^{\circ}_{m,Ny6}}\right)\frac{1}{\phi_{MXD}}=-\frac{BV_{Ny6}}{\Delta H_{Ny6}}\frac{\phi_{MXD}}{T_{m,Ny6}} \quad (1)$$

where $T^{\circ}_{m,Ny6}$ is the melting temperature of Ny6 homopolymer, and ϕ_x, V_x and ΔH_x are the volume fraction, the molar volume and the enthalpy of fusion, respectively, of component x. The interaction parameter B is related to the so-called Flory–Huggins interaction parameter, χ, by the following equation:

$$\chi=\frac{BV_{MXD}}{RT} \quad (2)$$

where R and T are the gas constant and absolute temperature, respectively. The volume fraction ϕ was estimated by using the average densities d_x of Ny6 and MXD ($d_{Ny6}=1.14\,g\,cm^{-3}$ and $d_{MXD}=1.21\,g\,cm^{-3}$). *Figure 11* shows the plot based on equation (1) for blend samples of $\tau=60$ min. By substituting $V_{Ny6}=99.12\,cm^3mol^{-1}$ and $V_{MXD}=208.26\,cm^3mol^{-1}$ we get $\chi=-0.185$ ($T=275$°C). This value seems to be significantly larger than the value ($|\chi|<1$) for amide–amide blends[9]. This may be due to an overestimation of the slope since the linearity of the plot is rather poor. The observed value of χ is comparable with that for a crystalline–amorphous blend reported by Nishi and Wang[16], who obtained $\chi=-0.295$ ($T=160$°C) for a poly(vinylidene fluoride)/poly(methyl methacrylate) blend.

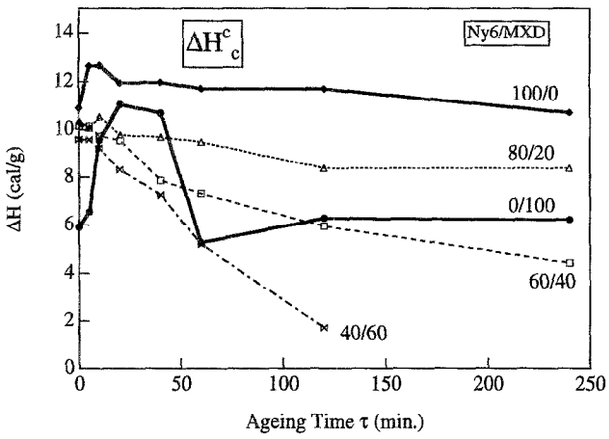

Figure 10 Dependence of enthalpy of crystallization exothem ΔH_c^c on ageing time τ

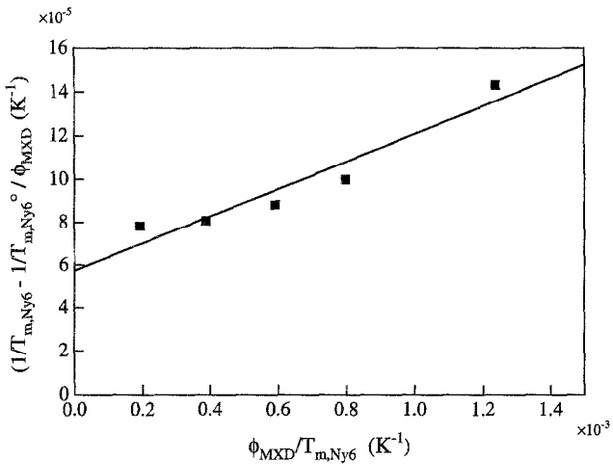

Figure 11 Melting point depression plots for Ny6/MXD blends. T°_m is the melting temperature for Ny6 homopolymer, ϕ_{MXD} is the volume fraction of MXD

Equation (1) was derived for crystalline–amorphous blends. The blend studied in this work, however, is a crystalline–crystalline blend. When we discuss the melting point depression of Ny6, we can treat the MXD crystalline phase as a non-interaction filler because of $T_{m,MXD} > T_{m,Ny6}$: Thus the following correction can be made

$$\left(\frac{1}{T_{m,Ny6}}-\frac{1}{T^{\circ}_{m,Ny6}}\right)\frac{1}{\phi'_{MXD}}=-\frac{BV_{Ny6}}{\Delta H_{Ny6}}\frac{\phi'_{MXD}}{T_{m,Ny6}} \quad (3)$$

where

$$\phi'_{MXD}=\frac{(1-\phi^{\circ}_{MXD,C})\phi_{MXD}}{(1-\phi^{\circ}_{MXD,C})\phi_{MXD}+\phi_{Ny6}} \quad (4)$$

In this case, we obtained $\chi=-0.194$ ($T=275$°C) upon taking the value $\phi^{\circ}_{MXD,C}=0.23$ for the degree of crystallization of pure MXD. In both cases, χ is negative, indicating that the Ny6/MXD blends are miscible.

The same analysis was conducted for the same blend at $\tau=0$ min and χ was estimated to be -0.111 (uncorrected, $T=275$°C, $\tau=0$ min) and -0.154 (corrected, $T=275$°C, $\tau=0$ min). Thus the following relationship was obtained

$$\chi(\tau=60\,\text{min})<\chi(\tau=0\,\text{min})<0 \quad (5)$$

Although the absolute value of χ may be uncertain, the tendency of χ change with τ clearly indicates progressive miscibility.

It should be pointed out here that the blends at $\tau=0$ min may not be fully homogenized despite $\chi<0$. This is ascribed to an insufficient blending time in the preparation process. In this case, the amide exchange reaction starts from the surface of the domain of the minor component and propagates into the inner part, which requires a more sophisticated analysis. On the other hand, the blending time cannot be extended so as to keep the Ny6 and MXD crystalline phases separate. As studied here, the amide exchange reaction significantly reduces the ability to crystallize. Therefore, a precise control of ageing time and temperature is required to obtain a blend with suitable mechanical and gas-barrier properties. Morphological studies are now in progress and will be reported in a forthcoming paper[17].

CONCLUSIONS

Evidence of miscibility enhancement in Ny6/MXD blends was studied as a function of blend composition. The blend samples were cured for different ageing times, τ at 275°C. Parameters obtained by D.S.C., such as the melting temperature $T_{m,x}$, the enthalpy of fusion $\Delta H_{m,x}$, the crystallization temperature T_c^c and the enthalpy of crystallization ΔH_c^c were strongly dependent on τ, where x denotes either Ny6 or MXD. These indicate that

progressive miscibility enhancement takes place during ageing at elevated temperature due to the amide exchange reaction. Comparison of the interaction parameters estimated from the melting point depression for samples before and after ageing clearly shows a progressive enhancement of the blend miscibility, i.e. $\chi(\tau = 60\,\text{min}) < \chi(\tau = 0\,\text{min}) < 0$. This effect was highest for the blend with composition closest to the stoichiometric ratio.

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