Thermodynamic properties affect the molecular motion of novolac type phenolic resin blended with polyamide

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Abstract

The effect of association reaction length on the substantial increase of molecular motion as well as entropy $(-T\Delta S_m)$ of phenolic–polyamide blends is investigated with the ^{13}C solid-state NMR and DSC. The H-bonding strength by forming the phenolic–polyamide interaction is great enough to overcome the breaking off the self-association of phenolic. With respect to decreasing the association reaction, the polyamide resonance intensity of ^{13}C solid-state NMR spectra is weakened due to the reduction of the cross-polarization efficiency at a high mobile sample. The glass transition temperature of phenolic–polyamide blend as well as $T_{1\rho}^{H}$ value from NMR experiments is also decreased. The decreasing strength of H-bonding resulting from blending causes higher entropy $(-T\Delta S_m)$ and higher molecular mobility of the phenolic–polyamide blends. Accordingly, the polyamide-66 possesses higher H-bonding force and exhibits more mobile role in this phenolic/polyamide blends family. It can be concluded that the molecular segmental motion and entropy are progressively decreased while increasing the *inter*-association force of the polyamide within the miscible window.
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1. Introduction

The strength of H-bonding between particular functional groups has recently been reported as a mean to express the miscibility of polymer blend [1,2,6,9,12]. The theory of miscibility of polymer blends has been well identified and established in previous study [1]. It is well known that the miscibility of a polymer blend decreases while increasing the repeated unit length of the guest backbone. When the guest polymer is added, the competition between *intra*- and *inter*-association will in-

fluence the inherent H-bonding strength and the thermodynamic properties of the blend [2–5]. It is anticipated that the molecular mobility of a blend should depend on the strength of H-bonding. Because of the stronger inter-molecular interaction [2], the shorter repeated unit with the higher density H-bonded functional group should display a better miscibility than the longer one. This effect therefore should bring about entropy loss and result in less mobility of the blend. It gives rise to a question whether molecular motion of a polymer is able to prompt the entropy change through blending a suitable guest polymer.

The modification of phenolic properties is expected because contained C=O (carbonyl group) of the polyamide in the backbone is able to interact with the OH (hydroxyl group) of the phenolic resin and form

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the inter-molecular H-bonding [6]. The H-bonding strength of the blend is determined by the competition of the inter-molecular H-bonding strength and the intra-molecular H-bonding of the original polymers [7]. For example, when the increase of the inter-molecular H-bonding is sufficient to compensate the loss of self-association of the original polymers, the overall averaged H-bonding strength within the polymer blend is increased.

The repeated unit length of the polyamide is related to the molecular mobility and entropy change of the phenolic/polyamide blends within the miscible window [9]. The T_g behavior of the polymer blend that reveals the information regarding the entropy change on blending and the solid-state NMR methodologies (such as the chemical shift, line shape and relaxation behavior, $T_{1\rho}^H$) were employed to investigate the molecular mobility of the phenolic/polyamide blends. In the meantime, understanding the relationship between the repeated unit length of polyamide and entropy change as well as molecular mobility of phenolic/polyamide blends were also inspected.
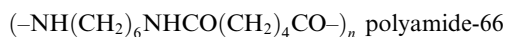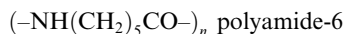
2. Experimental section

2.1. Sample preparation

The characters of the novolac type phenolic resin (phenolic) and the polyamide have been described previously [6,8,9]. Structures of the phenolic and the polyamide family are exhibited as followed:

Novolac type phenolic resin

$(-NH(CH_2)_5CO-)_n$ polyamide-6

$(-NH(CH_2)_6NHCO(CH_2)_4CO-)_n$ polyamide-66
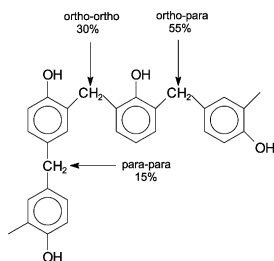
The phenolic and the polyamide were mixed in phenol (1% (w/v)) at room temperature according to the designed compositions at 100 °C. The mixed solution was stirred for 6–8 h, and then allowed to evaporate slowly at 100 °C for 24 h. The blended films were then dried at 120 °C for two days and annealed at 140 °C for 2 h under a vacuum.

2.2. Glass transition temperatures and melt enthalpies of blends

The glass transition temperatures (T_g) of the polymer blends were measured by a differential scanning calorimeter (Du-Pont, DSC Model 2900). The heating rate was 20 °C/min within a range of 20–280 °C. The measurements were conducted with 3–4 mg samples on a DSC sample pan. After the specimens were quickly cooled to room temperature, the first scan would follow. This procedure was employed in order to ensure the entire mixing of the polymer blends and to remove the residual solvent and water in the specimen. T_g values were determined at the midpoint of the transition point of the heat capacity (C_p) changed, and the reproducibility of T_g values was estimated to be within ± 2 °C.

2.3. NMR experiments

High-resolution solid-state NMR experiments were applied by a Bruker DSX-300 spectrometer operating at resonance frequencies of 300.13 and 75.475 MHz for ^{1}H and ^{13}C, respectively. All NMR spectra were achieved at a temperature of 300 K with broadband decoupling, normal cross-polarization (CP) pulse sequence and the magic angle spinning (MAS) of 5.4 kHz. The ^{13}C CP/MAS spectra were measured with a pulse angle 90°; pulse width, 3.9 μs; pulse delay time, 3 s; acquisition time, 30 ms; spectral width, 200 ppm; number of data points per spectrum, 4k, and number of scans, 2k. Proton spin–lattice relaxation time, $T_{1\rho}^H$, in the rotating frame is measured via carbon signal intensities using a 90°-τ-spin lock pulse sequence prior to CP. Data acquisition is performed via ^{1}H decoupling with delay time (τ) in a range of 0.1–16 ms.

3. Results and discussion

3.1. Glass transition temperatures of the phenolic/polyamide blends family

Conventionally, the differential scanning calorimeter can be employed to differentiate the miscibility and entropy change of a polymer blend. The theoretical treatments of glass transition temperature have stimulated several important findings with respect to the thermodynamic property. Fig. 1 shows the DSC traces of various phenolic/polyamide-6 blends compositions. In regard to the pure polyamide, the T_g values that present an increasing order of polyamide-66 and polyamide-6 are 47 ± 2 and 43 ± 2 °C [6,8], respectively. The T_g value of the pure phenolic is 70 ± 2 °C [6,8], which is substantially higher than other polymers under analogous molecular weights due to its high intra-molecular
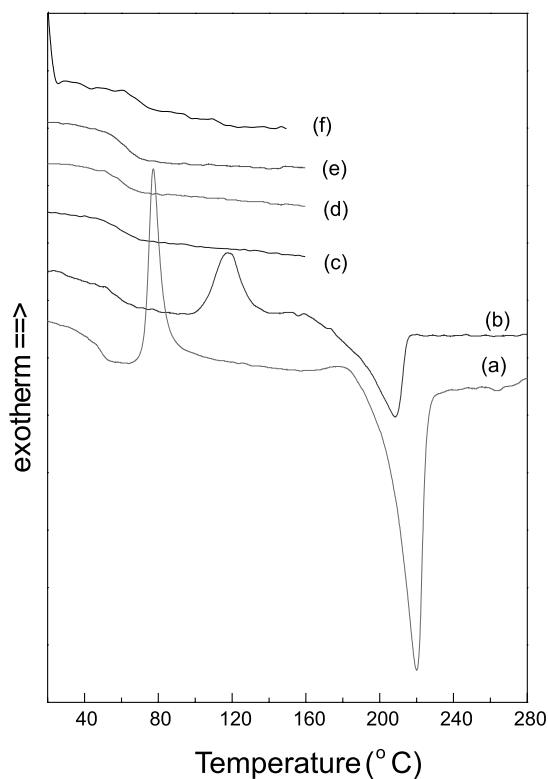
Fig. 1. The DSC traces of various phenolic/polyamide-6 blends (wt.%): (a) 10/90, (b) 30/70, (c) 60/40, (d) 80/20, (e) 90/10, (f) 100/0 phenolic/polyamide-6 blends.

H-bonding density. Both blends are miscible because only a single T_g point is observed throughout the whole range of blend compositions. It appears that the polyamide is able to penetrate into the phenolic matrix. An obvious melting peak is observed when the polyamide content is greater than 50% by weight. Furthermore, the melting temperature is gradually shifted to a higher temperature with the simultaneous increase of the polyamide-6 content, which is shown in Fig. 1.

The T_g value of a miscible blend unusually follows the weight sum average value. The deviation is defined as

$$\Delta T_g = T_g - (\omega_a T_{ga}^o + \omega_b T_{gb}^o), \qquad (1)$$

where ω_i is the weight fraction of component i, and T_{gi}^o is the glass transition temperature of the pure component, i. The T_g deviation (ΔT_g) as well as the raw T_g temperatures of the various phenolic/polyamide-6 and phenolic/polyamide-66 blends in phenolic rich region are summarized in Fig. 2. Essentially, all the T_g deviation curves are negative, and its deviation increasing order is shown to be polyamide-66 followed by polyamide-6. This order coincides with the order of H-bonding in the backbone of the polyamide family. The T_g deviation is a result of entropy change corresponding to the change in
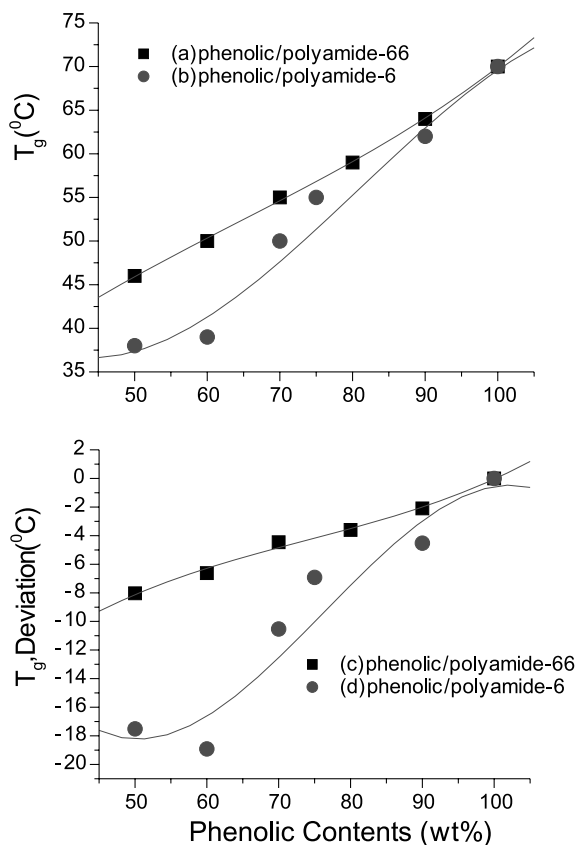

Fig. 2. The composition dependence of the glass transition temperature (T_g) of (a) phenolic/polyamide-66, (b) phenolic/polyamide-6 blends, and the T_g deviation of (c) phenolic/polyamide-66, (d) phenolic/polyamide-6 blends.

the number of H-bonding interactions [10]. The strength of H-bonding of phenolic/polyamide-66 is higher than that of phenolic/polyamide-6. As a result, the T_g reduction of the phenolic/polyamide-66 blends is not as substantial as that of the phenolic/polyamide-6 blends. It is shown in Fig. 2. The strength of the H-bonding interaction (summarizing both the inter- and intra-molecular H-bonding) in the phenolic/polyamide-6 blends is weaker than that in the phenolic/polyamide-66 blends.

This obvious evidence provides the relationship between the molecular structure and mobility that was demonstrated by solid-state NMR from the parameters of ^{13}C chemical shifts, CP dynamics and $T_{1\rho}^H$ relaxation time.

3.2. ^{13}C CP/MAS NMR spectra

Fig. 3 shows the ^{13}C solid-state NMR spectra of phenolic, polyamide-6 and their blends with standard ^{13}C CP/MAS pulse sequence. In Fig. 4, the ^{13}C solid-state NMR spectra of phenolic, polyamide-66 and their

(a) Pure Polyamide 6
(b) Phenolic/Polyamide 6=60/40
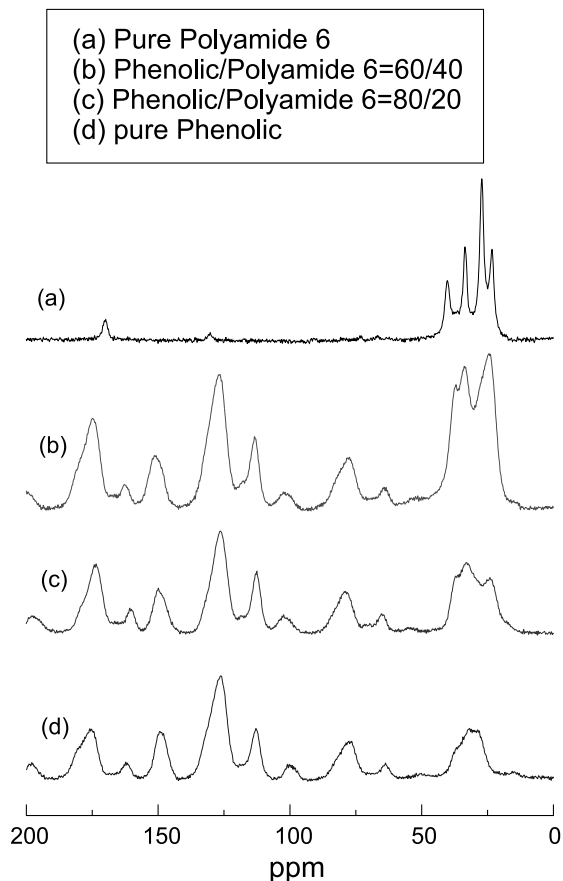(c) Phenolic/Polyamide 6=80/20
(d) pure Phenolic

Fig. 3. Solid-state ^{13}C NMR CP/MAS spectra polyamide-6/ phenolic resin blends with various compositions (wt.%): (a) 100/0, (b) 40/60, (c) 20/80, (d) 0/100.

(a) pure Polyamide 66
(b) Phenolic/Polyamide 66=60/40
(c) Phenolic/Polyamide 66=80/20
(d) pure Phenolic

Fig. 4. Solid-state ^{13}C NMR CP/MAS spectra polyamide-66/ phenolic resin blends with various compositions (wt.%): (a) 100/0, (b) 40/60, (c) 20/80, (d) 0/100.

blends with standard ^{13}C CP/MAS pulse sequence are presented. The chemical shifts of major peaks of the phenolic and the polyamide are summarized in Table 1. The chemical shifts of the OH–carbon in the phenol ring (phenolic, 150 ppm) and C=O group (polyamide, 170 ppm) for various phenolic/polyamide blends compositions are indicated in Figs. 3 and 4. The relaxation time of various phenolic/polyamide blends compositions (i.e. 100/0, 80/20 and 60/40) and pure polyamide was measured at 128 ppm and 170 ppm, respectively. Due to the fact that pure polyamide is a crystalline polymer, two different $T_{1\rho}^{H}$ values are obtained from the crystalline and amorphous regions [15]. Apparently, owing to the fact that the interaction of H-bonding would carry out small perturbation to the magnetic shielding on the nucleus, it resulted in the chemical shift being switched downfield. As compared to the one without H-bonding, which had no such shift [11]. The degree of downfield shift reflects the strength of the H-bonding [12]. As shown in Figs. 3 and 4, the chemical shift of OH–carbon in the phenol ring is shifted downfield with the increase
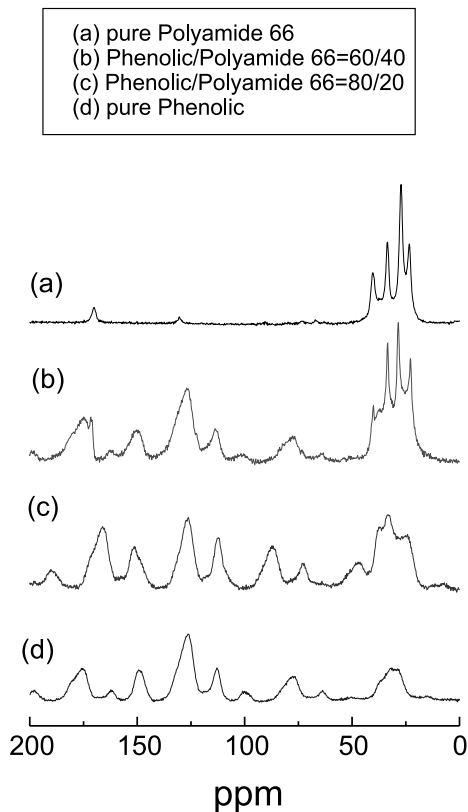
Table 1
The major chemical shifts of the phenolic/polyamide blends family in the ^{13}C-NMR spectrum with peak symbols in this text

Material	Chemical shift	Description
Phenolic	32 ppm	Methylene
Phenolic	114 ppm	Ortho-substituted in phenol ring
Phenolic	151 ppm	OH–carbon in phenol ring
Phenolic	128 ppm	Other carbon in phenol ring
Polyamide	25–35 ppm	Methylene of poly(adipic ester) backbone
Polyamide	170 ppm	C=O group

of the polyamide content. Both results suggest that the variation of local electronic density provides the direct evidence of the formation of H-bonding interaction between OH and C=O in the blend. The downfield shift of OH–carbon of phenolic is due to the decrease of shielding. It indicates that the strength of the H-bonding, which increased gradually, resulted from blending with a variety of polyamide contents. Furthermore, the increase of inter-molecular H-bonding is sufficient to

compensate the loss of intra-molecular H-bonding of phenolic.

The individual ^{13}C NMR resonance also reveals that the change of molecular mobility as blending is employed. As seen in Figs. 3 and 4, the variation of peak intensity definitely associated with the individual blend shows non-monotone changes with blend composition. The peak intensity is modulated by both the efficiency of the CP and molecular mobility that are related to the rate near the ^{1}H decoupling field [13–15]. It is difficult to deduce unambiguously the information of the molecular mobility without knowing the detailed CP dynamics. However, it is enough to judge that the molecular mobility of polyamide is increased significantly due to the resonance of polyamide being weakened as the content of polyamide is reduced.

As shown in Fig. 5, while comparing the ^{13}C NMR spectra of both phenolic/polyamide-6 and phenolic/polyamide-66 blends with a ratio of 60/40 in the range between 100 and 200 ppm are measured by the normal CP/MAS method with a contact time of 1 ms. The phenolic peak intensity (128–150 ppm) in the phenolic/polyamide-66 blend is the one with greater suppression which can be attributed to the low efficiency of CP. It

appears that the phenolic/polyamide-66 blend in phenolic/polyamide blends (i.e. phenolic/polyamide-6 and phenolic/polyamide-66) with this composition has greater molecular mobility. The different repeated unit of polyamide predominantly reduces the possibility of the intra-molecular H-bonding of phenolic and results in higher entropy as well as higher molecular mobility simultaneously. This is consistent with the observed T_g deviation tendency in the phenolic/polyamide blends family.

The line width of NMR spectra provides information on morphological heterogeneity at the molecular level. In Fig. 5, a new splitting peak at 171 ppm, was formed blends with a ratio of 60/40 (60% phenolic), as the polyamide content is reduced. The line width of this peak as mentioned above continues broadening while the content of polyamide is further reduced. It exhibits the formation of inter-molecular H-bonding and would produce a rather heterogeneous environment and some changes in the molecular mobility with the rate near the ^{1}H decoupling field for the phenolic rich region.

With respect to the relationship of molecular mobility to repeated unit length, they are presented in the following $T_{1\rho}^H$ relaxation study.

3.3. Relaxation times of $T_{1\rho}^H$ of the phenolic/polyamide blends family

Proton $T_{1\rho}$ via resolved carbon resonance has been demonstrated to be a convincing method to analyze the molecular motion and domain heterogeneity in polymer blends. In a homogeneous system, the carbon signal decays in a manner following a simple exponential equation [16].

$$M(\tau) = M_0 e^{-\tau/T_{1\rho}}, \qquad (2)$$

where τ and $T_{1\rho}$ are delay time and spin–lattice relaxation time in the rotating frame, respectively. Molecular motion in different environments should exhibit a different relaxation behavior. When the coupling effect or the spin-diffusion effect is totally neglected, a pluralism relaxation can be utilized to model the heterogeneity of the system. In general, in the hard collision limit, the more mobile environments should display a relative lower value of $T_{1\rho}^H$, while the rigid domains give a relative higher value of $T_{1\rho}^H$. Fig. 6 shows the magnetization plots of logarithmic ^{13}C intensity (related to the benzene ring) versus the spin-lock time with 1 ms contact time for various phenolic/polyamide blends with the ratio of 80/20. Table 2 summarizes the $T_{1\rho}^H$ values of the phenolic/polyamide blends family in the phenolic rich region. The NMR specimen was annealed at 140 °C for 1 h and cooled rapidly to room temperature. Due to pure polyamide being a crystalline polymer, two different $T_{1\rho}^H$ values (0.6 and 9.9 ms) resulted from the amorphous and
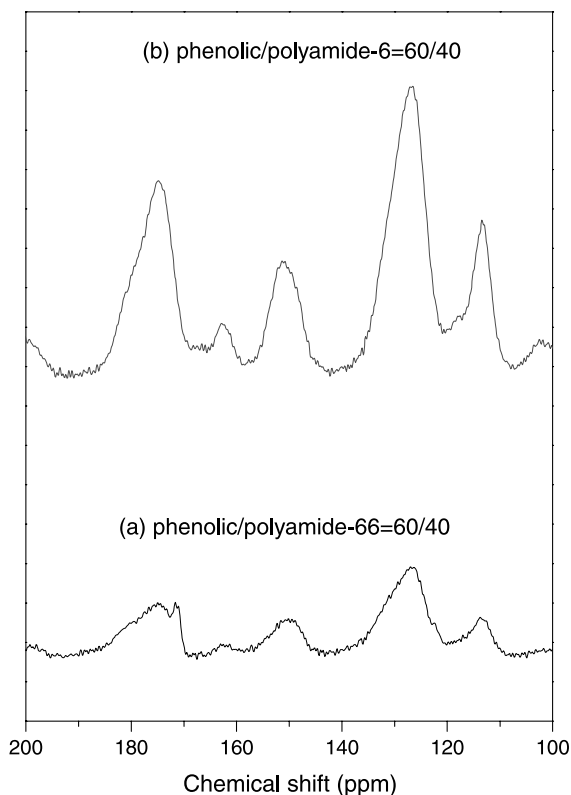

Fig. 5. The ^{13}C CP/MAS NMR spectra of (a) phenolic/polyamide-66 = 60/40, and (b) phenolic/polyamide-6 = 60/40 blends measured by the normal CP/MAS method.
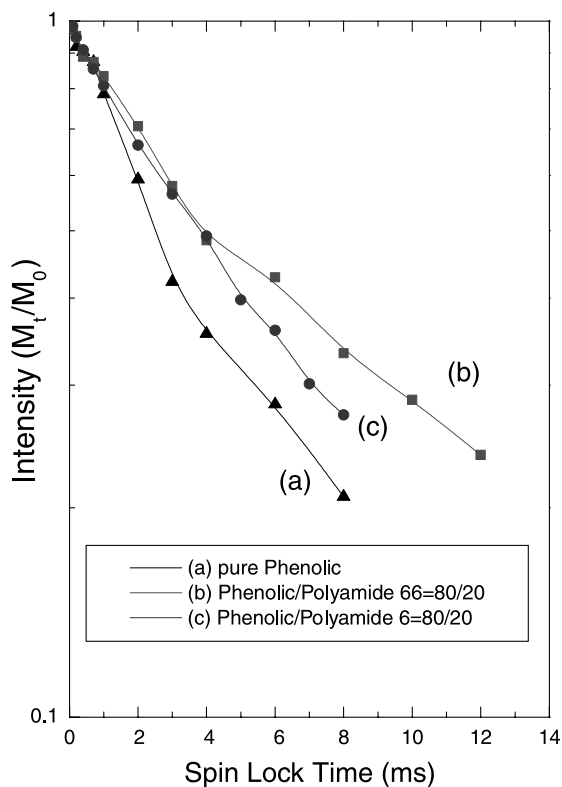
Fig. 6. The logarithmic plots of the magnetization intensities (related to the benzene ring) versus the spin-lock time with 1 ms contact time for uncured (a) pure phenolic; (b) phenolic/polyamide-66 = 80/20; and (c) phenolic/polyamide-6 = 80/20 blends.

Table 2
$T_{1\rho}^{H}$ relaxation time of various phenolic/polyamide blends compositions at 300 K

Phenolic resin/ polyamide blend (w/w)	Phenolic resin/ polyamide-6 (ms)	Phenolic resin/ polyamide-66 (ms)
100/0	4.5 (128 ppm)	4.5 (128 ppm)
80/20	–	4.12 (128 ppm)
60/40	3.03 (128 ppm)	0.52 (128 ppm)
0/100	1.0, 18 (170 ppm)	0.6, 9.9 (170 ppm)

Based on the benzene ring (128 ppm) and carbonyl group (170 ppm).

crystalline regions, respectively. Nevertheless, both blends indicate single component $T_{1\rho}^{H}$ relaxation behavior, which implies that these materials are classified under the homogeneous phase. The declined $T_{1\rho}^{H}$ value is related to the addition of the polyamide as concluded from Fig. 6 and Table 2. Obviously, the mobility of the blend is improved upon blending the phenolic with the polyamide and such improvement refers to the increase of the polyamide content. The hindering effect of the

intra-association in the phenolic is increased with addition of the polyamide. Meanwhile, the entropy of the polymer blend is increased as confirmed by DSC data.

The reduced association of the phenolic blend is caused by the hindrance of the intra-association in greater molecular segment mobility of the phenolic as indicated by the solid-state NMR spectra and relaxation behavior. The polyamide-66 should be a better prompt mobility of phenolic before the phase separation occurs.

3.4. Thermodynamic behavior of the phenolic/polyamide blends family

The Miscibility Guide & Phase Calculator software was employed to calculate the thermodynamic properties of a polymer blend [1,9]. The entropy reduction is due to the formation of the phenolic–polyamide interaction. Such effect is great enough to overcome the increasing entropy that is created from the breaking-off of the self-association of phenolic. As a result of lower overall H-bonding density, the framework of these blends becomes looser and the observed negative T_g deviation is therefore concluded firmly in these phenolic/polyamide blends. Moreover, the polyamide-66 increases the H-bonding density and enlarges the entropy on blending more sub-
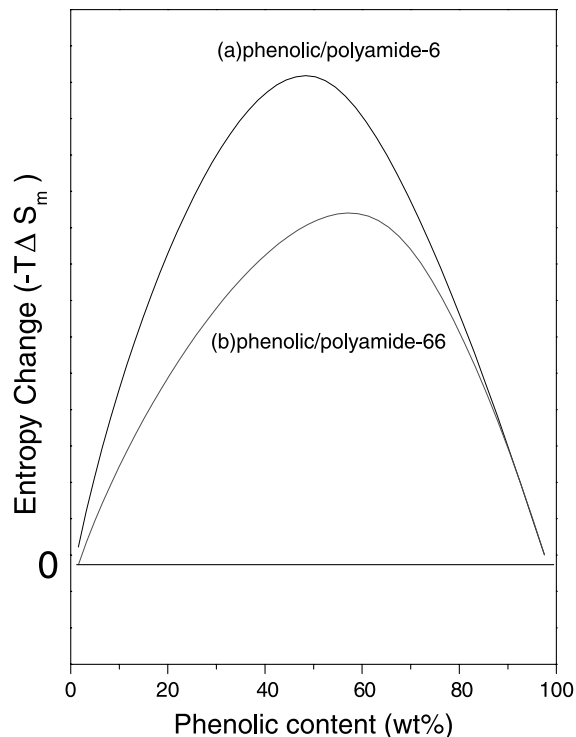

Fig. 7. Variation of the entropy change $(-T\Delta S_m)$ on blending with polyamide as a function of composition: (a) phenolic/polyamide-6; (b) phenolic/polyamide-66 blends.

stantially and thus gives rise to T_g reduction more sharp than that of the polyamide-6. As shown in Fig. 7, apparently, entropy change $(-T\Delta S_m)$ in the phenolic/polyamide-6 blends is larger than that in the phenolic/polyamide-66 blends.

4. Conclusions

This study has further demonstrated that the polyamide-66 increases molecular mobility better than that of polyamide-6 within the miscible window. The molecular motion is related to thermodynamic behavior that is discussed with employing the T_g deviation, efficiency of CP, and $T_{1\rho}^H$ relaxation behavior. The observed negative T_g deviation in phenolic/polyamide blends is attributed to the enlarged entropy $(-T\Delta S_m)$. The greater T_g deviation that the phenolic/polyamide-6 blends exhibits because of the effect of the repeated unit length on the hindrance of phenolic self-association is more severe than that of the phenolic/polyamide-66 blends. Therefore, lower $T_{1\rho}^H$ relaxation, lower efficiency of CP and higher mobility in the phenolic/polyamide-66 blends is concluded. However, the polyamide-66 chain in phenolic/polyamide-66 exhibits more effective in prompting the molecular motion than the polyamide-6 chain in phenolic/polyamide-6.

Particularly, the results as shown here reveal a new idea for prompting the mobility of polymer blends: the strength of inter-molecular interaction between both individual polymers should also be taken into consideration as the mechanism of toughness within the miscible window.

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