

Preparation and Characterization of Novolac type Phenolic Resin Blended with Poly(dimethylsiloxane adipamide)

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ABSTRACT: Phenolic resin/poly(dimethylsiloxane adipamide) (PDMSA) blends, which have been prepared, show miscibility due to intermolecular H-bonding existing between phenolic resin and the PDMSA. The specific H-bonding of novolac type phenolic/PDMSA blends was characterized by means of glass transition temperature behavior and Fourier Transform Infrared Spectroscopy (FTIR). The strength of intermolecular H-bonding within the phenolic blend is a function of the H-bonded group of the PDMSA modifier and corresponds to the deviation glass transition

temperature (ΔT_g). Phenolic/PDMSA blends were completely miscible, as confirmed by the T_g study. The FTIR result is in good agreement with the inference from T_g behavior. The char yield of phenolic/PDMSA corresponds to the phenolic resin content. The molecular mobility of phenolic/PDMSA blends increases with PDMSA content in the phenolic-rich region. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 984–992, 2002

Key words: blends; thermogravimetric analysis (TGA); resins

INTRODUCTION

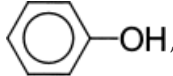
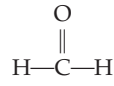
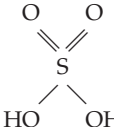
Phenolic resins have been widely used as paints, adhesives, and composites, etc., due to their excellent flame resistance, dimensional stability, and chemical resistance.^{1–3} In recent years, much emphasis has been focused on fireproof structures and decorations in buildings for public security, and, phenolic resin is one of the most popular resins for this purpose. However, its brittleness has significantly limited its applications. Improvement in the toughness of phenolic resin is important for further application.^{4–7} The miscibility of phenolic blends depends on both the strength of self-association of the phenolic resin and the interassociation between the phenolic resin and modifier.^{8–16} A simple and useful method to analyze the miscibility of a polymer blend is by determining the T_g as a function of composition.^{15,16} Over the years, numerous theories have been proposed to correlate the T_g of a miscible blend with its composition,^{16–25} interpreted in terms of specific interactions within a polymer blend. The carbonyl stretching vibration has been proved to be an excellent probe to detect the molecular mixing for a number of polymer blends.^{26–33} This information should lead to a better understanding of the relationship between H-bonding and T_g .

Polysiloxane has been widely used in industry, as a result of its low glass transition temperature (T_g), low surface tension of wetting, and low energy barrier of rotation. Because of silicon atoms and organic groups in polysiloxane, the chemical structures of its derivatives possess organic and inorganic properties.¹² The chemical structure of the siloxane group in a polysiloxane causes lower glass transition temperature (T_g) and lower surface tension of wetting, owing to its lower energy barrier for rotation and the soft segment of the siloxane group. Polysiloxane has been used as a toughening agent for epoxy, phenolic, and polyacrylate resin because of its chemical resistance, thermal stability, electrical insulation, and weather resistance.

In this study, poly(dimethylsiloxane adipamide), PDMSA, blended with novolac-type phenolic resin is proposed to improve the physical properties of phenolic resin. The amide group of PDMSA interacts with a hydroxyl group of the phenolic resin to form H-bonding. The strength of the intermolecular H-bonding within the phenolic blend is explored by the T_g deviation at various compositions. The FTIR technique is used to demonstrate the inference of the result of T_g behavior of the phenolic blends. The effects of the strength of interassociation and crystallinity on the deviation T_g in various phenolic blends are discussed in this study. The miscibility and thermal stability of phenolic/PDMSA blend are also investigated.

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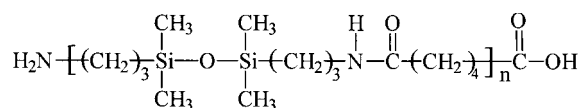
TABLE I
Materials Used in This Study

No.	Reagent	Structure	Supplier
1	Phenol	 $M_w = 94.11$ purity > 98.0%	Union Chemical Works Ltd., Taiwan
2	Formalin	 37 wt % water solution	Union Chemical Works Ltd., Taiwan
3	Concentrated Sulfuric acid	 $M_w = 190.21$ Purity > 96.0%	Hayashi Pure Chemical Industries Ltd., Japan
4	adipic acid	HOOC(CH ₂) ₄ COOH	Showa Chemical Inc., Japan
5	1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyl-disiloxane	C ₁₀ H ₂₈ N ₂ OSi ₂	United Chemical Technologies, Inc., USA

EXPERIMENTAL

Materials

The synthesis method and the analytical techniques of novolac-type phenolic resin were described in previous reports.⁸⁻¹⁰ The synthesis of poly(dimethylsiloxane-adipamide) (PDMSA) was as follows. The PDMSA prepolymer was synthesized in a 1.0-L glass reactor equipped with a thermometer, a reflux condenser, and a stirrer. The reactants, 73.08 g adipic acid (0.5 mol) and 124.26 g 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyl-disiloxane (0.5 mol), were fed into a flask reactor and reacted at 60°C for 1 h. At the end of reaction, PDMSA prepolymer was purified in 300 mL tetrahydrofuran (THF) and then stirred for 30 min. The PDMSA prepolymer was prepared via molten polymerization under 760 mmHg at 200°C. Materials used in this study are summarized in Table I.



Poly(dimethylsiloxane adipamide), PDMSA

Sample preparation

The preparation of DSC specimens was as follows: the phenolic/PDMSA blends were prepared by mixing blends in DMF [1%(w/v)] at 70°C. The mixed solution was stirred for 30–60 min, then dried at 180°C for 1 day under vacuum and annealed at 90°C for 2 h. The

IR specimens were prepared by pulverizing DSC samples.

Properties characterization

Solution ¹H NMR and GPC

The PDMSA were identified by using Bruker AM 400 spectrometer operated at 300 MHz for ¹H. Deuterated chloroform (CDCl₃) and DMSO were used as lock solvents for PDMSA. The tetramethylsilane was used as an internal standard. All spectra were obtained at 300 K (Figs. 2 and 3). Moreover, the chemical shifts and related description of PDMSA in ¹H- and ¹³C-NMR spectra are summarized in Tables II and III, respectively.

The molecular weight of PDMSA, as shown in Figure 4, was measured with a GPC column styragel HR series. DMF was used as the mobile phase, the flow rate was 1 mL/min at 40°C.

TABLE II
The Chemical Shifts of PDMSA in ¹H-NMR

Chemical shift (ppm)	Description
0.11	Si—CH ₃
0.48	Si—CH ₂
1.52	CH ₂ (adipic acid)
1.66	CH ₂ (siloxane)
2.26	CONH—CH ₂
3.11	CH ₂ —NHCO
6.65;7.10	CONH

TABLE III
The Chemical Shifts of PDMSA in ^{13}C -NMR

Chemical shift (ppm)	Description
0.1	Si—CH ₃
15.2	Si—CH ₂
25.1	CH ₂ (siloxane)
34.8	CH ₂ (adipic acid)
41.7	—CH ₂ —NHCO—
171.5	—CONH—
174	—COOH (end group)

Differential scanning calorimetry (DSC)

The glass transition temperatures (T_g) of the polymer blend films were determined by a differential scanning calorimeter (Du-Pont, DSC Model 2900). The scan rate was 10°C/min, within a temperature range of 0 to 300°C. The measurements were conducted with 3–4 mg samples on DSC sample pans after the specimens were quickly cooled to 0°C following the first scan. This procedure was adopted to ensure entirely mixing of the polymer blends and to remove the residual solvent and water in the specimen completely. The T_g values were determined at the midpoint of the transition point of the heat capacity (C_p) change and reproducibility of T_g values was estimated to be within $\pm 2^\circ\text{C}$ (Fig. 5).

Fourier transform infrared spectroscopy (FTIR)

Infrared spectra were recorded with a Nicolet 5 DXC spectrometer. Thin films were prepared by the solution-casting method. All the samples were annealed at 110°C for 2 h to remove residual solvent and ensure the polymer blend mixing completely. A minimum of 16 scans was signal averaged with a resolution of 2 cm^{-1} in the range of 4000–400 cm^{-1} . The hydroxyl stretching and carbonyl stretching region of the IR spectrum was analyzed for various phenolic resins (Figs. 7 and 8).

Thermogravimetric analysis (TGA)

Thermal degradation of the blends was performed by TGA (DU-Pont-951) from room temperature to 800°C with a heating rate of 10°C/min under nitrogen atmosphere. The measurements were conducted on 6–10-mg samples. Weight-loss/temperature curves also were recorded appropriately (Fig. 9).

Solid-state ^{13}C -NMR

High-resolution solid-state ^{13}C -NMR experiments were carried out on a Bruker DSX-300 spectrometer operated at resonance frequencies of 300.13 and 75.475 MHz for ^1H and ^{13}C , respectively. 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 point per spectrum, 4 k, and number of scans, 1 k. All NMR spectra were taken 300 K with broaden band decoupling, normal crosspolarization (CP) pulse sequence, and the magic angle sample spinning (MAS) of 4 kHz. The chemical shifts of ^{13}C -NMR spectra are reported in ppm relative to glycine by taking the carbonyl at 176.04 ppm (referred to TMS) as a secondary external standard. The signal-to-noise ratio of methylene of glycine was higher than 50 as measured with four scans and a pulse angle of 90°.

Proton spin-lattice relaxation time, $T_{1\rho}$ (in the rotating frame), was measured via carbon signal intensities using a 90°- τ -spin lock pulse sequence prior to cross-polarization. Data acquisition was performed via ^1H decoupling with delay time (τ) ranging from 0.1 to 16 ms. The relaxation time of $T_{1\rho}$ was obtained at 300 K.

RESULTS AND DISCUSSION

Molecular structure identification of PDMSA

Figure 1 shows the IR spectra of adipic acid, 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyl-disiloxane, poly(dimethylsiloxane adipamide) (PDMSA), in the absorption region of 400–4000 cm^{-1} at room temperature. The stretching peak of C=O functional group shifts from 1682 cm^{-1} [Fig. 1(a)] to 1640 cm^{-1} [Fig. 1(c)] that indicates that COOH reacts with NH₂ and CONH is formed. Figure 1(c) shows the peaks of spectra at 2690 cm^{-1} (CH₂), 827 cm^{-1} (Si—CH₂), 1251 cm^{-1} (Si—CH₃) used to confirm the structure of PDMSA.

Figure 2 and Figure 3 show ^1H - and ^{13}C -NMR spectra of PDMSA. All peaks in the spectra have been assigned to PDMSA. The molecular weight of PDMSA polymer was 1.9×10^4 obtained from GPC (Fig. 4). According to the ^1H -NMR and ^{13}C -NMR spectra of PDMSA, chemical shifts of PDMSA can be obtained

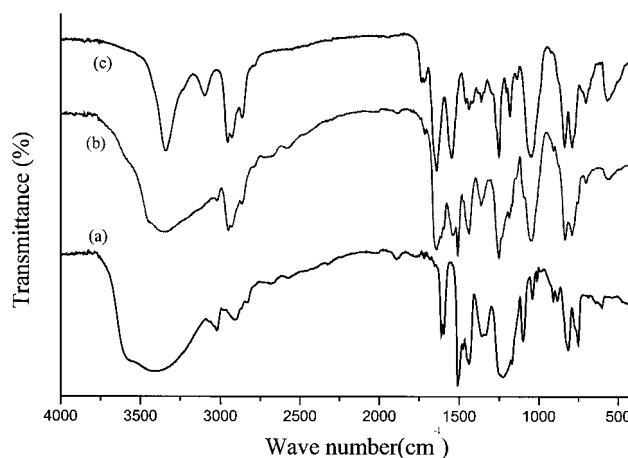


Figure 1 The IR spectra: (a) adipic acid, (b) 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, and (c) poly(dimethylsiloxane adipamide).

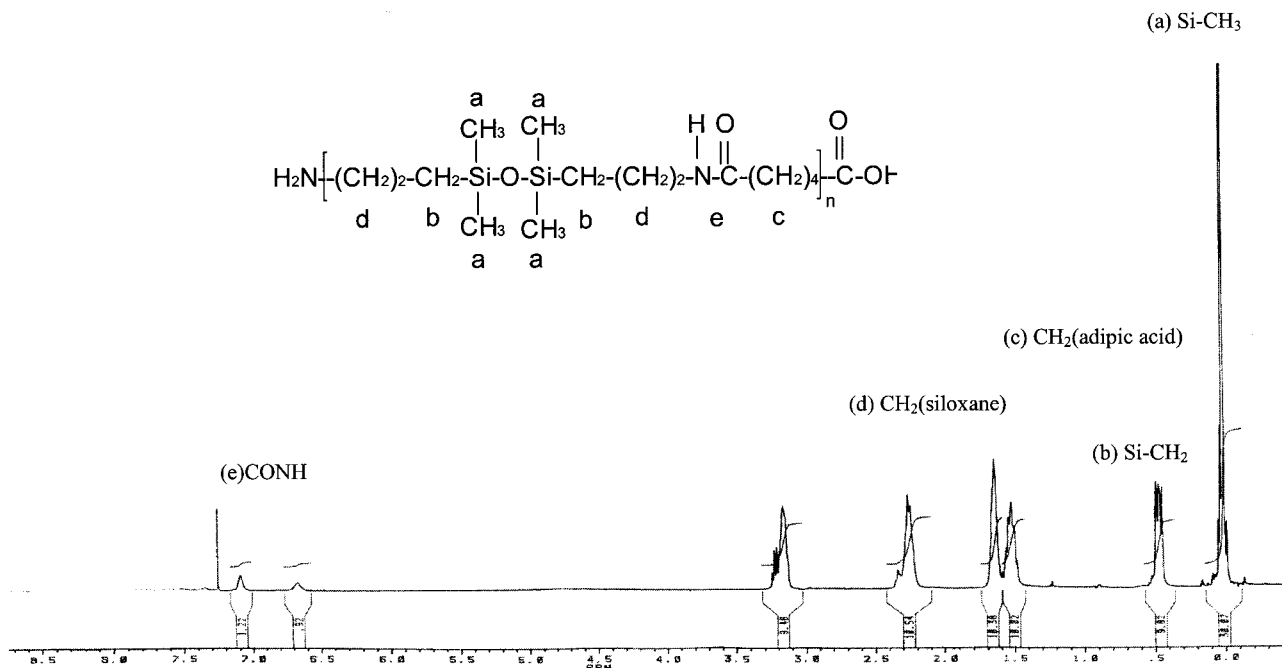


Figure 2 The ^1H -NMR spectrum of poly(dimethylsiloxane adipamide), PDMSA.

and are summarized in Tables II and III. The chemical shifts for hydrogen and carbon in $\text{Si}-\text{CH}_3$ are 0.11 and 0.1 ppm, respectively. The chemical shift of the amide group in the ^1H -NMR spectrum is shown to be in the range of 6.65 and 7.1 ppm. It can be concluded from this that PDMSA has been synthesized.

Glass transition temperature of phenolic/PDMSA blends

Thermal analysis is a good method to study the miscibility of a polymer blend. In general, a single T_g will

be exhibited when the polymer blend is miscible. Figure 5 shows the DSC curves of uncured phenolic/PDMSA blends with various compositions, respectively. The T_g of pure phenolic resin is $70 \pm 2^\circ\text{C}$, while the T_g of PDMSA is $-43 \pm 2^\circ\text{C}$. A single glass transition temperature can be clearly observed by DSC except in the phenolic-poor region, which indicates that the polymer blend is highly miscible in the phenolic-rich region.

Phenolic resin shows an unusual higher T_g than other similar low molecular weight polymers due to

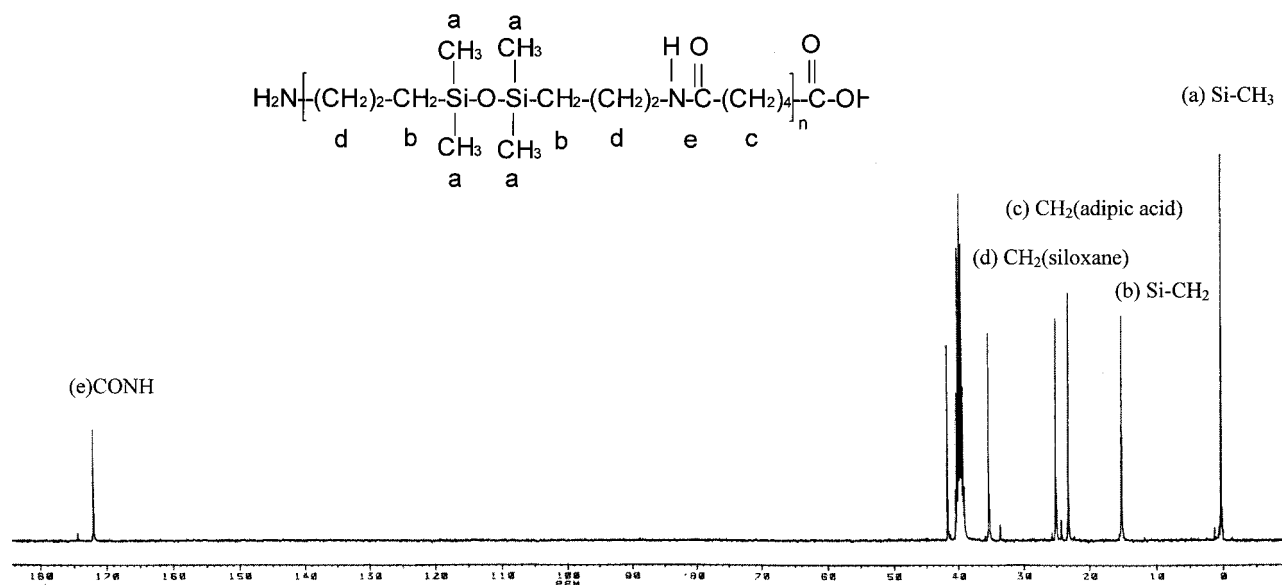


Figure 3 The ^{13}C -NMR spectrum of poly(dimethylsiloxane adipamide), PDMSA.

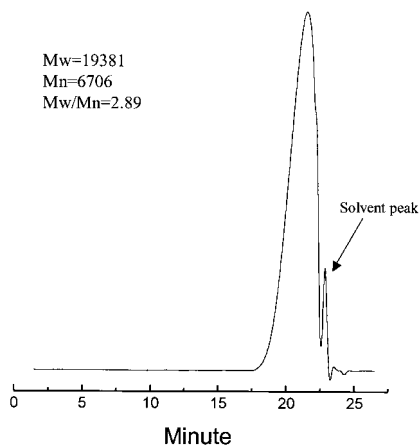


Figure 4 GPC curve of neat PDMSA.

its higher density of intramolecular H-bonding. The PDMSA is a polymer with high crystallinity, while phenolic resin is an amorphous and relatively rigid polymer. The flexible chain of PDMSA intersects into the network structure of phenolic resin providing more functional groups to interact with phenolic resin and form intermolecular H-bonding between the two polymers. When the PDMSA was added into phenolic resin, both the number and the strength of hydrogen bonding increased.

A notable feature can be seen from the DSC curves of phenolic/PDMSA blends in Figure 5, there is a heat of fusion generated at 230–250°C, even occurring with the 45/55 (wt %) phenolic/PDMSA blend. An obvious

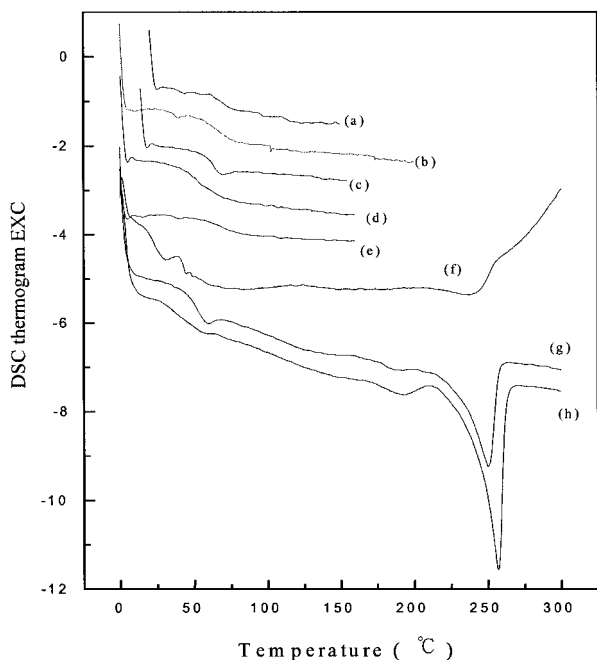


Figure 5 The DSC thermogram curves of PDMSA/Novolac-type phenolic resin blends with various compositions (wt %): (a) 0/100, (b) 10/90, (c) 25/75, (d) 30/70, (e) 40/60, (f) 55/45, (g) 70/30, and (h) 90/10.

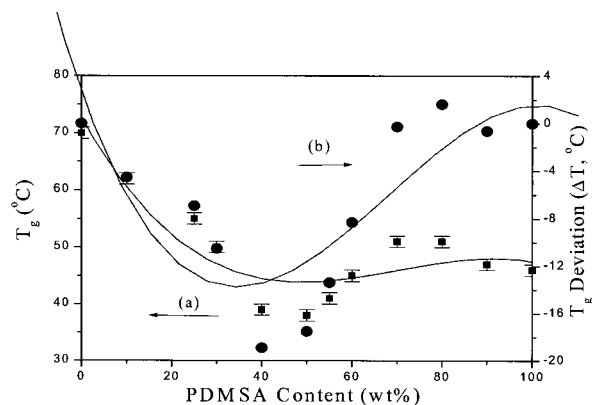


Figure 6 T_g and T_g deviation vs. composition of the phenolic resin/PDMSA blends. (a) T_g (■), and (b) T_g deviation (●).

melting peak appears when the polyamide content is greater than 50 wt %. Furthermore, the melting temperature is gradually shifted to higher temperature with increasing PDMSA content, as shown in Figure 5.

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

$$\Delta T_g = T_g - (\omega_a T_{g_a}^0 + \omega_b T_{g_b}^0) \quad (1)$$

where ω_i is the weight fraction of component i , and $T_{g_i}^0$ 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/PDMSA blends, are summarized in Figure 6. Essentially, all the T_g deviations are negative. T_g deviation is a result of an entropy change corresponding to the change in the number of H-bonding interactions.¹⁶

This direct evidence confirms the relationship between the molecular structure and mobility demonstrated by the following solid-state NMR from the

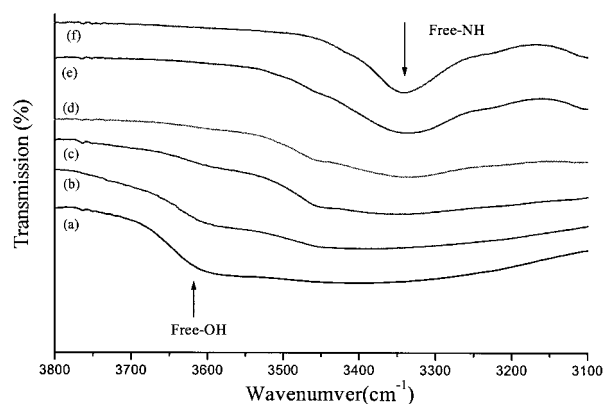


Figure 7 The IR spectra of the phenolic resin/PDMSA blends with various composition (wt %) (a) neat phenolic resin, (b) 80/20 (w/w), (c) 60/60 (w/w), (d) 30/70 (w/w), (e) 10/90 (w/w), and (f) neat PDMSA at 3800–3100 cm^{-1} .

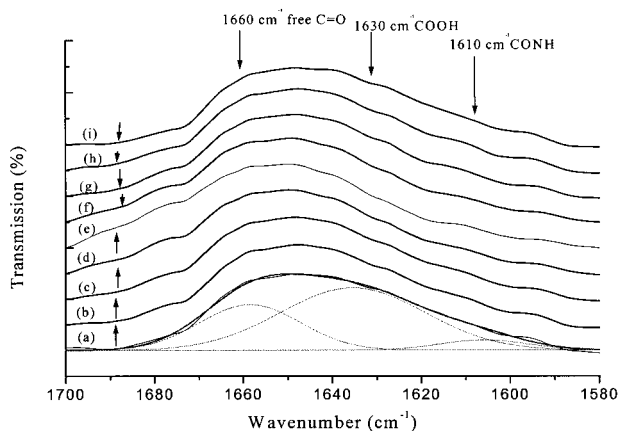


Figure 8 The IR spectra of the phenolic resin/PDMSA (30/70, w/w) blends recorded as a function of temperature: (a) 30°C, (b) 80°C, (c) 100°C, (d) 150°C, (e) 200°C, (f) 150°C, (g) 100°C, (h) 80°C, and (i) 30°C (↑: temp increased. ↓: temp decreased.)

parameters of ^{13}C chemical shifts, and $T_{1\rho}^{\text{H}}$ relaxation time.

FTIR spectra of phenolic/PDMSA blends

Figure 7 shows the H-bonding of the hydroxyl group in the IR absorption spectra with various PDMSA contents in the range of 4000–3000 cm^{-1} at room temperature. The presence of the IR transmittance component supports the fact that H-bonding exists in the polymer blends. All hydroxyl bands could be further resolved into “free” hydroxyl (free H-bonded hydroxyl) peaks in the range between 3450 and 3550 cm^{-1} , and “associated” H-bonded hydroxyl peaks in the range of 3300 to 3450 cm^{-1} , which are attributed to a wide distribution of H-bonded hydroxyl stretch frequencies. The H-bonding of polymer blend that is dynamic bonding is affected by temperature. The intramolecular H-bonding (CONH) and intermolecular H-bonding (COOH) can be determined by IR absorption in 1500–1700 cm^{-1} . The H-bonding is dynamic

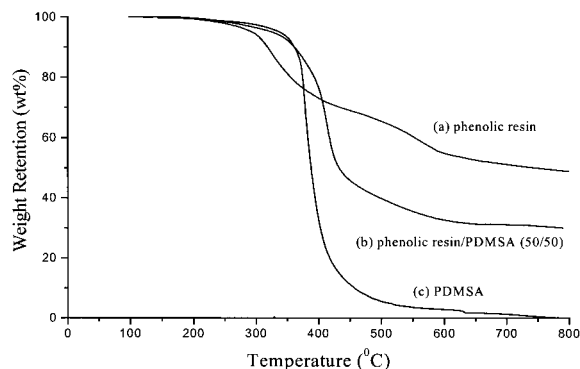


Figure 9 TGA of the phenolic/PDMSA copolymer at various compositions: (a) pure phenolic, (b) phenolic/PDMSA (50/50), and (c) pure PDMSA.

bonding, as proved by the IR spectra of phenolic/PDMSA blends with various temperatures in the range of 1500–1700 cm^{-1} .^{8,9} Figure 8 and Table IV confirm that COOH and CONH peaks decrease with an increase of temperature, while the “free” hydrogen bonding is increased with an increase of temperature.

Thermogravimetric analysis

Figure 9 illustrates the thermogravimetric analysis (TGA) of phenolic resin, PDMSA, and their blends in N_2 . From the derivative weight loss curve, the temperatures of 5% weight loss of modified phenolic resin with various PDMSA contents in N_2 are summarized in Table V. From Figure 9, one can conclude that the char yield of phenolic resin/PDMSA is associated with raised phenolic resin content.

CP/MAS of ^{13}C -NMR spectra of phenolic/PDMSA blends

Typical CP/MAS of ^{13}C -NMR spectra of phenolic/PDMSA blends, considered in the present study, are depicted in Figure 10. The main peak locations of the phenolic resin and the PDMSA are summarized in

TABLE IV
Curve Fitting Data γ , $\omega_{1/2}$, Af from Infrared Spectrum of the Phenolic Resin/PDMSA Blends (30/70) in the Range of 1700–1575 cm^{-1} with Various Temperatures

Temp °C	“Free” C=O			H-bonded COOH			H-bonded CONH			f_b
	ν cm^{-1}	$\omega_{1/2}$ cm^{-1}	Af %	ν cm^{-1}	$\omega_{1/2}$ cm^{-1}	Af %	ν cm^{-1}	$\omega_{1/2}$ cm^{-1}	Af %	
30	1658.5	22.646	989.63	1635.4	32.388	506.62	1605.9	19.802	100.66	0.290325
70	1653.4	28.546	1210.2	1630.1	23.173	284.56	1608.9	20.189	161.19	0.197143
100	1651.5	33.231	1262.4	1631.7	18.3	251.96	1613.7	25.367	155.98	0.177247
150	1650.7	39.069	1588.9	1633	14.806	169.25	1610.9	25.711	14.87	0.071713
200	1652.6	42.125	1710.9	1638.8	22.137	110.02	1607.4	22.684	2.6837	0.042068
150	1650.8	39.362	1598.5	1632.2	13.716	164.75	1609	25.555	20.314	0.071652
100	1652.2	32.544	1301.9	1632.3	18.503	274.48	1613	23.894	124.73	0.169728
70	1651.5	31.911	1221	1628.9	20.928	249.69	1609.5	21.172	186.67	0.19241
30	1659.6	19.065	1015	1639.3	34.52	317.82	1607.6	19.512	291.49	0.285818

TABLE V
The Temperature of 5% Weight Loss of Modified Phenolic Resin with Various PDMSA Contents in Nitrogen Atmosphere

Phenolic/PDMSA (w/w)	5% Weight loss temperature (°C)
100/0	289.8
50/50	326.8
0/100	340.6

Table VI. The chemical shifts of the hydroxyl-substituted (α) carbon in phenolic ring (phenolic, ~ 150 ppm) and C=O group (PDMSA, ~ 170 ppm) for various phenolic/PDMSA blends are shown in Figure 10. The relaxation time of various phenolic/PDMSA blends was measured at 128 ppm, and that of pure PDMSA was measured at 170 ppm. The PDMSA is a crystalline polymer, therefore, there are two difference $T_{1\rho}$ values for the crystalline region and the amorphous region. The interaction of H-bonding would produce small perturbations to the magnetic shielding on the nucleus and shifts downfield, compared to the one without H-bonding. The alteration of ^{13}C chemical shifts also reflects the varying strengths of H-bonding that provides evidence for the H-bonding reaction between phenolic resin and PDMSA. As shown in Figure 10, the α carbon resonance is assigned as 149.6 ppm, while the α carbon of uncured phenolic/PDMSA blends appeared between 149.6 and 152.6 ppm. This resonance shows a downfield shift with decreasing phenolic content, and that directly attracted α carbon of phenolic resin would exhibit deshielding associated with the increasing of H-bonding strength upon blending. The stronger H-bonding strength (than the intramolecular H-bonding of phenolic resin) between phenolic resin and PDMSA is believed to be the driving force for breaking up the PDMSA crystalline domain. The intensity of phenolic

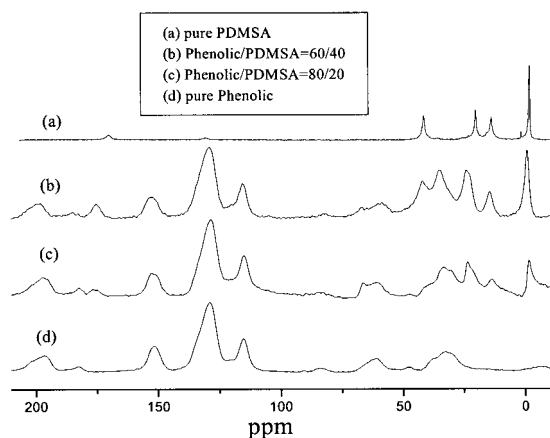


Figure 10 The CP/MAS of ^{13}C -NMR spectra of uncured phenolic resin, PDMSA and the phenolic resin/PDMSA blends with various compositions (w/w): (a) 100/0, (b) 60/40, (c) 80/20, and (d) 0/100 at 300 K.

TABLE VI
Chemical Shifts of the Phenolic Resin and PDMSA in ^{13}C -NMR Spectra

Material	Chemical shift (ppm)	Description
Phenolic	32.0	Methylene group
Phenolic	113.0	<i>Ortho</i> -substituted in phenol ring
Phenolic	149.6	Hydroxyl-substituted in phenol ring
Phenolic	126.5	Other carbon in phenol ring
PDMSA	170.6	Carbonyl group

bonding is weakened significantly with the decreasing phenolic resin content. In other words, the mobility of phenolic/PDMSA blend is increasing with the addition of PDMSA. In the phenolic-rich region, the intermolecular H-bonding is higher than that of the self-association H-bonding of phenolic resin.

From Figure 10 it was confirmed that the chemical shift of hydroxyl group substituted α -C of phenolic resin shifted downfield with increasing PDMSA content, and the chemical shift is 151 ppm, as listed in Table VI. In the phenolic/PDMSA blend, the tendency of the chemical shift downfield is due to the effect of magnetic shielding of promoted H-bonding; the chemical shift of hydroxyl group substituted α -C of phenolic resin is 174.6 ppm.

Relaxation time, $t_{1\rho}$, of phenolic/PDMSA blends

Proton $T_{1\rho}$ via resolved carbon resonances has been demonstrated to be a powerful measure to analyze molecular motion and domain heterogeneity in polymer blends. In a homogeneous system, the carbon signal decays in a manner following a simple exponential equation³³

$$M(\tau) = M_0 e^{-\tau/\tau_{1\rho}} \quad (2)$$

where τ is the relaxation time of spin lock; $M(\tau)$ is the strength of ^{13}C signal in τ time; M_0 is the strength of ^{13}C signal, at $\tau = 0$. The results from eq. (2) show that the phenolic/PDMSA blend is miscible.

Molecular motion in different environments should exhibit different relaxation behavior. When the coupling effect or the spin-diffusion effect is totally neglected, a pluralism relaxation can be used to model the inhomogeneity of the system. In general, in the hard collision limit, the more mobile environments should exhibit a relatively lower value of $T_{1\rho}^{\text{H}}$, while the rigid domains give a relatively higher value of $T_{1\rho}^{\text{H}}$. Figure 11 shows the magnetization plots of logarithmic ^{13}C intensity (relates to benzene ring) vs. the spin-lock time with 1 ms contact time for phenolic/PDMSA blends. Table VII summarizes the $T_{1\rho}^{\text{H}}$ values of phenolic/PDMSA blends in phenolic-rich region. The

NMR specimen was annealed at 140°C for 1 h and cooled quickly to room temperature. Pure PDMSA is a crystalline polymer, therefore, there are two different $T_{1\rho}^H$ values for the crystalline region and the amorphous region. Both blends (80/20 and 60/40) show single component $T_{1\rho}^H$ relaxation behavior, which implies that for those materials, there is a homogeneous phase. The value of $T_{1\rho}^H$ decreases with the addition of PDMSA, as shown in Figure 11 and Table VII. It is apparent that the mobility of a phenolic blend is improved upon blending with PDMSA, and such improvement increases with PDMSA content. The efficiency of hindering the intra-association of phenolic is increased with increasing PDMSA. Therefore, the entropy of polymer blend increases as confirmed by DSC data.

The reduced association of the phenolic blend caused by hindrance of the intra-association resulted in greater molecular segment mobility of the phenolic as indicated by the solid-state NMR spectra and relaxation behavior: the PDMSA prompted mobility of the phenolic before phase separation occurred.

CONCLUSIONS

1. When the novolac type phenolic resin was blended with PDMSA, the intramolecular H-bonding of phenolic resin and the crystallinity of PDMSA were destroyed and converted to intermolecular H-bonding and amorphous phase, respectively. The "free" H-bonding increased with an increase of temperature and the H-bonding (intra- and inter-) decreased with an increase of temperature.
2. The flexible chain of PDMSA intersects into the network of phenolic resin and may improve the brittleness of phenolic resin. The flexible chain of PDMSA will absorb energy that impacts on the

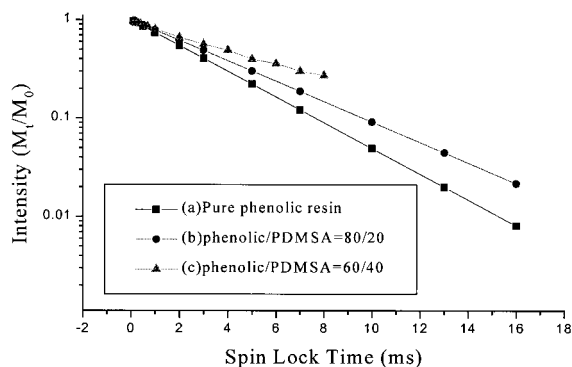


Figure 11 The logarithmic plots of the magnetization intensities of hydroxyl substituted in phenol ring of phenolic resin vs. the spin-lock time ($T_{1\rho}$) for uncured phenolic resin/PDMSA blends (w/w): (a) 100/0, (b) 80/20, and (c) 60/40.

TABLE VII
 $T_{1\rho}$ Relaxation Times of Phenolic/PDMSA Blends at 300° K

Phenolic resin/PDMSA blend (w/w)	Phenolic resin/PDMSA (ms)
100/0	4.5 (128 ppm)
80/20	4.18 (128 ppm)
60/40	3.32 (128 ppm)
0/100	0.8, 12 (170 ppm)

phenolic resin. These mechanisms occurred in the blend system simultaneously.

3. According to the TGA data, the thermal stability of the phenolic/PDMSA blend was enhanced with increasing PDMSA content. The char yield of phenolic/PDMSA blend was associated with raised phenolic resin content.
4. The close packing of phenolic is weakened significantly with decreasing phenolic resin content. In other words, the mobility of the phenolic resin increases with the addition of PDMSA. In PDMSA-rich region, the intermolecular H-bonding is higher than that of the intramolecular H-bonding of phenolic resin.
5. In the phenolic-rich region, $T_{1\rho}$ of the phenolic/PDMSA blend decreases with increasing PDMSA content and the mobility of the phenolic/PDMSA blend.

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