Mechanical Properties, Thermal Stability, and Flame Retardance of Novolac-Type Phenolic Resin Blended with Poly(dimethylsiloxaneadipamide)

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ABSTRACT: Mechanical properties (flexural strength, flexural modulus, and notched Izod impact strength), thermal stability, and flame retardance of poly(dimethylsiloxane adipamide) (PDMSA)-toughened novolac type phenolic resin were investigated. Mechanical properties of modified novolac-type phenolic resin increase with PDMSA contents, because the soft segment of PDMSA absorbs the loads in the network of brittle novolac-type phenolic resins. TGA results show that the thermal degradation temperatures are higher than 400°C, and the temperature of 10% weight loss increases with increasing the PDMSA content. The char yield increases with novolac-type phenolic resin content. The morphologies of the fracture surface of the modified novolac-type phenolic resin were investigated by scanning electron microscopy (SEM). Morphological results agree with those from mechanical properties of the modified novolac-type phenolic resin. The modified novolac-type phenolic resin also shows excellent flame retardance that is UL-94, V-1, and the limited oxygen index is higher than 35. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 631–637, 2001

Key words: mechanical properties; thermal stability; flame retardance; PDMSA; novolac-type phenolic resin

INTRODUCTION

Phenolic resin has been widely used commercially in the applications such as paint, adhesives, and composites due to its lower manufacturing cost, dimensional stability, and chemical resistance.[1–3] Polysiloxane has been widely used in industry, due to its low glass transition temperature (T_g), low surface tension of wetting, and low energy barrier of rotation. Because of the silicon atom and organic groups in polysiloxane and its derivatives, their chemical structures possess organic and inorganic properties.[4] The siloxane portion of polysiloxane causes lower glass transition temperature (T_g) and lower surface tension of wetting, due to lower energy barrier for rotation and the soft segment of the siloxane group. Consequently, polysiloxane can be used as a toughening agent for epoxy, phenolic, and polyacrylate resin.[5–8] As described in previous reports,[9–13] the novolac type phenolic resin provides intermolecular hydrogen bonding as a dominant driving force to interact with hydroxyl, carbonyl, amide groups, and other hydrogen-bonded functional groups of thermoplastic miscible polymers. Mechanical properties of modified novolac type phenolic increase with

thermoplastic polymer added, because either amide or other hydrogen-bonded functional groups are more flexible than phenolic resin; consequently, the ability to absorb the loads will be enhanced.

In this study, a novel method of blending the novolac type phenolic resin with poly(dimethylsiloxaneadipamide) (PDMSA) is proposed. The amide group of PDMSA would interact with the hydrogen bonding of novolac phenolic resin to improve the mechanical properties (including tensile strength, flexural modulus, and notched Izod impact strength) of the modified phenolic resin.[6]

The thermal stability of phenolic/PDMSA blend is also investigated in the study.
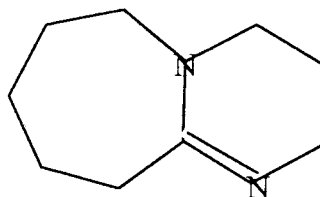
EXPERIMENTAL

Materials

The curing agent used is the bisphenol A-type epoxy resin, diglycidyl ether of bisphenol A (DGEBA) (Epon828, Shell Chemical Co., U.S.A.). The catalyst, 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), was purchased from the Lancaster Synthesis Ltd, U.S.A. The structures of DGEBA and DBU are described as follows:
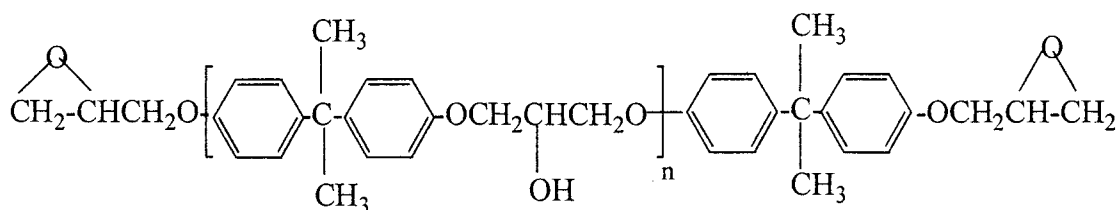

diglycidyl ether of bisphenol-A (DGEBA)

1,8-Diazabicyclo(5.4.0)-7-undencene (DBU)

The syntheses of novolac type phenolic resin and poly(dimethylsiloxaneadipamide) (PDMSA) are described below, and the materials used are summarized in Table I.
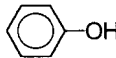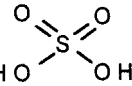
The poly(dimethylsiloxaneadipamide) (PDMSA) prepolymer was synthesized in a 1.0-L glass reactor equipped with a thermometer, reflux condenser, and a stirrer. Adipic acid (73.08 g) (0.5 mol) and 124.26 g 1,3-bis(3-aminopropyl)-

1,1,3,3-tetramethyldisiloxane (0.5 mol), were fed into the flask reactor and were reacted at 60°C, 1 h. At the end of the reaction the PDMSA prepolymer was purified in 300 mL tetrahydrofuran (THF) and then stirred for 30 min. The PDMSA prepolymer was thermally melt polymerized under 76 mmHg at 185°C until the desired molecular weight of PDMSA was obtained
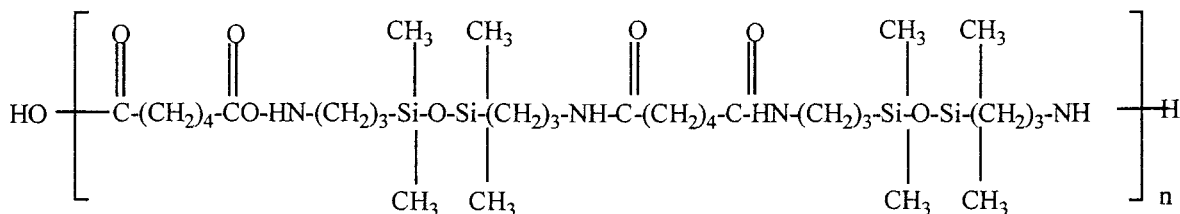
poly(dimethylsiloxaneadipamide) (PDMSA)

Table I Reagents Used in This Study

No.	Reagent	Structure	Supplier
1	Phenol	$M_w = 94.11$ purity > 98.0%	Union Chemical Works Ltd., Taiwan
2	Formaline	$\overset{O}{\overset{\|}{H-C-H}}$ 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	$HOOC(CH_2)_4COOH$	Showa Chemical Inc., Japan
5	1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane	$C_{10}H_{28}N_2OSi_2$	United Chemical Technologies, Inc., USA
6	1,8-Diazabicyclo[5.4.0]-7-undecene (DBU)	$M_w = 152.24$; f.1 = 116°C	Lancaster Synthesis Ltd., United Kingdom
7	Diglycidyl ether of bisphenol-A (DGEBA) (Epon-828)		Shell Chemical Co., S/A

Sample Preparation

Diglycidyl ether of bisphenol A epoxy (DGEBA) was used as a curing agent and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) was used as a catalyst. Various contents of PDMSA were blended with novolac-type phenolic resin in THF. Compositions of cured samples are summarized in Table II. Samples were put in an oven at 55°C for 2 h, and then the temperature was increased to 70°C overnight in vacuum. The postcured temperature was 150°C, and curing time was 5 h, to ensure complete mixing of the polymer blend and to remove the residual solvent and water in the specimens completely.

The preparation of the IR and TGA specimens are described as follows: the phenolic/PDMSA blend was prepared by mixing it with THF [1% (w/v)] at room temperature according to the designed composition. The mixed solution was stirred for 6–8 min, and THF was evaporated slowly at 70°C under vacuum for 1 day.

Properties Measurements

Flexural modulus was measured according to ASTM D-256. The sample dimensions were 63 × 10 × 3 mm (length × width × thickness), the span between the two supports was 50 mm, and the crosshead speed was 1.3 mm/min. The notched Izod impact strength was measured following the specifications of ASTM D-256, with dimensions of 63 × 10 × 3 (length × width × thickness).

The infrared spectrophotometer used was a Perkin Elmer 842. The IR spectra was scanned at the range of 4000–400 cm^{-1}, and was utilized to study the intermolecular hydrogen bonded between phenolic resin and PDMSA. Thermogravimetric analysis (TGA) was conducted with a Dupont TGA951 from room temperature to 800°C using a heating rate of 10°C/min under nitrogen gas atmosphere. A scanning electron microscope (Model JSM-5300 from JEOL) was used for the morphological study.

Table II Compositions of Cured Samples

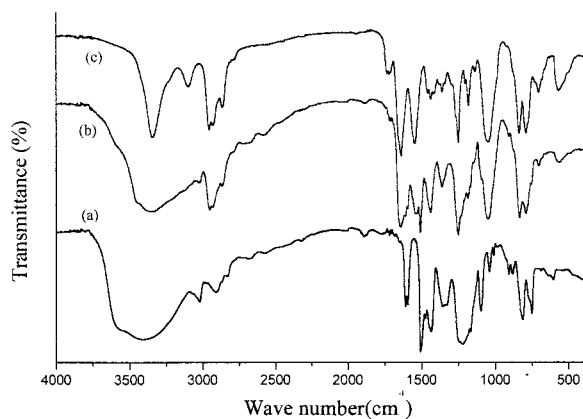| PDMSA Content (phr)	Phenolic (g)	SiNHCO (g)	Epoxy (g)	DBU (g)
1	30	0.3	15	0.6
3	30	0.9	15	0.6
5	30	1.5	15	0.6
7	30	2.1	15	0.6

Figure 1 IR spectra: (a) adipic acid; (b) 1,3bis(3-aminopropyl)-1,1,3,3-tetramethyl-disiloxane, (c) poly-(dimethylsiloxane adipamide).

Flame retardance was measured according to the UL-94 Standard.[14] Five specimens with dimensions of 125 ± 5 mm long and 13.0 ± 0.5 mm wide were tested. Methane gas was supplied to the burner shell, and the burner was adjusted to produce a blue flame of 20 ± 1 mm high. By applying the flame centrally to the middle point of the bottom edge of the specimen, the top of the burner was 10 mm below the point of the lower end of the specimen, and that distance was maintained for 10 s. If only one specimen from one set of five specimens did not comply with the requirements, another set of five specimens was tested. The limiting oxygen index (LOI) was tested according to ASTM D-2863.

RESULTS AND DISCUSSION

Molecular Structure Identification

IR measurements, to provide further information regarding interaction in the polymer blends, were determinations of the spectrum of the hydroxyl group of various phenolic blends. Figure 1 shows the IR spectra of poly(dimethylsiloxaneadipamide), 1,3bis(3-aminopropyl)-1,1,3,3-tetramethyl-disiloxane, poly(dimethylsiloxaneadipamide), 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)], and indicates that COOH reacts with NH$_2$ and CONH is formed. Figure 1(c) shows the spectra peaks at 2690 cm^{-1} (CH$_2$), 827 cm^{-1} (Si—CH$_2$), 1251 cm^{-1} (Si—CH$_3$), and confirms the structure of poly(dimethylsiloxaneadipamide).
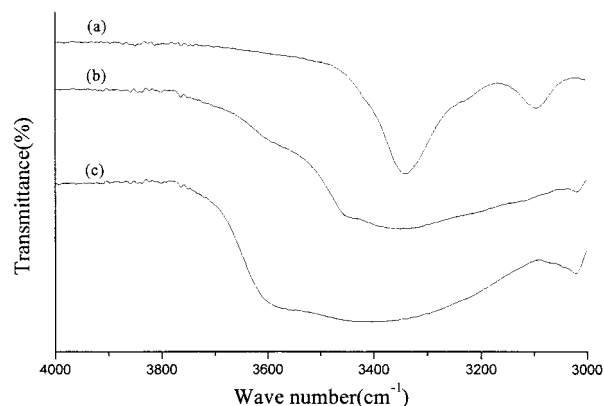

Figure 2 IR spectra: (a) poly(dimethylsiloxane adipamide), (b) pehnolic/PDMSA (50/50), (c) phenolic resin.

Figure 2 shows the IR transmittance bands of hydroxyl absorption in the range of $4000–3000$ cm^{-1} for pure phenolic resin, 50/50 ph/PDMSA, and pure PDMSA at room temperature. The presence of the IR transmittance component is evidence that hydrogen bonds exist in the polymer blends. All of the hydroxyl bands could be further resolved into "free" hydroxyl (free hydrogen-bonded hydroxyl) peaks in the range from 3450 cm^{-1} to 3550 cm^{-1}, and the "associated" hydrogen-bonded hydroxyl peak in the range from 3300 cm^{-1} to 3450 cm^{-1}, which is attributed to a wide distribution of hydrogen-bonded hydroxyl stretch frequencies. The amide group of PDMSA appeared mostly in the hydrogen-bonded configuration, corresponding to PDMSA containing a high-density amide group that is more flexible in the backbone than the phenolic resin. Both functional groups provide the opportunity to form intramolecular hydrogen bonds.
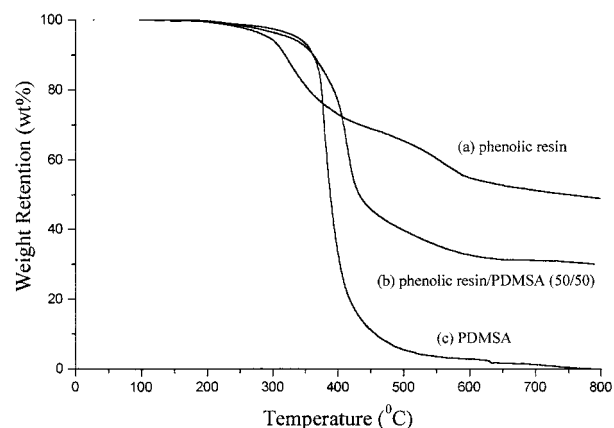

Figure 3 TGA of the phenolic/PDMSA copolymer at various compositions: (a) pure phenolic, (b) phenolic/OPDMSA (50/50), (c) pure PDMSA.

Table III The Temperature of 5% Weight Loss of Phenolic/PDMSA Copolymer with Various Compositions

Phenolic/PDMSA (w/w)	Temperature (°C)
100/0	289.8
50/50	326.8
0/100	340.6

Thermal Properties

Thermal Stability

Figure 3 illustrates the thermogravimetric analysis (TGA) results of the phenolic/PDMSA blend. PDMSA in the blend caused it to decompose gradually at a higher temperature than that of the phenolic resin. From the derivative weight loss curve, it is found that the temperature of the 5% weight loss of the blend was lowered with increased phenolic resin content, as summarized in Table III. The initial decomposition temperature of the phenolic/PDMSA blend is above 400°C, indicating that the blend posses good thermal stability.

Flame Retardance

The flame retardance of phenolic/PDMSA blends shows a high limiting oxygen index (LOI) value (>35) and the UL-94 is V-1, as summarized Table IV. These values are maintained up to 7 wt % PDMSA. The effect of the minor PDMSA content on the flame retardance was insignificant because the phenolic resin is a high char-yield material.

Mechanical Properties

Flexural Strength and Modulus

Figures 4 and 5 show the flexual strength and modulus of the phenolic resin toughened by PDMSA, as summarized in Table V. Flexural strength and modulus show maximum values

Table IV The Flame Resistance of Modified Novolac-Type Phenolic Resin Toughened by PDMSA

PDMSA content (phr)	0	1	3	5	7
UL-94	V-1	V-1	V-1	V-1	V-1
Limited oxygen index (LOI)	35	35	35	35	35
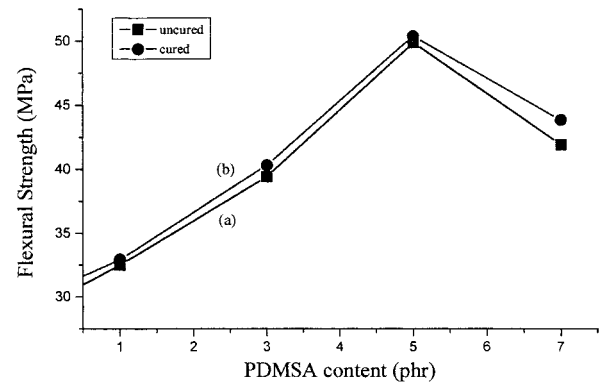
Figure 4 Flexural strength of novolac-type phenolic resin toughened by PDMSA at various PDMSA contents: (a) uncured, (b) cured.

when PDMSA content is 5 phr, and then decrease gradually when PDMSA content is more than 5 phr. This behavior can be interpreted as that, when the soft segment of PDMSA is incorporated into the backbone of the phenolic resin the soft segment will absorb any load applied first; hence, the flexural strength will be increased. However, when the PDMSA content is higher than 5 phr, phase separation may occur, and the flexural strength is decreased. The flexural strength of the cured composite is higher than that of the uncured one. The flexural modulus of cured composites is comparable to the uncured one.

Notched Izod Impact Strength

The effect of the PDMSA content on the notched Izod impact strength of composite is illustrated in Figure 6. The highest impact value also occurs when the blend contains 5 phr of PDMSA and a
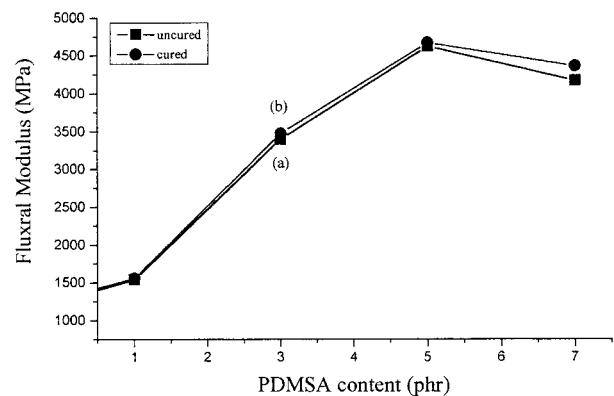

Figure 5 Flexural modulus of novolac-type phenolic resin toughened by PDMSA at various PDMSA contents: (a) uncured, (b) cured.

Table V   Mechanical Properties of PDMSA-Modified Phenolic Resin

Specimen	Property	PDMSA Content (Phr)				
		0	1	3	5	7
Uncured specimen	Flexural strength (MPa)	29.43	32.53	39.42	49.85	41.89
	Flexural modulus (MPa)	1261.6	1541.2	3399.2	4616.8	4166.1
	Notched Izod impact strength (kJ/m)	23.3	24.9	25.7	33.8	30.2
Cured specimen	Flexural strength (MPa)	30.35	32.97	40.33	50.37	43.82
	Flexural Modulus (MPa)	1301	1562	3478	4665	4358
	Notched Izod impact strength (J/m)	25.4	26.6	29.6	34.8	31.7

significant improvement in toughness is observed. The impact strength of the blended composite containing 5 phr of PDMSA is 34% higher than that of the pure phenolic. When the PDMSA content is higher than 5 phr, the impact strength is decreased because the phenolic resin and the PDMSA become immiscible at a higher PDMSA content. A macrophase separation forms in the modified phenolic resins instead of microphase separation. The notched Izod impact strength decreases with increasing PDMSA content. The cured composites show higher notched Izod impact strength than that of the uncured ones due to the more complete cure reaction.

Morphology of the Specimen

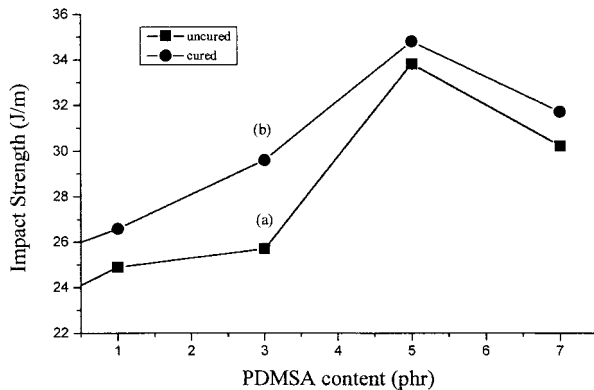The morphology of phenolic resin blended with PDMSA was investigated by SEM photography,

as shown in Figure 7. The SEM photographs in Figure 7 show crack propagation under cleavage fracture. There is clear crack propagation in Fig-

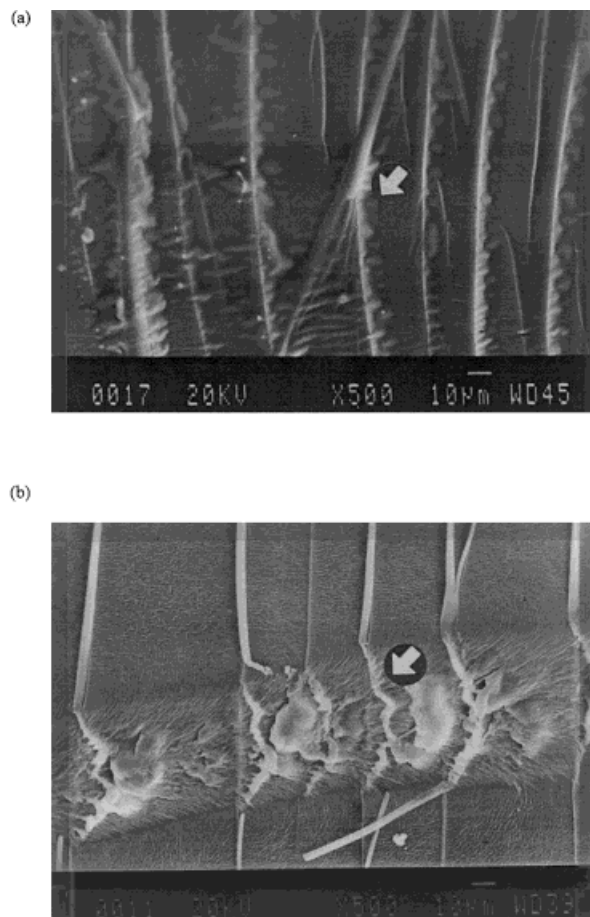**Figure 7**   SEMs of (a) novolac-type phenolic resin, and (b) PDMSA/phenolic: 5/95 (w/w).

Figure 6   Impact strength of novolac-type phenolic resin toughened by PDMSA at various PDMSA contents: (a) uncured, (b) cured.

ure 7(b), while that in Figure 7(a) is smooth, implying that the toughness of the matrix increased with the addition of PDMSA. The soft segment of PDMSA absorbs fracture energy by yielding, and softens the matrix. The notched Izod impact strength and flexural modulus of the specimen increases with the addition of the PDMSA at the beginning, and then decreases when the PDMSA content is higher than 5 phr.

CONCLUSIONS

1. Mechanical properties (including flexural modulus, notched Izod impact strength) of modified novolac-type phenolic resin show the highest values for a blend that contains 5 phr PDMSA. The cured specimen shows higher mechanical properties than that of the uncured one.
2. The phenolic/PDMSA blend is a completely miscible system at low PDMSA content in which the flexible siloxane chain of the PDMSA backbone penetrates into the rigid phenolic matrix, which serves to toughen the phenolic resin.
3. The decomposition temperature of the phenolic/PDMSA blend was above 400°C for all specimens, although its temperature decreased with the increase of the PDMSA content.
4. The flame retardance of blends containing up to 7 phr PDMSA in modified phenolic resin composites shows the values of UL-94, V-1, and LOI higher than 35, which demonstrate that the blended composites possess excellent fire resistance.

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