Mechanical Properties, Morphology, and Flame Retardance of Glass Fiber-Reinforced Polyamide-Toughened Novolac-Type Phenolic Resin

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ABSTRACT: The mechanical properties (tensile, flexural modulus, and impact strength) and the flame retardance of glass fiber-reinforced novolac-type phenolic resin modified with polyamide (PA-6, PA-66) were investigated. Results show that polyamide improves the mechanical properties of composites, especially for the impact strength up to 1.5-fold which shows a maximum value at 7 wt % of polyamide content. The interface between the matrix and glass fiber is increased due to the hydrogen-bonding function present in the polyamide chain. This modified phenolic composite shows excellent flame retardance, that is, UL-94, V-0, and LOI is higher than 55. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 881–887, 1999

Key words: novolac-type phenolic resin; glass fiber surface mat; polyamide (PA-6, PA-66); mechanical properties; flame retardance

INTRODUCTION

Phenolic resin has been widely used in industry because of its good flame retardance, electrical insulation, dimensional stability, and chemical resistance.[1–4] However, the poor wet-out between glass fiber and phenolic resin and the brittleness of phenolic resin are serious problems of the glass fiber-reinforced phenolic composite.

In recent years, much emphasis has been placed on the fireproof structure and decoration in buildings for public security. Phenolic resin is one of the most popular resins for this purpose. However, its brittleness has limited its application significantly. Improvement in the toughness of phenolic resin is an important task for further application.[5,6] All the mechanical properties of modified phenolics can be increased with a thermoplastic modifier added, for example, either ester groups or other hydrogen-bonding functional groups are more flexible than the phenolic resin. Hence, the modified phenolic resin will absorb more load.

In this study, polyamide was blended with novolac-type phenolic resin in order to improve the toughness of novolac-type phenolic resin and the bonding between fiber and matrix.[7] Both functions improve the mechanical properties (including the tensile strength, flexural modulus, and Izod impact strength) of the resultant composite. The morphology and flame retardance of the phenolic/polyamide blend were also investigated.

EXPERIMENTAL

Materials

The polyamide 6.6 (PA-66) used in this study was obtained from Taiwan Chemical Co. (Taipei, Tai-

Table I　Reagents Used in This Study

Reagent	Structure	Supplier
Phenol	$M_w = 94.11$ Purity > 98.0%	Union Chemical Works Ltd. (Hsin-Chu, Taiwan)
Formaline	$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H$$ 37 wt % water solution	Union Chemical Works Ltd. (Hsin-Chu, Taiwan)
Concentrated sulfuric acid	$M_w = 190.21$ Purity > 96.0%	Hayashi Pure Chemical Industries Ltd. (Tokyo, Japan)
PA-6	$+NH(CH_2)_5CO+_n$ Dupont101L	Dupont Chemical Co. (Wilmington, DE)
PA-6.6	$+NH(CH_2)_6NHCO(CH_2)_4CO+_n$	Taiwan Chemical Co. (Taipei, Taiwan)
Hexamethylene tetramine (hexamine)	Purified industry grade	Chu-Chung Resin Co. (Hsin-Chu, Taiwan)
Glass fiber surface mat	P250 R.A. 1.250mx	Regina Fibra Glass Pty Ltd. (Sydney, Australia)

wan) and polyamide 6 (PA-6) was obtained from DuPont Co. (Wilmington, DE). Phenol and formaldehyde monomers were EP grade supplied by the Union Chemical Works Ltd. (Hsin-Chu, Taiwan). The novolac-type phenolic prepolymer was synthesized in this laboratory. Hexamethylenetetramine (hexamine) was a purified industry-grade reagent obtained from the Chu-Chung Resin Co. (Hsin-Chu, Taiwan). The concentrated sulfuric acid used was a guaranteed reagent, which was obtained from the Osaka Chemical Co. (Osaka, Japan). The glass fiber mat used has a mat thickness of 0.014 mm and was supplied by Regina Fibre Glass Pty Ltd. (Sydney, Australia).

The chemical structure and specification of these reagents are listed in Table I.

Sample Preparation

The novolac-type phenolic prepolymer was synthesized in a 5.0 L glass reactor equipped with a thermometer, reflux condenser, and stirrer. The reactants, 1694 g phenol (18 mol) and 1217.5 g formalin (in 37 wt % water solution, 15 mol formaldehyde), were fed into a flask reactor. The reaction was catalyzed by adding diluted sulfuric acid solution (4 g of concentrated sulfuric acid dissolved in 20 mL of water) and reacting at 100°C for 7 h in the reactor. The reaction was continued

Table II   Mechanical Properties (Flexural Modulus, Impact Strength, and Tensile Strength) of Cured and Uncured Glass Fiber-reinforced Novolac-type Phenolic Composites Modified with Polyamide

Polyamide	Wt %	Flexural Modulus (GPa)		% Increase[a]	
		U	P	U	P
	0	30.6	34.2	—	—
PA-6	7	32.7	36.6	6.79	8.14
PA-66	7	33.8	38.3	10.5	11.3

	Wt %	Impact Strength (kJ/m)		% Increase[a]	
		U	P	U	P
	0	1.36	1.56	—	—
PA-6	7	1.99	2.33	46.2	48.7
PA-66	7	2.03	2.36	49.3	50.7

	Wt %	Tensile Strength (MPa)		% Increase[a]	
		U	P	U	P
	0	436	451	—	—
PA-6	7	441	460	1.10	2.00
PA-66	7	442	478	1.35	5.964

Glass fiber content: 65 wt %. U, cured resin before postcure; P, cured resin after postcure (180°C, 1 h).
[a] Comparison between unmodified phenolic resin and modified phenolic resin.

until the prepolymer with a desired viscosity (500–2000 cps at 25°C) was obtained. At the end of the reaction, the calculated amount (1.558 g) of $Ca(OH)_2$ was dispersed in 5 mL of water and added to neutralize the sulfuric acid catalyst and then stirred for an additional 3 min. The mixture was dehydrated under a pressure of 100 mmH_2O at 120–130°C until the resin was clear.

The dimensions of the compression mold were $25 \times 25 \times 0.12$ cm. The heating temperature profile of the mold used two heating plates along the compression direction. The surfaces of the stainless-steel mold were treated by chromium plating.

The preparation of the thermogravimetric analysis (TGA) specimen is described as follows: The phenolic/polyamide blend was prepared by mixing it with phenol at 100°C according to the designated composition. The mixed solution was evaporated slowly at 100°C for 30 h.

Property Measurement

The flexural modulus was measured according to ASTM D-790. The dimensions of the test speci-men were $50 \times 2.5 \times 0.8$ mm (length $\times$ width $\times$ thickness), and the crosshead speed was 0.5 mm/min. The tensile strength was measured with an Instron 4201 according to ASTM D-638. The dimensions of the test specimen were $40 \times 20 \times 0.8$ mm (length $\times$ width $\times$ thickness) and the crosshead speed was 2 mm/min. The notched Izod impact strength was measured according to ASTM D-256.

Thermogravimetric analysis was conducted with a DuPont TGA TGS-2 from room temperature to 800°C using a heating rate of 10°C/min under air. A scanning electron microscope (Model JSM-5300 from JEOL Co.) was used for the morphology study.

The limiting oxygen index (LOI) was tested according to ASTM D-2863. The flame retardance was measured according to the UL-94 Standard.[8] The specimen was 125 ± 5 mm long and 13.5 ± 0.5 mm wide.

RESULTS AND DISCUSSION

Mechanical Properties

All mechanical properties such as tensile, flex-ural, and impact strengths are summarized in

Figure 1 Effect of PA-6 and PA-66 content on the flexural modulus of glass fiber-reinforced novolac-type phenolic resin composites modified with polyamide.

Table II. Figure 1 shows the flexural modulus of the compression-molded fiber-reinforced novolac-type phenolic resin modified with various PA-6 and PA-66 polyamide contents. Since the loads applied will be absorbed by the soft segment of polyamide, that leads to an increase in impact strength and flexural strength. The wet-out between the matrix and fiber is poor due to the viscosity being higher than 100,000 cps at high polyamide content. The highest flexural modulus of the composites occurred at 7 wt % of polyamide and exhibited a significant improvement of 8% (PA-6/phenolic) and 11% (PA-66/phenolic) in stiffness.

The effect of the polyamide content on the notched Izod impact strength of the composite is illustrated in Figure 2. The highest impact strength appeared at 7 wt % polyamide and exhibits a significant improvement in toughness of 49% (PA-6/phenolic) and 51% (PA-66/phenolic). Owing to the high viscosity, 100,000 cps, causing poor wet-out between the matrix and fiber, at higher polyamide contents the notched Izod im-

pact strength of the composite decreased with polyamide content.

Figure 3 shows the tensile strength of a modified phenolic composite with various polyamide contents. The tensile strength of the composite depends on both the polymer properties and the wet-out of the matrix and the fiber. It is apparent that the presence of polyamide improves the tensile strength of the composite due to its flexibility. On the other hand, the high viscosity with the addition of polyamide reduces the wet-out of the glass fiber and leads to the reduction of the tensile strength. The highest tensile appeared at 7 wt % content and exhibited an improvement of 2.0% (PA-6) and 6.0% (PA-66). The effect of the wet-out on the mechanical properties is demonstrated and further discussed by SEM photographs in the next section.

The mechanical properties of the postcured composites show higher values than those before postcure because the reaction of the postcured one is more complete. The mechanical properties of

Figure 2 Effect of PA-6 and PA-66 content on the impact strength of glass fiber-reinforced novolac-type phenolic resin composites modified with polyamide.

Figure 3 Effect of PA-6 and PA-66 content on the tensile strength of glass fiber-reinforced novolac-type phenolic resin composite modified with polyamide.

the PA-66-modified composite were better than those of the PA-6-modified one. In our previous study, it was found that intermolecular hydrogen bonding is higher than the self-association of phenolic and polyamide.[9] The intermolecular hydrogen bonding within phenolic/PA-66 is higher than that within phenolic/PA-6. The miscibility of phenolic/PA-66 at the molecular level is higher than that of phenolic/PA-6.

TGA and Flame Retardance

Figure 4 shows the TGA of the pure phenolic resin and pure polyamides. The decomposition temperature of polyamide is higher than that of pure phenolic due to its intrinsic properties. Figures 5 and 6 illustrate the TGA of polyamide-modified phenolic resin. From the derivative of the weight-loss curve, one can find the decomposition temperature of the modified phenolic resin increased

with increasing polyamide content, as summarized in Table III. It is observed that the decomposition temperature of the 50/50 phenolic/polyamide blend is higher than predicted. In addition, the decomposition temperature of the 50/50 phenolic/PA-66 is higher than that of the 50/50 phenolic/PA-6 blend. These results provide evidence that the intermolecular hydrogen bonding within this blend system is higher than the intramolecular hydrogen bonding and the intermolecular hydrogen bonding within 50/50 phenolic/PA-66 is higher than that of 50/50 phenolic/PA-6 blend. The decomposition temperature of the modified phenolic resin is above 400°C, indicating that the modified phenolic resin has good thermal stability.

The flame retardance of the compression-molded glass fiber-reinforced modified phenolic resin shows an extremely high LOI value (>55) and the property of UL-94, V-0, even when the polyamide content is as high as 9 wt % content. The effect of minor polyamide content on flame retardance was insignificant because the phenolic

Figure 4 TGA curves of neat (a) novolac, (b) PA-6, and (c) PA-66 at a heating rate of 10°C/min in air.

Figure 5 TGA curves of (a) novolac-type phenolic resin, (b) PA-6/novolac: 50/50 (w/w), and (c) neat PA-6 at a heating rate of 10°C/min in air.

resin and the glass fiber are high char-yield materials. Table IV lists all data of the flammability test.

Morphology of the Composite

The morphology of the composite was investigated by SEM photography as shown in Figure 7. From Figure 7(a), it can be observed that the wet-out of the fiber by neat phenolic resin is poor. Figure 7(b) shows that the fiber wet-out of the fiber-reinforced modified phenolic composites is better than that of the unmodified phenolic composite [Fig. 7(a)]. Because the amide group of polyamide can interact with a hydroxyl group of the phenolic, the mobility of phenolic resin is increased, and the wet-out between matrix and glass fiber is also enhanced. The SEM photographs in Figure 7 show crack propagation under cleavage fracture. There is clear crack propagation in Figure 7(b), while that in Figure 7(a) is smooth, implying that the toughness of the ma-

Figure 6 TGA curves of (a) novolac-type phenolic resin, (b) PA-66/novolac: 50/50 (w/w), and (c) neat PA-66 at a heating rate of 10°C/min in air.

trix increased with the addition of polyamide. The wave pattern becomes more severe, as is observed when the polyamide content increases as shown in Figure 7. The soft segment of polyamide absorbs fracture energy by yielding and softens the matrix. The mechanical properties depend on both the polyamide content and wet-out of the glass fiber. The notched Izod impact strength and flexural modulus of the composite increased with

Table III   Weight Loss of PA-6/Novolac and PA-6.6/Novolac Blends by TGA Analysis

	$T_{5\%}$[a] (°C)	$T_{10\%}$[b] (°C)
Neat Novolac	255	**297**
50 wt % PA-6	295	356
Neat PA-6	370	401
50 wt % PA-6.6	243	377
Neat PA-6.6	377	408

[a] Temperature (°C) for 5% weight loss.
[b] Temperature (°C) for 10% weight loss.

the initial addition of the polyamide and decreased when the polyamide content was more than 7 wt %.

CONCLUSIONS

1. The soft segments of polyamide reinforce the rigid structure of phenolic resin by intermolecular hydrogen bonding when the phenolic resin is modified; hence, the loads applied are absorbed by the soft segments of polyamide and, the toughness of the phenolic resin is improved significantly.
2. At high polyamide content, the high viscosity will cause poor wet-out between the matrix and glass fiber and the mechanical properties of the composite will decrease when the polyamide content is more than 7 wt %.
3. The mechanical properties of the postcured composite show higher values than those before postcure because the reaction of the postcured one is more complete.
4. The decomposition temperature of the polyamide-modified phenolic resin is above 400°C, indicating that the modified phenolic resin possesses good thermal stability.
5. The wet-out of fiber by neat phenolic resin is poor. The amide group of polyamide can interact with the hydroxyl group of phenolic resin and increase the mobility of phenolic resin; hence, the wet-out between the matrix and the glass fiber is also enhanced.

Table IV   UL-94 and LOI Test Results (Flammability) of Novolac/PA-6 and PA-66 Blends

Wt % of Polyamide	Flamming Drops	Cotton Ignited	UL-94 Standard	LOI
1, 3, 5, 7, 9	N/A	N/A	V-0	> 55
1, 3, 5, 7, 9	N/A	N/A	V-0	> 55

N/A, not available. Condition of cure: 130°C (top plate) and 150°C (bottom plate) for 1 h. Condition of postcure: 180°C for 1 h.

Figure 7   SEM photograph of (a) novolac-type phenolic resin and (b) PA-66/Novolac: 5/95 (w/w).

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