

Processability and Properties of Phenoxy Resin Toughened Phenolic Resin Composites

HEW-DER WU, CHEN-CHI M. MA,* JIA-MIN LIN

Institute of Chemical Engineering, National Tsing-Hua University, Hsinchu, Taiwan, 30043, Republic of China

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ABSTRACT: A novel method has been developed to toughen phenolic resin using phenoxy resin. Phenoxy resin was dissolved in phenol to form a glutinous mixture at 110°C, and an acid catalyst (*p*-toluene sulfonic acid, PTSA) was utilized to reduce the viscosity of mixture. The mixture was blended with resole-type phenolic resin.

IR spectra confirmed that the amount and strength of hydrogen bonds increased with PTSA content, and the viscosity decreased with PTSA content in the polymer blends.

The wet-out of glass fiber by modified resin was improved. The flexural and notched Izod impact strength of the polymer-blend composites increased significantly. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 911–917, 1997

Key words: polymer blend; phenolic; phenoxy; toughness; hydrogen bond

INTRODUCTION

Phenolic resin is one of the earliest synthetic resins to possess excellent fire retardance and low smoke density and toxic emission.^{1–4} It is widely used in the construction and electrical industries, etc.^{3,5} However, unmodified phenolic resin is a brittle material with limited application. Much research has been conducted to improve the properties of phenolic resin. The polyester-phenolic copolymer has been synthesized to improve the mechanical properties and heat resistance.⁶ Phenolic resin blended with polyurethane also can provide higher mechanical properties.⁷

Two main types of polymer blending processes have been studied, i.e., melt-blending and solution-blending methods.⁹ The former is not suitable for the active resole-type phenolic resin, since it will cure under a melt-blending process. The solu-

tion method is suitable for active resole-type phenolic resin to blend with the thermoplastic resin. However, a higher modifier content solution will increase the viscosity and reduce the processability of the polymer blend system. In order to select a suitable solvent for the polymer blend, it must have a higher modifier content and possess good processability in solution. In this study, a novel blend process for phenoxy and phenolic resin blending was developed, giving a lower viscosity at a high modifier content. It can be used for blends with resole-type phenolic resin at lower viscosity to improve mechanical properties.

The effect of the relative IR absorption spectrum of the free and hydrogen-bonded hydroxyl band on the specific miscibility of the polymer blend was studied. The rheological behavior of the phenoxy/phenol solution and the mechanical properties of the composite were also investigated.

EXPERIMENTAL

Materials

Phenoxy resin, PKHH, was obtained from the Union Carbide Co., USA with a molecular weight

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M_n of 23,000. Phenolic resin, PF-750 a resole-type phenolic with 75 wt % solid content, was obtained from the Chung-Chen Resin Co., Hsin-Chu, Taiwan. The catalyst, *p*-toluene sulfonic acid, was obtained from the Hayashi Pure Chemical Industries Ltd., Japan. The reactive solvent, phenol, was purchased from the Merck Co. The E-glass fiber roving was obtained from the PPG Co., USA.

Samples Preparation

The mixture with various phenoxy/phenol ratios was heated at 110°C for one-half hour. Then 5 wt % of *p*-toluene sulfonic acid (based on the amount of phenolic resin) was added to the phenoxy/phenol solution at 110°C for another one-half hour.

The solution with *p*-toluene sulfonic acid and phenolic resin was stored at 80°C. The solution and phenolic resin were mixed in a stirrer glass reactor until the mixture was cooled to ambient.

IR Measurements

A Perkin-Elmer infrared spectrometer with the NaCl disk method was used to measure the IR spectra. All of the spectra were scanned at a resolution of 2 cm^{-1} .

Viscosity Measurement

In order to investigate the effect of the *p*-toluene sulfonic acid (PTSA) on the viscosity of the phenoxy/phenol solution and the pot life of the polymer blend, the viscosity was measured at 110°C using a Brookfield viscometer, following the specification of ASTM-D2373. The relationship was recorded at constant temperature using LV-1, LV-2 and LV-3 type spindles.

Pultruded Composite Specimen

The pultrusion machine used has been described elsewhere.⁷ The dimensions of the die were $82 \times 1.27 \times 0.33$ cm. The heating temperature profile of the die was controlled by two heating plates along the pultrusion direction. The surfaces of the stainless steel die were treated by chrome plating. The pulling rate was 30 cm/min at die temperatures of 180°C and 200°C.

Mechanical Properties

Notched Izod impact strength (ASTM-D256), tensile strength (ASTM-D638), and flexural strength

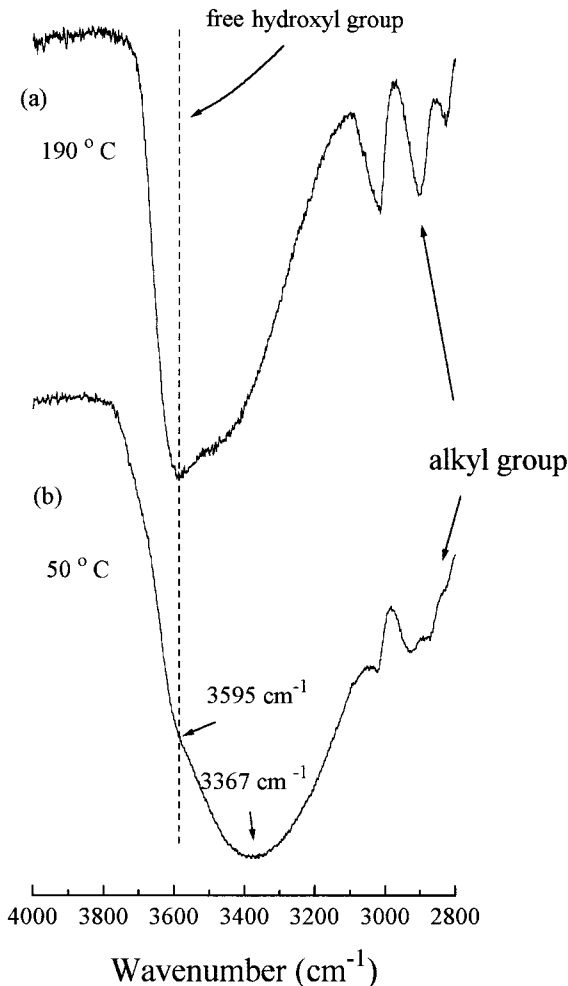


Figure 1 The IR spectra of hydroxyl stretching of the pure phenolic resin scanned at different temperatures: (a) 50°C, (b) 190°C.

(ASTM-D790), were carried out at ambient conditions.

RESULTS AND DISCUSSION

Miscibility Study

Infrared Spectrum of Pure Phenolic Resin

As shown in Figure 1, there is a broad band in the high-frequency region from 3800 to 2800 cm^{-1} , where the hydroxyl stretching vibration can be observed. At room temperature, the hydroxyl group is characterized by a very broad band at 3367 cm^{-1} , which is attributed to the wide distribution of the hydrogen-bonded hydroxyl group, whereas a narrower band is observed at 3595 cm^{-1} , which is the free hydroxyl group. As the

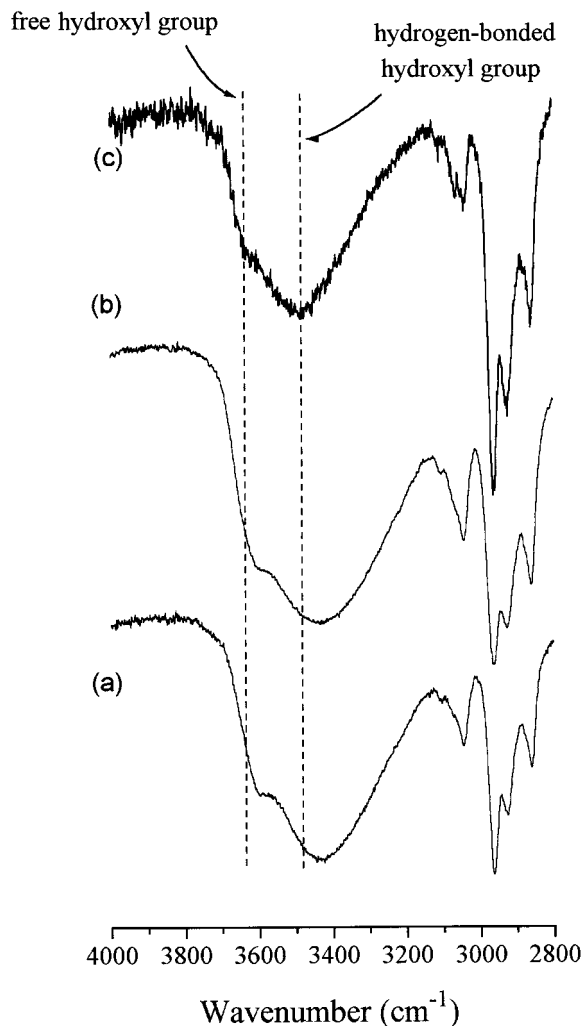


Figure 2 The IR spectra of the hydroxyl stretching of phenoxy/phenol solutions with various weight ratios: (a) 15/25, (b) 15/15, (c) 15/0.

temperature increased, the relative absorption of the free hydroxyl group increased while that of the hydrogen-bonded hydroxyl group decreased. In addition, the peak of the hydrogen-bonded hydroxyl shifted to the higher frequency region, which is attributed to the decrease of the average bond strength of hydrogen-bonded species at higher temperatures.

Infrared Spectrum of Phenoxy Dissolved in Phenol

The IR spectra of the solutions with various phenoxy/phenol ratios made by the hot-melt method were measured at room temperature. Figure 2 shows the IR spectra of the hydroxyl stretching ($3800\text{--}2800\text{ cm}^{-1}$) of phenoxy/phenol solutions.

The pure phenoxy exhibits two peaks in the hydroxyl stretching region of the infrared spectrum. The first peak occurs at 3614 cm^{-1} , corresponding to the free hydroxyl group. The second peak is a broader band appearing at 3476 cm^{-1} , which is attributed to the hydrogen-bonded hydroxyl (self-association) group. The hydroxyl group in the phenoxy was almost completely self-associated. The free hydroxyl band increased in the blends with increasing phenol content. The band of the hydrogen-bonded hydroxyl shifted to lower frequency with increasing phenol.

There are three major components in the spectra of the solutions. The first is the free hydroxyl, the second is the self-association of hydrogen-bonded hydroxyl, and the third is the intermolecular associated hydroxyl group between phenol and phenoxy.¹⁰ Figure 2 shows the average strength of the hydrogen bond between phenoxy resin and phenol, as measured by the difference in the frequency from that of the hydroxyl ($\sim 179\text{ cm}^{-1}$), which is higher than that of the average strength of the self-associated pure phenol ($\sim 167\text{ cm}^{-1}$) and pure phenoxy ($\sim 138\text{ cm}^{-1}$). The average strength of the hydrogen bond of the solution is stronger than both the average strength of the pure phenol and the pure phenoxy. The strength of the hydrogen bonds increased when the phenoxy was dissolved in the phenol.

Figure 3 shows the infrared spectra of phenoxy/phenol solutions with PTSA prepared by the hot-melt method. The band at 3400 cm^{-1} (hydrogen-bonded hydroxyl) can be observed for all of the PTSA-containing solutions [Figure 3 (b,c)]. The hydrogen-bonded hydroxyl band solution containing PTSA was broader and larger than that of the PTSA-free solution [Figure 3(a)], and shifted to lower frequency. The spectra features have been observed in compatible phenoxy/poly(vinyl methyl ether) blends.¹² The band of hydrogen-bonded hydroxyl group shifts to lower frequency in a miscible polymer system. The band of free hydroxyl group at 3598 cm^{-1} does not shift or change to any measurable extent. The average strength of the hydrogen bond of PTSA-containing solution ($\sim 198\text{ cm}^{-1}$), as measured by the difference in frequency between the hydrogen-bonded and free hydroxyl group, is higher than that of the average strength of the hydrogen bond of the PTSA-free solution ($\sim 179\text{ cm}^{-1}$). The higher average strength of the hydrogen bond causes a significant decrease of viscosity. From Table I one can find that the viscosity of the phenoxy/phenol

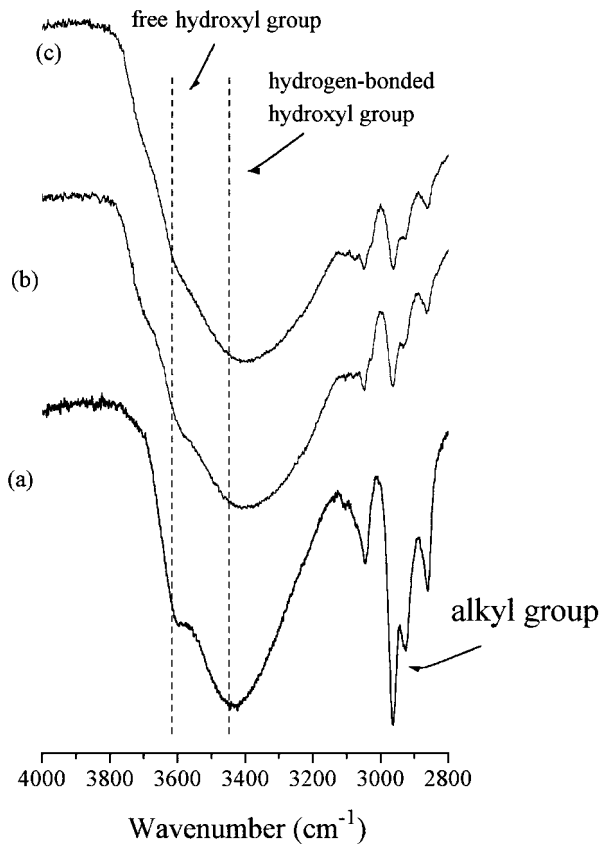


Figure 3 The IR spectra of the hydroxyl stretching of phenoxy/phenol/PTSA solutions with various PTSA weight ratios: (a) 9/15/0, (b) 9/15/1, (c) 9/15/5.

(15/15) decreased from 12,000 to 300 cps when the PTSA was added to the phenoxy/phenol solution. The PTSA donates protons to the blend system and increases the amount and the strength of the hydrogen bonds significantly. The phenoxy chain in the phenol can move more easily than in the PTSA-free solution; hence the viscosity is reduced.

Infrared Spectrum of Uncured and Cured Blended Phenolic Resin

The IR spectra of the uncured and cured polymer blends of phenolic resin (100 phr) with phenol (15 phr), phenoxy (9 phr) and PTSA (5 phr) are shown in Figure 4. The relative strength of the hydrogen-bonding interaction involved in the phenolic blends was studied. After curing at 160°C for two hours, the hydroxyl-stretching band of the blends became narrower and shifted to higher frequency. The relative absorbency of the hydrogen-bonded hydroxyl group decreased when the poly-

mer blend was heated. The band at 3599 cm^{-1} (free hydroxyl), observed for the cured blends, does not shift or change to any measurable extent. It indicates that both the intra- and intermolecular hydrogen bonds were destroyed in the phenolic network after heating at 160°C for 2 hours. The formation of the network of cured phenolic restricted segmental motion, hence reduced the interaction between hydroxyls. The segmental motion of phenoxy was frozen by the phenolic network.

Effect of PTSA Content on the Viscosity of the Solution

For a sticky polymer solution, the change of viscosity may depend on the degree of molecular en-

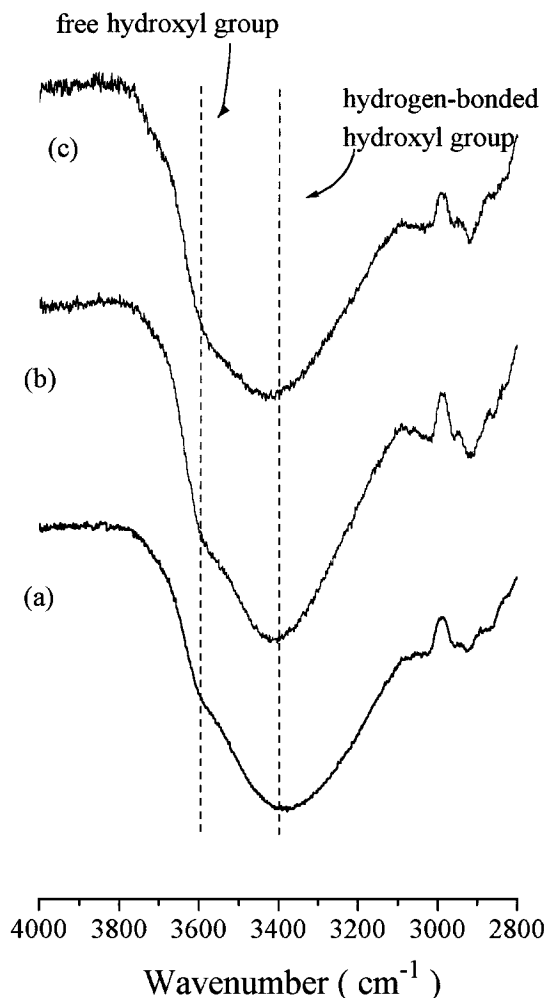
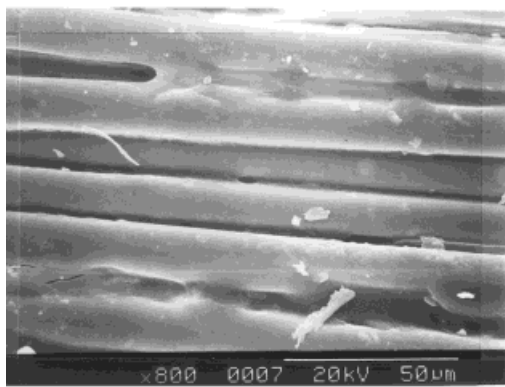


Figure 4 The IR spectra of the hydroxyl stretching of phenolic/phenoxy/phenol/PTSA (100/9/15/5 by weight) blends at various cured times at 180°C: (a) 0 min, (b) 5 min, (c) 2 h.

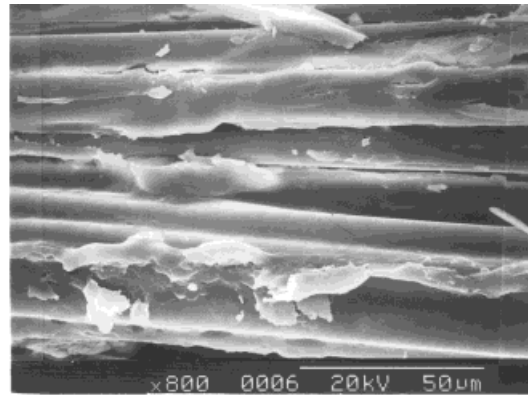
Table I The Viscosity of the Various Ratios of Phenoxy/Phenol

| Ratio of Phenoxy/Phenol (wt ratio) | 3/15 | 6/15 | 9/15 | 12/15 | 15/15 | 18/15 |
|---|------|-------|-------|--------|---------|---------|
| Viscosity of the PTSA-free Solution (cps) | 200 | 1,310 | 8,900 | 30,000 | 120,000 | 320,000 |
| Viscosity of the PTSA- containing Solution (cps) | 40 | 60 | 180 | 220 | 300 | 420 |

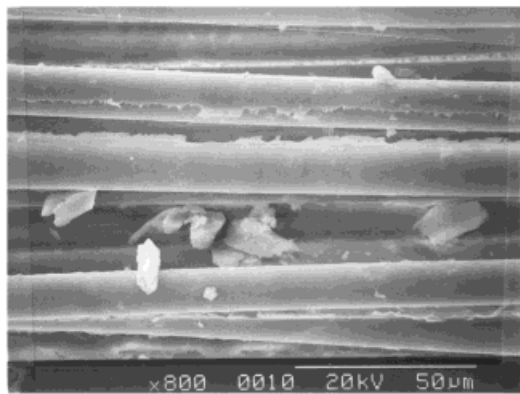
The weight of PTSA is based on 1/15 of the weight of phenol.
The test temperature is 110°C.



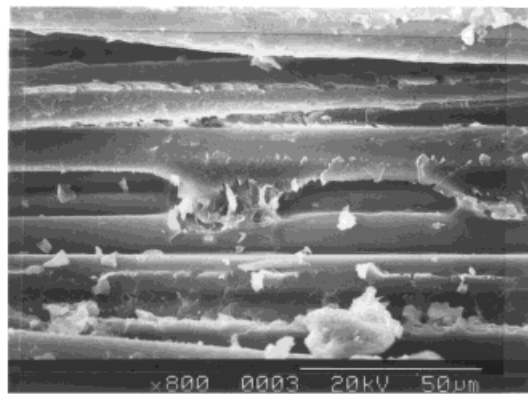
(a)



(c)



(b)



(d)

Figure 5 The SEM photographs of the pultruded fiber-reinforced phenoxy-toughened phenolic resin composite with various phenoxy contents: (a) 0 phr (pure phenolic), (b) 6 phr, (c) 12 phr, (d) 18 phr.

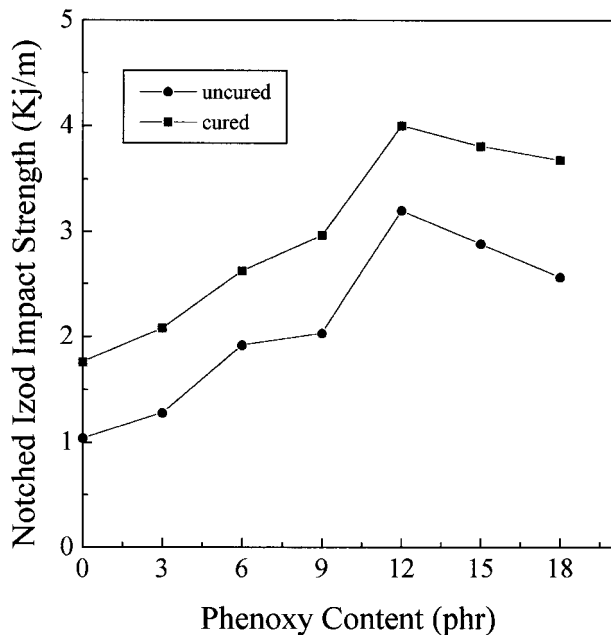


Figure 6 The notched Izod impact strengths of pultruded fiber-reinforced phenoxy resin-toughened phenolic resin: (●) uncured; (■) cured.

tanglement.^{11,12} The physical crosslinks due to entanglements will affect the viscosity of the sticky solution. The PTSA-free solution shows a sticky solution because the phenoxy chain has a lower extension, hence the lower interaction with phenols. When PTSA is added to the solution, the amount and the average strength of the hydrogen-bonded interaction between phenol and phenoxy increases, and the degree of entanglements decreases. PTSA donates protons to the phenoxy/phenol solution, causing the increase of the amount and strength of interaction between phenoxy resin and phenol. Figure 3 shows that the amount of the hydrogen-bonded hydroxyl increases significantly. The increasing amount of the hydrogen bond results in a lower viscosity. A suitable organic acid can adjust the viscosity of the phenoxy/phenol solution for blending. The viscosities of PTSA-free and PTSA-containing phenoxy/phenol solution are shown in Table I.

Morphology of Pultruded Composites

The morphology of pultruded fiber-reinforced phenoxy-toughened phenolic resin composite was investigated by SEM photographs as shown in Figure 5. From Figure 5(a), it is observed that the fiber bundles are distributed evenly in the pure phenolic matrices; however, the wet-out of the fi-

ber is poor. Figures 5(b), 5(c), and 5(d) show that the fiber wet-out of the fiber-reinforced phenoxy/phenolic composite is better than that of the unmodified phenolic composite [Figure 5(a)]. The fiber wet-out in the polymer blend containing 18 wt % phenoxy is the best one. The hydroxyl groups of the phenoxy can interact with the hydroxyl groups of the glass fiber. Consequently, phenoxy resin improves the interfacial bonding between the glass fiber and the matrix.

The SEM photograph in Figure 5(a) shows crack propagation under cleavage fracture. From Figures 5(b), 5(c), and 5(d), it can be seen that when the phenoxy content increases, the wave pattern becomes more severe, since the soft segment of phenoxy absorbs fracture energy by yielding and thus softens the matrix. The results show that the notched Izod impact strength increases with the phenoxy content.

Mechanical Properties

Improvement of the mechanical properties of the polymer blends based on composites containing phenolic, phenoxy and phenol have been demonstrated clearly in this study. Figure 6 shows that the impact strength of the polymer blend-based composites increases with phenoxy content, the maximum value appearing at the 12 phr phenoxy

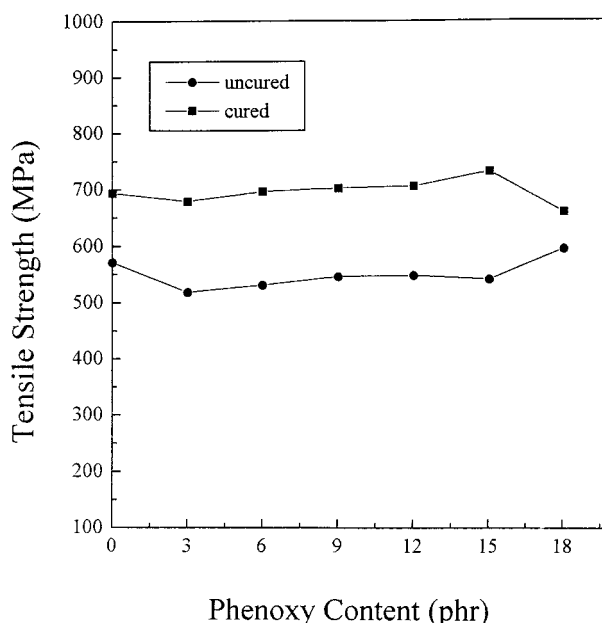


Figure 7 The tensile strengths of pultruded fiber-reinforced phenoxy resin-toughened phenolic resin: (●) uncured; (■) cured.

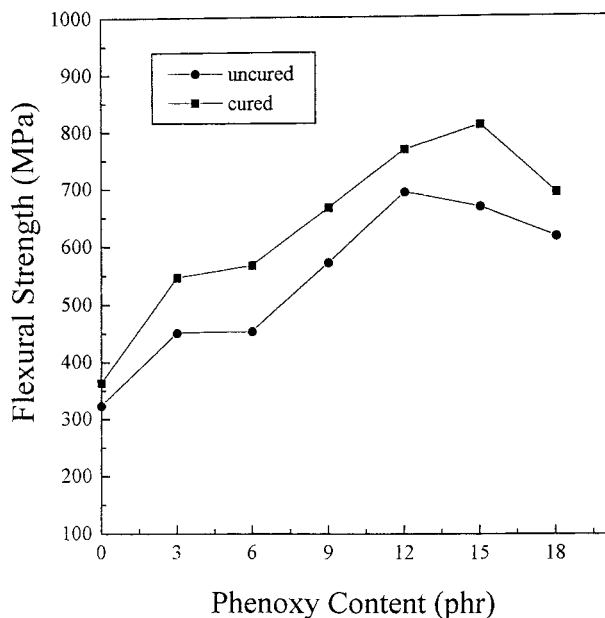


Figure 8 The flexural strengths of pultruded fiber-reinforced phenoxy resin-toughened phenolic resin: (●) uncured; (■) cured.

level. Figure 7 shows that the tensile strength of the polymer blend-based composite is almost independent of the phenoxy content of the phenolic matrix. The tensile strength of the composite depends on the wet-out of the fiber and on the matrix. In this system, the solvent (phenol) in the matrix increases the crosslink density and reduces the wet-out of glass fiber; hence the polymer is brittle. On the other hand, the presence of the phenoxy improves the interface between the matrix and glass fiber. Both factors balance and cause the tensile strength to be almost independent of the phenoxy content. Figure 8 shows that the flexural strength of the polymer blend-based composites increases with phenoxy content, the maximum value also appearing at the 12 phr phenoxy level. The mechanical properties of the post-cured composites are higher than those of uncured ones, since the postcured specimens may react more completely.

CONCLUSIONS

The presence of the organic-acid catalyst in a phenoxy/phenol solution improved the processability of the polymer blend. The amount and strength of hydrogen bonding in the phenoxy/phenol solution

increased significantly when the organic-acid catalyst was added. The interaction between phenol and the phenoxy chains increased, and the viscosity of the phenol/phenoxy solution was reduced.

When the phenolic/phenoxy/phenol blends were cured, the hydrogen bonding decreased significantly within the phenolic network. The phenolic network may freeze the motion of phenoxy segments.

The interface between the matrix and glass fiber of the phenoxy-toughened resole-type phenolic resin was improved; consequently, the mechanical properties of the composites increased significantly.

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