Pultruded Fiber-Reinforced Polyurethane-Toughened Phenolic Resin. II. Mechanical Properties, Thermal Properties, and Flame Resistance

HEW-DER WU, MING-SHIU LEE, YIU-DON WU, YI-FENG SU, and CHEN-CHI M. MA*

Institute of Chemical Engineering, National Tsing Hua University, Hsin-Chu, Taiwan, 30043

SYNOPSIS

A novel process has been developed to toughen phenolic resin by polyurethane for fiber-reinforced pultruded composites. The mechanical properties of the composites (tensile strength, flexural strength, and notched Izod impact strength) approach maximum values at 10 wt % of the blocked polyurethane content. The fabricated composites show good mechanical properties and possess low void fraction. Notched Izod impact strength of the composite (with 5 wt % polyurethane content) increases by more than 30% compared to the virgin composite. The thermogravimetric analysis (TGA) showed that the temperature for the 5% weight loss of the phenolic/polyurethane copolymer decreases with the increasing of the polyurethane content; however, the thermal degradation temperature is still higher than 350°C. Differential scanning calorimetric analysis (DSC) showed that the onset point of copolymer is 20°C higher than that of the virgin one. The presence of the blocked polyurethane may hinder the polymerization of phenolic resin. The modified composite shows excellent dimensional stability. The copolymer composite also possesses good fire resistance. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Phenol-formaldehyde thermosetting resins have been widely used in industry, due to their good heat resistance, electrical insulation, dimensional stability, flame resistance, and chemical resistance.[1-7] However, there are some limitations for wide applications; for instance, water and formaldehyde generated in the condensation reaction would cause crazing and porosity in the cured resin. The phenolic resin is brittle with poor fiber wet-out; hence, its applications are limited. Recently, many approaches have been proposed to improve the toughness of the phenolic resin.[8-11] Matsumoto et al. modified the phenolic resin with p-Hydroxyphenylmaleimide/ Acrylic ester copolymer to improve the toughness of resin.[11] The ester based copolymer shows higher toughness than the unmodified phenolic resin be-

cause the ester based copolymer is more flexible than the virgin resin. In this study, a novel method by blending the phenolic resin with ester-based blocked polyurethane is proposed to overcome these deficiencies. The modified resin has been toughened, and the void content of the composite has also been reduced. When the blocked polyurethane is deblocked, it can react with the hydroxyl groups of the phenolic resin and with the surface of glass fiber.[12] Consequently, the block polyurethane serves as a toughening agent and a coupling agent.[12] Both functions improve the mechanical properties of the resultant composite.

In this study, the mechanical properties (including tensile strength, flexural strength, and notched Izod impact strength) of the phenolic/polyurethane copolymer composites show maximum values at 10 wt % polyurethane content. The void fraction decreases with the polyurethane content. Phenolic polymer is a high char-yielded polymer material that is suitable to be designed as a high-temperature flame-resistant material.[1]

EXPERIMENTAL

Materials

The materials used in this study are listed in Table I. The catalyst, p-toluene sulfonic acid (PTSA), was dissolved in dipropylene glycol with stirring under a nitrogen atmosphere at 80°C. Phenolic resin, blocked polyurethane, and catalyst solution were blended under nitrogen atmosphere at room temperature.

Sample Preparation

Polymer systems containing 0 to 20 wt % of blocked-polyurethane, 5 wt % of catalyst (PTSA), 5 wt % of dipropylene glycol, and 70–90 wt % of phenolic resin were blended.

The pultrusion machine used was described previously.[13] The dimensions of die were 82 × 1.27 × 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 have been treated by chrome plating. The pulling rate was 30 cm/min at die temperatures of 180 and 200°C. The diameter of E-glass type Glass fiber used was 13.1 μm in the pultrusion system.

The postcured process was conducted by heating the sample at 200°C for 1 hour.

Property Measurement

Tensile strength was measured on an Instron 4201 following the specification of ASTM D-3039. The sample dimensions were 20.8 × 1.27 × 0.33 cm (length × width × thickness), and the crosshead speed was 5 mm/min. Flexural strength and flexural modulus were measured following the specification of ASTM D-790. The sample dimensions were 12.7 × 1.27 × 0.33 cm, the span was 9 cm, and the crosshead speed was 2 mm/min. The notched Izod impact strength was measured following the specification of ASTM D256.

The thermogravimetric analysis was conducted with a DuPont TGA from room temperature to 800°C at a rate of 5°C/min under a nitrogen gas atmosphere. Differential scanning calorimetric (DSC) analysis was performed on a DuPont DSC-2000 instrument at atmospheric pressure. The sample was heated in a DSC sample cell at 5°C/min from room temperature to 250°C with nitrogen gas flow.

Thermal expansion of the phenolic resin composite was measured using a conventional quartz dilatometer and a thermal mechanical analyzer.[14] The dimensions of specimen for expansion measurement of the phenolic resin composite are 10 mm in diameter and 3.3 mm in thickness. All thermal expansion measurements were carried out in a nitrogen atmosphere. The heating rate was 10°C/min from 25 to 200°C.

Table I   Materials Used in This Study

Material	Specification	Supplier
Phenolic resin	PF-750 resole type viscosity < 1500 cp phenol < 1% formadehylde < 1%	Chang Chun Resin Co. Taiwan
Blocked polyurethane	Desmodur BL 1100 NCO equiv. = 1355 based on polyester polyol	Bayer Co. Germany
Dipropylene glycol	MW = 134.18	Hayashi Pure Chemical Industries Ltd., Japan
P-toluene sulfonic acid	purity > 96.0% MW = 190.21	Hayashi Pure Chemical Industries Ltd., Japan
E-glass fiber roving	764-NT-218 diameter = 13.1 μm	PPG Co., USA

Table II   Material Classifications for Flammability Test[15]

Criteria Conditions	94V-0	94V-1	94V-2
Afterflame time for each individual speciment (t_1 or t_2)	≤10 s	≤30 s	≤30 s
Total afterflame time for any condition set (t_1 plus t_2 for the 5 specimens)	≤50 s	≤250 s	≤250 s
Afterflame plus afterglow time for each individual specimen after the second flame application ($t_2 + t_3$)	≤30 s	≤60 s	≤60 s
Afterflame or afterglow of any specimen up to the holding clamp	No	No	No
Cotton indicator ignited by flaming particles or drops	No	No	Yes

The following are to be observed and recorded: Afterflame time after first flame application, t_1; afterflame time after second flame application, t_2; afterglow time after second flame application, t_3; whether or not specimens burn up to the holding clamp; and whether or not specimens drip flaming particles which ignite the cotton indicator. See *UL94 Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances* (Ref. 15).

Void content was measured following the specifications of ASTM D-2584 and D-3171. The samples were placed in an oven at 625°C until all of the resin was burned out. The weight loss of specimen was measured, and the void fraction was calculated.

Flame resistance was measured following the specification of UL 94 Standard.[15] Five specimens with the 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 is 10 mm below the point of lower end of the specimen, then maintained it at that distance for 10 seconds. If only one specimen from one set of five specimens does not comply with the requirements, another set of five specimens is to be tested. Table II shows the specification of the material classifications for flammability test. The limited oxygen index (LOI) was tested following the specification of ASTM D-2863.[15]
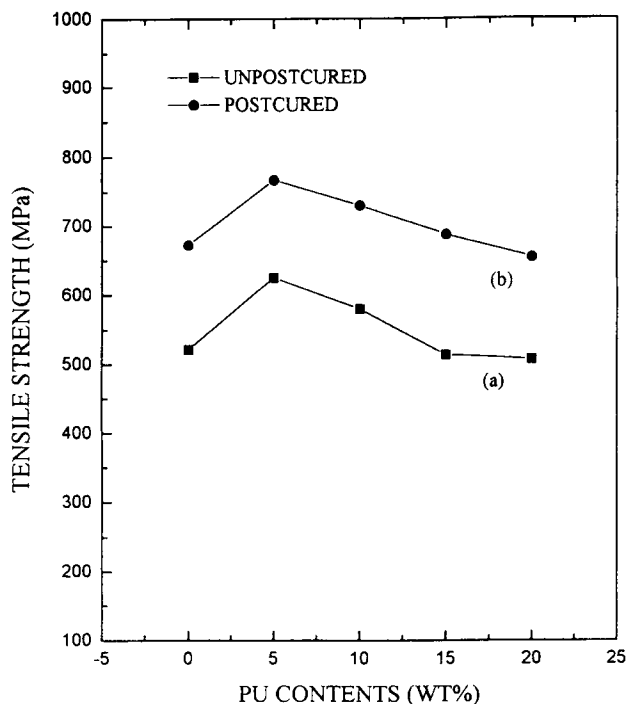
RESULTS AND DISCUSSION

Mechanical Properties

Tensile Strength

Figure 1 shows the tensile strength of pultruded fiber-reinforced polyurethane-toughened phenolic resin. The tensile strength of the modified system shows a maximum value at 5 wt % polyurethane content. This phenomenon is attributed to the decrease of the void fraction of the phenolic matrix by blending with polyurethane. The modified resin system shows excellent wetting and bonding ability to fiber and improves the tensile strength of the composites.[12] On the other hand, the presence of the ester-based polyurethane in the phenolic resin may reduce the cross-linking density and soften the matrix. Consequently, the mechanical properties of the composite decrease. The postcured composites show higher tensile strength than that of the unpostcured counterparts since the postcured samples were reacted completely.

Figure 1   Tensile Strength versus pultruded fiber-reinforced phenolic resin toughened by various polyurethane contents: (a) unpostcured, (b) postcured.

Flexural Strength and Modulus

Figures 2 and 3 show the flexural strength and modulus of the pultruded fiber reinforced phenolic resin toughened by the polyurethane. Flexural strength and modulus show maximum values in the range between 5 and 10 wt % of polyurethane content and then decrease gradually when the polyurethane content is greater than 10 wt %. This behavior can be interpreted when the soft segment of polyurethane is incorporated into the backbone of the phenolic resin, as follows: any load applied will be absorbed by the soft segment first; hence, the flexural strength will be increased. However, when the polyurethane content was more than 10 wt %, phase separation may occur and the flexural strength was decreased. The flexural strength of the postcured composite is higher than that of the unpostcured one. The flexural modulus of the postcured composites is comparable to the unpostcured one.

Notched Izod Impact Strength

The effect of the polyurethane content on the notched Izod impact strength of composite is illustrated in Figure 4. The highest impact value is between 5 and 10 wt % of polyurethane content and a significant improvement in toughness was ob-
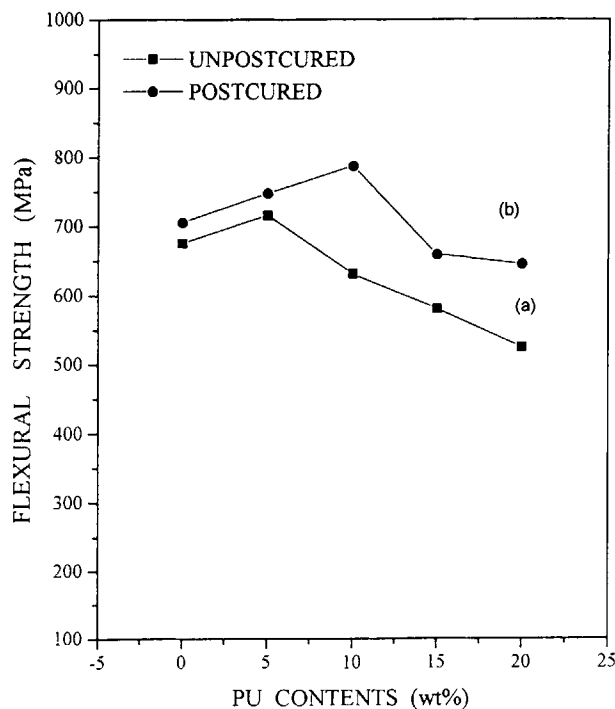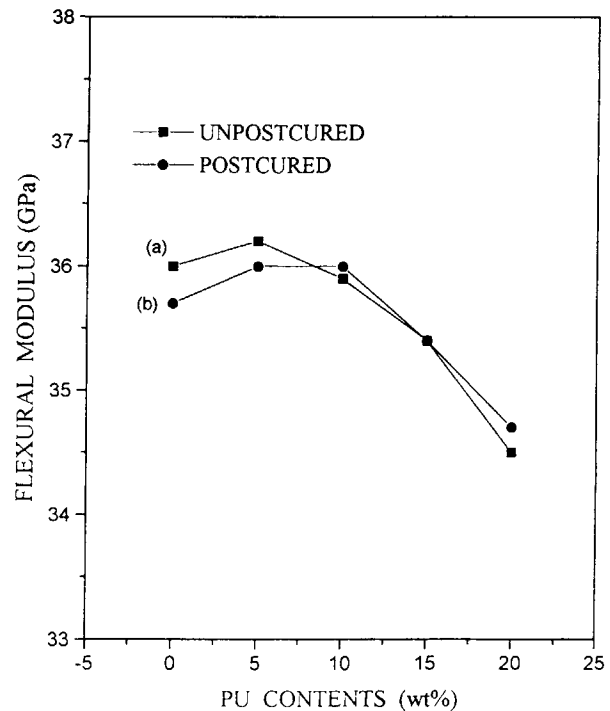

Figure 3 Flexural modulus versus pultruded fiber-reinforced phenolic resin toughened by various polyurethane contents: (a) unpostcured, (b) postcured.

served. The impact strength of the copolymer composite containing 5 wt % of polyurethane is 30% higher than that of the pure phenolic composite. The composites containing higher, flexible, ester-based polyurethane result in a better wet-out of glass fiber.[12] When the polyurethane content is greater than 15 wt %, the impact strength is decreased because the phenolic resin and the blocked polyurethane become immiscible at a higher polyurethane content. A macrophase separation formed in the modified phenolic resins instead of microphase separation. The notched Izod impact strength decreases with the increasing of polyurethane content. The postcured composites show higher notched Izod strength than that of unpostcured due to the reaction of postcured is more complete.

Thermal Properties

Thermogravimetric Analysis

Figure 5 illustrates the thermogravimetric analysis (TGA) of the phenolic/polyurethane copolymer. The polyurethane in the copolymer decomposed gradually at a lower temperature than that of the phenolic resin. From the derivative weight loss curve, it is found that the temperature of the 5%
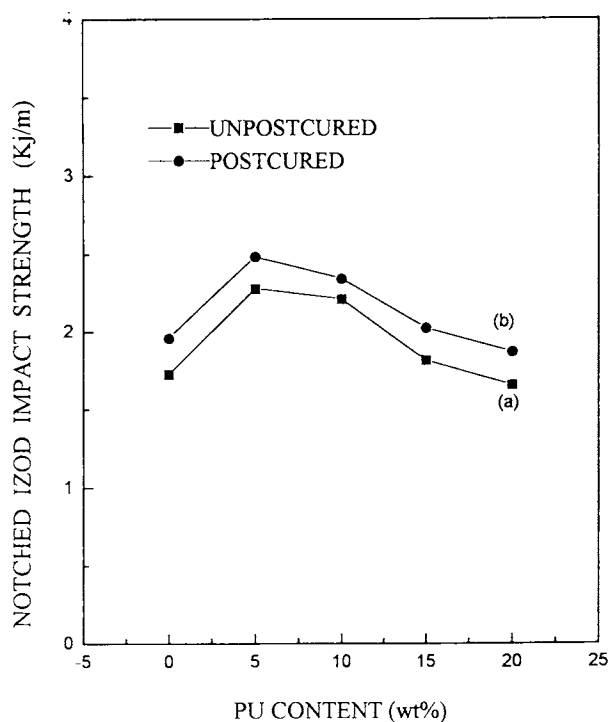

Figure 2 Flexural strength versus pultruded fiber-reinforced phenolic resin toughened by various polyurethane contents: (a) unpostcured, (b) postcured.

Figure 4 Notched Izod impact strength vs. pultruded fiber-reinforced phenolic resin toughened by various polyurethane contents: (a) unpostcured, (b) postcured.

Figure 5 TGA of the phenolic/polyurethane copolymer at various polyurethane contents: (a) 0 wt %, (b) 10 wt %, (c) 20 wt %.

weight loss of copolymer was lowered with the increase of the polyurethane content, as summarized in Table III. The 5% weight loss of the copolymer is over 350°C, indicating that the copolymer possesses good thermal stability.

DSC Analysis

Figure 6 shows the DSC analysis of pure phenolic resin and phenolic/polyurethane copolymer blends under nitrogen surrounding and ambient pressure. Curve (a) of Figure 6 shows that the onset point of the pure phenolic resin is at 126°C. There are two peaks that appear in the DSC trace for pure phenolic resin. The first peak is a larger exothermic peak, relating to the methylene and dimethylene ether bridge at 130–185°C. The second smaller exothermic peak indicates that the reaction will be completed at higher temperature (185–230°C), where the hydroxyl and methylol groups are converted to water and formaldehyde.

Curve (b) of Figure 6 shows the onset point of the copolymer containing 10 wt % polyurethane is at 146°C. In this system, the blocked polyurethane may hinder the reaction between phenolic prepolymer and blocked polyurethane. No reaction occurred below 145°C. When the temperature is higher
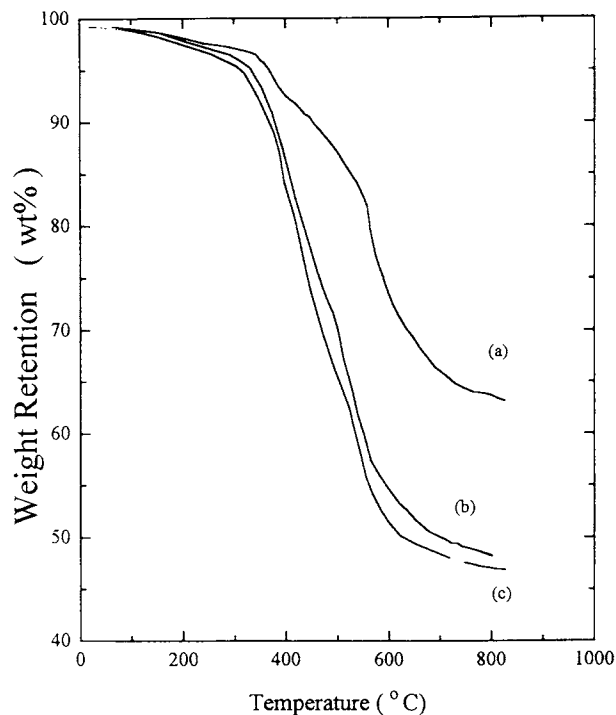
than 150°C, the blocked polyurethane starts to deblock gradually, and the NCO group attracts the hydroxyl group of phenolic resin. The linkage of phenolic resin is extended by polyurethane block instead of the methylene and the dimethylene ether bridge, as described in a previous study.[12] This reaction is very rapid and exhibits exothermic behavior. Curve (c) of Figure 6 shows the on-set point of the copolymer with 20 wt % polyurethane content is at 153°C. The on-set point increases with the increase of blocked-polyurethane content.

Thermal Expansion Ratio

Figures 7 and 8 show the thermal expansion ratio of phenolic composites containing various contents

Table III   The Temperature of 5% Weight Loss of Phenolic/Polyurethane Copolymer with Various PU Contents

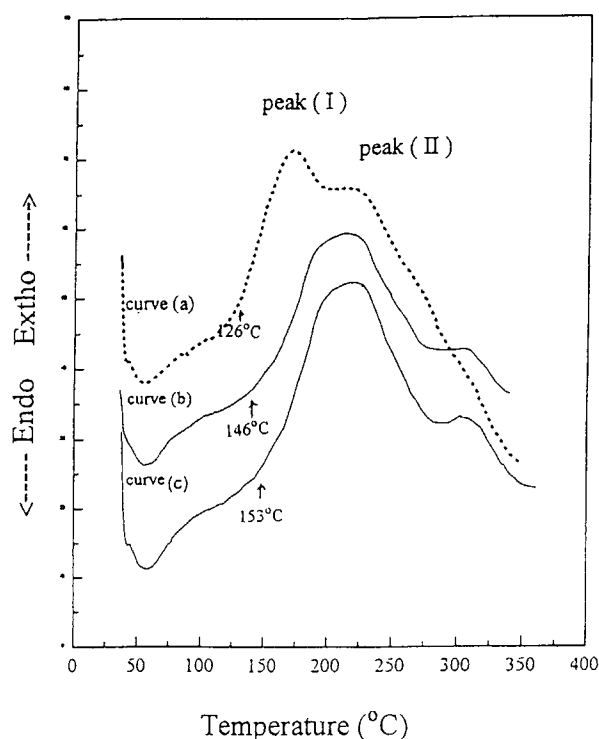| Polyurethane Content	Temperature (°C)
0 wt %	399
10 wt %	355
20 wt %	350

Figure 6   DSC analysis of pure phenolic and phenolic/ polyurethane copolymer: (a) pure phenolic resin, (b) phenolic/PU copolymer with 10 wt % polyurethane, (c) phenolic/PU copolymer with 20 wt % polyurethane.

of the blocked polyurethane before and after postcure, respectively. Figure 7 shows the thermal expansion curves of the unpostcured ones, which have minimum values, indicating the reaction was not complete at lower temperature. The unpostcured copolymer specimen may be reacted further with the hydroxy of phenolic and polyurethane at higher temperature. The coefficient of thermal expansion from 50 to 130°C decreases due to the loss of volatiles (water and formaldehyde), causing the specimen to shrink. When volatiles are being driven off sufficiently at higher temperature, the coefficient of thermal expansion of the specimen will be increased with temperature at higher temperature region.[14] The coefficient of thermal expansion decreases with the increase in polyurethane content. The higher polyurethane content may decrease the amount of volatiles; therefore, the temperature of shrinkage is decreased due to less volatiles. Consequently, the coefficient of thermal expansion curves showed S-shape.

Figure 8 shows a two-stage thermal expansion ratio after postcuring. At a temperature below 100°C, the dimension is stable; but the thermal expansion ratio increases when the temperature is

higher than 100°C. The thermal expansion coefficients are 20, 23, and 30×10^{-6} m/m°C^{-1} for the composites with blocked-polyurethane contents of 25, 10, and 0 wt %, respectively. Higher blocked-polyurethane content results in a lower thermal expansion coefficient.

It is expected that the semicured specimens are less stable with higher expansion ratio than those of the fully cured specimens. The fully cured specimen has a more stable chemical structure. The higher PU content in the phenolic network results in a lower thermal expansion ratio of the copolymer than that of the virgin one.

Void Content

The void content of the composite decreases with the increase of polyurethane content, as illustrated in Figure 9. The copolymer composites containing polyurethane may decrease the amount of volatiles (water, formaldehyde, and by-products) generated during polymerization.

Flame Resistance

Flame resistance of pultruded fiber-reinforced phenolic composite toughened by polyurethane is sum-
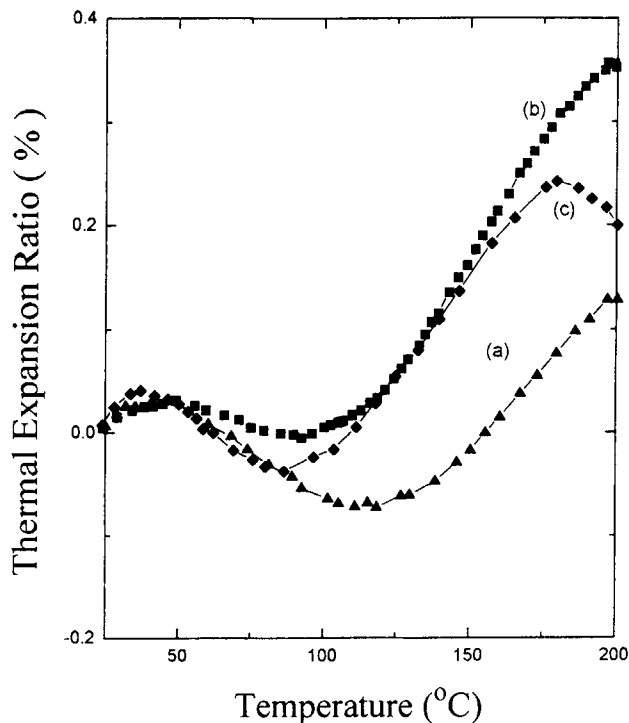

Figure 7   The thermal expansion ratio of PU-modified resole type phenolic unpostcured composite with various PU contents: (a) 0 wt %, (b) 10 wt %, (c) 25 wt %.
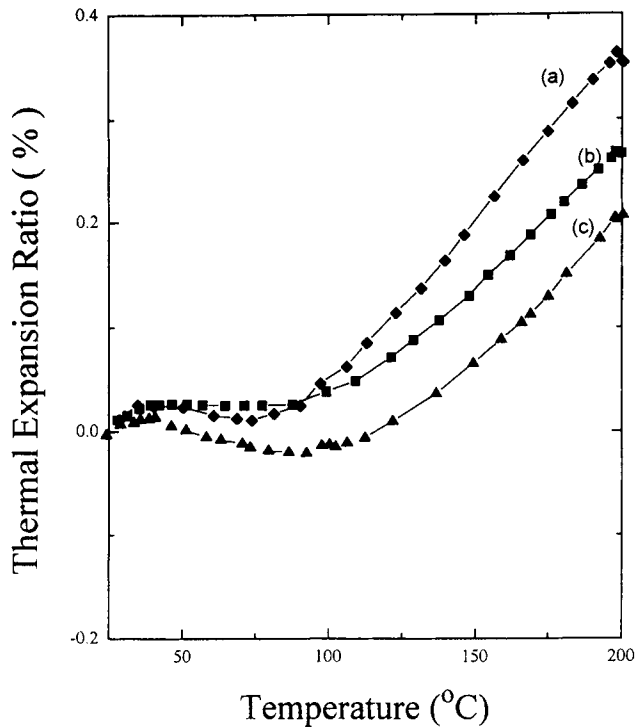
Figure 8 The thermal expansion ratio of PU-modified resole type phenolic postcured composite with various PU contents: (a) 0 wt %, (b) 10 wt %, (c) 25 wt %.

marized in Table IV. The flame resistance decreases with the increasing of polyurethane content. The linkages of phenolic are methylene and dimethylene ether. It is difficult for oxygen to react with pure phenolic resin.[1,3] In the phenolic/polyurethane copolymer system, methylene is extended by polyurethane[12] and diproplene glycol; hence, oxygen may react with copolymer easier than with pure phenolic polymer. The phenolic matrix toughen with polyester based polyurethane shows a lower LOI value. The flame resistance of the copolymer-based composite decreases with the increasing of the polyurethane. The copolymer composite containing 10 wt % polyurethane possesses good flame resistance, such as UL-94 V-0 and LOI of 49.

CONCLUSIONS

1. Tensile strength, flexural strength, and flexural modulus of the polyurethane-modified resole type phenolic resin system show maximum values with 5 to 10 wt % polyurethane content. The polyurethane blended with phenolic may reduce the void content of the

matrix. The postcured specimen shows higher mechanical properties than that of unpostcured since the reaction was complete.

2. The notched Izod impact strength of the copolymer composite shows a maximum value at 5 wt % polyurethane content. The impact strength of the copolymer-based composite is 30% higher than that of the pure phenolic composite.

3. From TGA, the temperature of the 5% weight loss of copolymer decreased with the increasing of polyurethane content.

4. From DSC, the blocked polyurethane may hinder the reaction of phenolic prepolymer. The onset point of the copolymerization with 20 wt % polyurethane is 27°C higher than that of the pure phenolic resin.

5. The coefficient of thermal expansion of the composite increases with the increasing of the polyurethane content. After postcuring, the coefficient of thermal expansion of the composite decreases.

6. The flame resistance of pultruded fiber-reinforced phenolic composite toughened by polyurethane decreases with the increase in the polyurethane content. Copolymer based
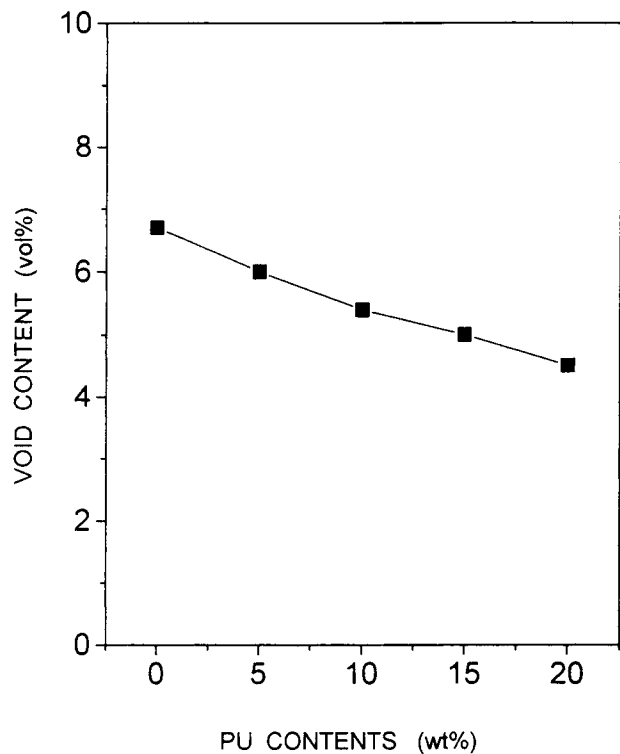

Figure 9 Void fraction vs. pultruded fiber-reinforced phenolic resin toughened by various polyurethane contents.

Table IV   The Flame Resistance of Pultruded Fiber Reinforced Phenolic Resin Toughened by Polyurethane

Polyurethane content (wt %)	0	5	10	15	20
Test for flammability (UL-94)	V-0	V-0	V-0	V-1	V-1
Limit oxygen index (LOI)	55	53	49	42	36

composite with 10 wt % polyurethane content possesses good flame resistance such as UL-94 V-0 and LOI of 49.

REFERENCES

1. Y. Zaks, J. Lo, D. Raucher, and E. M. Pearce, *J. Appl. Polym. Sci.*, **27**, 913 (1982).
2. *Reinf. Plast.*, **38**(6), 36 (1994) (editorial).
3. A. Knop and L. A. Pilot, *Phenolic Resin*, Springer-Verlag, Berlin, 1985, Chap. 1.
4. *Reinf. Plast.*, **36**(6), 30 (1992).
5. E. P. Rossa, *Plast. Eng.*, **44**, 39 (1988) (editorial).
6. G. R. Bishop and P. A. Sheard, *Comp. Struct.*, **21**, 85–89 (1992).
7. C. C. M. Ma and W. C. Shih, U.S. Pat. 4,873,128 (1989).
8. T. P. Yang, T. K. Kwei, and E. M. Pearce, *J. Appl. Polym. Sci.*, **41**, 1327–1332 (1991).
9. A. Matsumoto, K. Hasegawa, A. Fukuda, and K. Ot-suki, *J. Appl. Polym. Sci.*, **43**, 365–372 (1991).
10. A. Matsumoto, K. Hasegawa, A. Fukuda, and K. Ot-suki, *J. Appl. Polym. Sci.*, **44**, 205–212 (1992).
11. A. Matsumoto, K. Hasegawa, A. Fukuda, and K. Ot-suki, *J. Appl. Polym. Sci.*, **44**, 1547–1556 (1992).
12. H. D. Wu, C. C. M. Ma, M. S. Lee, and Y. D. Wu, *Die. Angew. Makromol. Chem.*, **235**, 35 (1996).
13. C. C. M. Ma, D. Y. Goang, J. L. Han, and K. H. Hsich, *Die Angew. Makromol. Chem.*, **218**, 41, 1994.
14. J. T. Mottram, B. Geary, and R. Taylor, *J. Mat. Sci.*, **27**, 5015–5026 (1992).
15. Underwriter's Laboratories, *UL 94 Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances*, 4th ed., UL-94, 1991.