

# Mechanical Properties, Thermal Stability, and Flame Retardance of Pultruded Fiber-Reinforced Poly(ethylene oxide)-Toughened Novolak-Type Phenolic Resin

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**ABSTRACT:** The mechanical properties (flexural modulus, static tensile strength, notched Izod impact strength), miscibility, thermal stability, and flame retardance of a poly(ethylene oxide) (PEO)-toughened phenolic resin glass pultruded composite were investigated. The mechanical properties of a pultruded glass fiber-reinforced modified phenolic resin composite increased while the soft segment of PEO absorbs the loads in the network of brittle phenolic resin. The phenolic/PEO blend is completely miscible, from the results of differential scanning calorimetry. Its thermal degradation temperature is always higher than 370°C and decreased with increasing PEO content. The morphology of the interface between the fiber and matrix is well wetted-out with increasing PEO content from the result with a scanning electron microscope (SEM). The modified phenolic composite also shows excellent flame retardance that is UL-94, V-0, and the limited oxygen index is more than 55. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1129–1136, 1998

**Key words:** pultrusion; novolak-type phenolic resin; poly(ethylene oxide); mechanical properties; thermal stability; flame retardance

## INTRODUCTION

Phenolic resin has been widely used commercially in applications such as paint, adhesives, and composites due to its lower manufacturing cost, dimensional stability, and chemical resistance.<sup>1–3</sup> In recent years, much emphasis has been placed on fireproof structures and decorations in buildings for public security. Phenolic resin is the most popular resin for this purpose. However, its brittleness has limited its application significantly.

Improving the toughness of phenolic resin is an important study for further application.<sup>4–7</sup> One method of modifying phenolic resin is to blend it with other miscible thermoplastic polymers. As described in previous reported work,<sup>5,7–11</sup> the phenolic resin provided intermolecular hydrogen bonding as a dominant driving force to interact with hydroxyl, carbonyl, and ester groups and other hydrogen-bonding functional groups of thermoplastic miscible polymers. All the mechanical properties of modified phenolic increased with the thermoplastic modifier added, since either ester or other hydrogen-bonding functional groups are more flexible than is the phenolic and will absorb the loads.

In this study, a novel method of blending the novolak-type phenolic resin with poly(ethylene oxide) (PEO) is proposed to improve the mechanical properties of phenolic. The ether group of PEO

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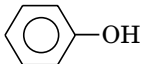
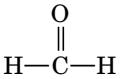
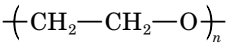
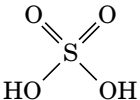
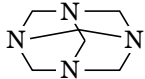
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**Table I Reagents Used in This Study**

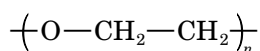
Materials	Specification
Phenol	 Purity > 98.0%, $M = 94.11$
Formaline	 37 wt % water solution
Poly(ethylene oxide)	 $M_n = 200,000$
Concentrated sulfuric acid	 Purity > 96.0%, $M = 190.21$
Hexamethylenetetramine (hexamine)	 Purified industry grade
E-glass fiber	764-NT-218 Diameter = 13.1 $\mu\text{m}$

would interact with the hydrogen bonding of the phenolic resin and also enhance the wet-out of the matrix and glass fiber.<sup>5</sup> Both functions improve the mechanical properties (including tensile strength, flexural modulus, and notched Izod impact strength) of the resultant composite. The miscibility and thermal stability of the phenolic/PEO blend were also investigated in this study.

## EXPERIMENTAL

### Materials

The synthesis and analysis of novolak-type phenolic resin were described in previous reports.<sup>7,12</sup> The materials used are summarized in Table I. Poly(ethylene oxide) (PEO) was obtained from Union Carbide Co. (U.S.A.) and the molecular weight ( $M_n$ ) is 200,000. The repeated PEO unit is described as follows:



### Preparation

PEO and 10 wt % hexamethylene tetramine (base to phenolic) are added to the novolak-type phenolic synthesized for pultrusion<sup>12</sup> (the viscosity ranged from 1000 to 2000 cps) according to the designed composition. The mixture was stirred for 2 days at 80°C. The pultrusion machine used was described previously.<sup>13</sup> The dimensions of the die were  $82 \times 1.27 \times 0.33$  cm. The heating-temperature profile 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 200 and 220°C. The diameter of the E-glass type glass fiber used was 13.1  $\mu\text{m}$  in the pultrusion system. The postcured process was conducted by heating the sample at 200°C for 1 h.

The preparation of the DSC specimen is described as follows: The phenolic/PEO 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 h, and THF was evaporated slowly at room temperature for 1 day. Then, the blend was dried at 50°C for 2 days and annealed at 140°C for 2 h under a vacuum.

### Properties Measurements

The tensile strength was measured with an Instron 4201 according to ASTM D-3039. The sample dimension was  $20.8 \times 1.27 \times 0.33$  cm (length  $\times$  width  $\times$  thickness), and the crosshead speed was 5 mm/min. The flexural modulus was measured according to ASTM D-790. The sample dimensions were  $12.7 \times 1.27 \times 0.33$  cm, the span between the two supports was 9 cm, and the crosshead speed was 2 mm/min. The notched Izod impact strength was measured following the specifications according to ASTM D256.

The glass transition temperatures ( $T_g$ s) was determined by a differential scanning calorimeter (DSC) (DuPont, DSC Model 2900). The heating rate was 20°C/min, ranging from -80 to 120°C. The measurements were made with 3–4-mg samples on a DSC sample plate after the specimens were quickly cooled to room temperature following the first scan. This procedure was adopted to ensure complete mixing of the polymer blends which removes the residual solvent and water in the specimen completely. The  $T_g$  values were de-

**Table II Material Classifications for Flammability Test<sup>14</sup>**

Criteria Conditions	94V-0	94V-1	94V-2
Afterflame time for each individual specimen t1 or t2	≤ 10 s	≤ 30 s	≤ 30 s
Total afterflame time for any condition set (t1 plus t2 for the five specimens)	≤ 50 s	≤ 250 s	≤ 250 s
Afterflame plus afterglow time each individual specimen after the second flame application (t2 + t3)	≤ 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: (A) afterflame time after first flame application, t1; (B) afterflame time after second flame application, t2; (C) afterglow time after second flame application, t3; (D) whether or not specimens burn up to the holding clamp; (E) whether or not specimen drips flaming particles that ignite the cotton indicator.

terminated at the midpoint of the transition point of the heat-capacity ( $C_p$ ) change, and the reproducibility of the  $T_g$  values was estimated to be within  $\pm 1^\circ\text{C}$ . Thermogravimetric analysis was conducted with a DuPont TGA from room temperature to  $800^\circ\text{C}$  using a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen gas atmosphere. A scanning electron microscope (Model JSM-5300 from JEOL Co.) was used for the morphology study.

Flame retardance was measured according to the UL 94 Standard.<sup>14</sup> Five specimens with the dimensions of  $125 \pm 5$  mm long and  $13.0 \pm 0.5$  mm wide were tested. Methane gas was supplied to the burner shell, and the burner was adjusted to produce a blue flame  $20 \pm 1$  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 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 to be tested. Table II shows the specifications of the material classifications for the flammability test.<sup>14</sup> The limited oxygen index (LOI) was tested according to ASTM D-2863.

## RESULTS AND DISCUSSION

### Mechanical Properties

All the mechanical properties are tabulated in Table III. Figure 1 shows the flexural modulus of the pultruded fiber-reinforced novolak-type phenolic resins toughened with various PEO contents. The flexural modulus shows maximum values at 6 wt % of PEO content and then decreases gradually when the PEO content is more than 6 wt %. Since the loads applied will be absorbed by the soft segment of PEO when phenolic resin is modified, that leads to an increased flexural modulus. The wet-

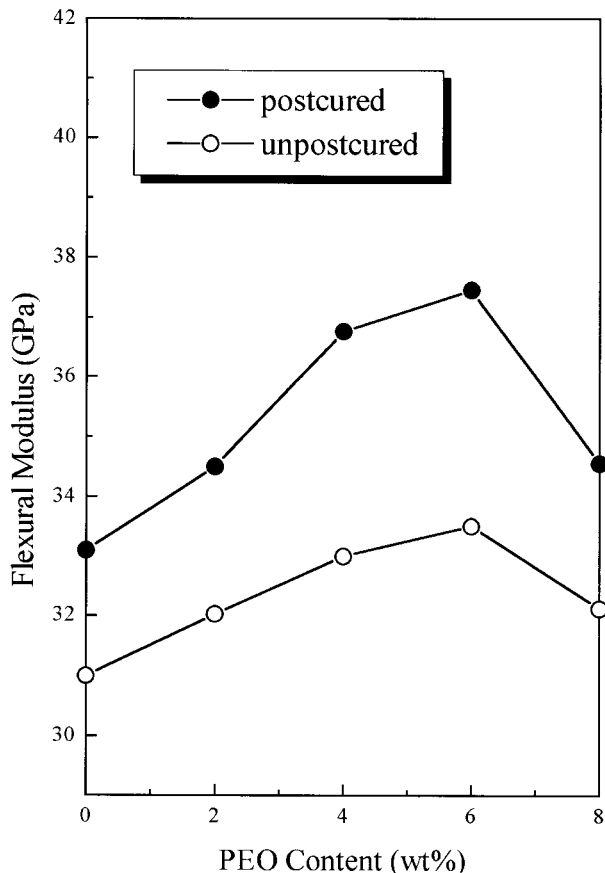
**Table III Mechanical Properties of PEO-Modified Phenolic Composite**

Specimen	Property	PEO Contents (wt %)				
		0	2	4	6	8
Uncured specimen	Flexural strength (GPa)	31.0	32.0	33.0	33.5	32.1
	Tensile strength (Ma)	559	562	562	566	564
	Notched Izod impact strength (kJ/m)	1.38	1.58	1.62	1.83	1.70
Cured specimen	Flexural strength (GPa)	33.1	34.5	36.8	37.5	34.6
	Tensile strength (Ma)	570	572	574	580	576
	Notched Izod impact strength (kJ/m)	1.61	1.76	1.99	2.18	2.03

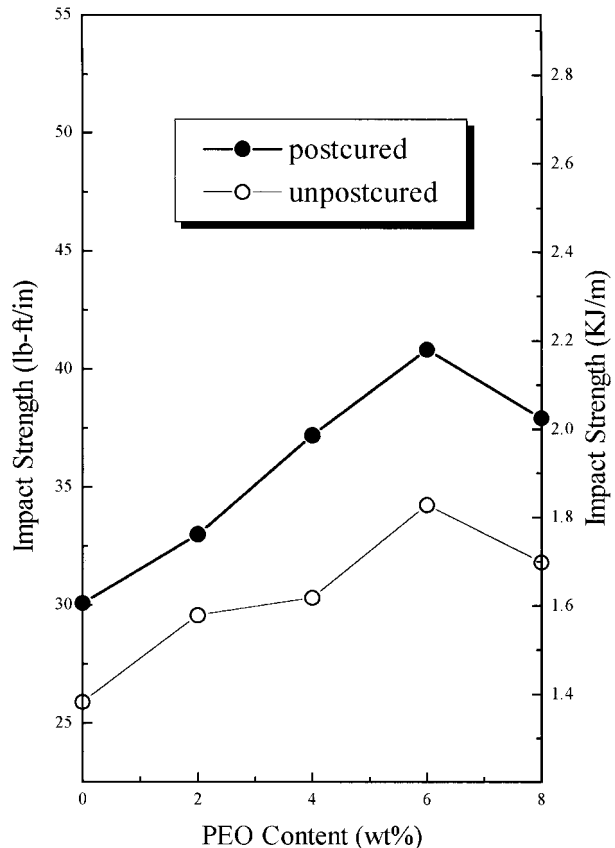
out between matrix and fiber becomes poor with higher viscosity at higher PEO content, causing the flexural modulus to decrease.

The effect of the PEO content on the notched Izod impact strength of the composite is illustrated in Figure 2. The highest impact strength appeared at PEO 6 wt % and exhibits a significant improvement of 35.7% in toughness. Owing to the higher viscosity causing poor wet-out between the matrix and fiber at higher PEO content, the notched Izod impact strength of the composites decreased when the PEO content was more than 6 wt %.

Figure 3 shows the tensile strength of a modified phenolic composite with various PEO contents. The tensile strength of a composite depends on both the polymer properties and the wet-out of the matrix and the fiber. In this system, the presence of PEO improves the tensile strength of the composite due to its flexibility. On the other



**Figure 1** Flexural modulus versus pultruded fiber-reinforced phenolic resin toughened by various PEO contents.



**Figure 2** Notched Izod impact strength versus pultruded fiber-reinforced phenolic resin toughened by various PEO contents.

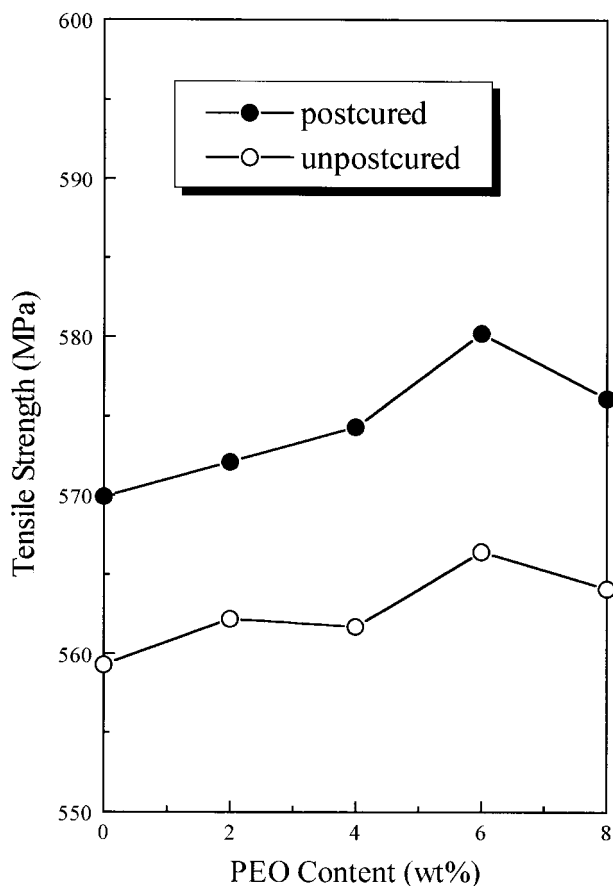
hand, the higher viscosity with the addition of PEO will reduce the wet-out of the glass fiber, reducing the tensile strength. It is considered that the tensile strength is almost independent of the PEO content because both factors are in balance. The effect of the wet-out on the mechanical properties will be demonstrated and further discussed by SEM photographs in the next section.

All the mechanical properties of the postcured composite show higher values than those of the unpostcured one because the reaction of the postcured one is more complete. The impact strength and flexural modulus of the postcured one containing 6 wt % of PEO is 35.7% and 13.2% higher than those of the unmodified phenolic one, respectively.

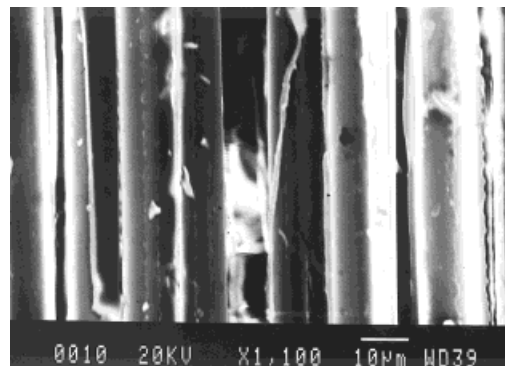
#### Morphology of the Pultruded Composites

The morphology of the composite was investigated by an SEM photograph, shown in Figure 4. From

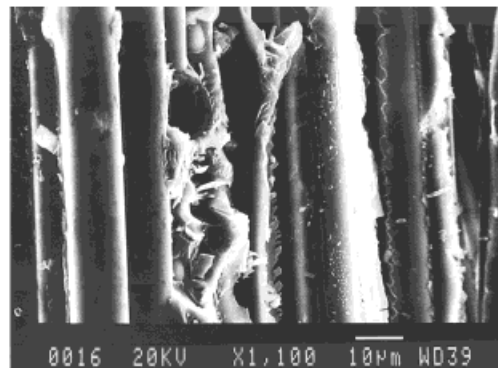
Figure 4(a), it is observed that the fiber bundles are distributed evenly in the pure phenolic matrices; however, the wet-out of the fiber is poor. Figure 4(b–d) show that the fiber wet-out of the fiber-reinforced modified phenolic composites are better than that of the unmodified phenolic composite [Fig. 4(a)]. The flexible ether group of PEO can interact with the hydroxyl group of phenolic and increase the mobility of the phenolic resin; the wet-out of the matrix and glass fiber is also enhanced. By comparing Figure 4(c) with Figure 4(d), one can see that the wet-out of the 8 wt % PEO content seems to be worse than that of 6 wt % PEO, since the higher PEO content increases the viscosity of the uncured phenolic resin and reduces the efficiency of the wet-out on the glass fiber. The SEM photographs in Figure 4 show crack propagation under a cleavage fracture. The wave pattern becomes more severe as is observed



**Figure 3** Tensile strength versus pultruded fiber-reinforced phenolic resin toughened by various PEO contents.



(a)



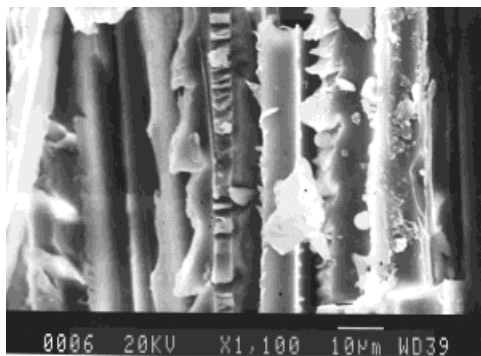
(b)

**Figure 4** SEM photographs of the pultruded fiber-reinforced PEO-toughened phenolic resin composite with various PEO contents: (a) 0 wt %; (b) 4 wt %; (c) 6 wt %; (d) 8 wt %.

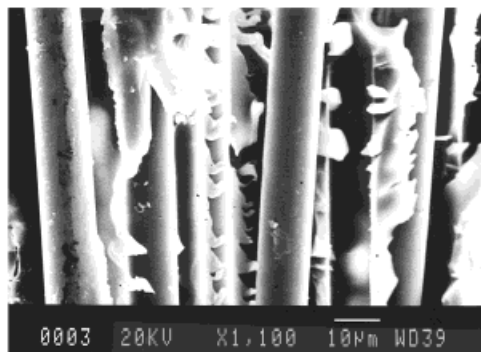
when the PEO content increases, as shown in Figure 4. The soft segment of PEO absorbs fracture energy by yielding and softens the matrix. The mechanical properties depend on both the PEO content and the wet-out of the glass fiber. The notched Izod impact strength and the flexural modulus of the composite increased with the initial addition of PEO and decreased when the PEO content was more than 6 wt %. The miscibility of the phenolic/PEO blend also affects the mechanical properties, which will be discussed in the next section.

#### Glass Transition Temperature of Phenolic/PEO Blend

Figure 5 shows the DSC curves of phenolic resin blended with various PEO contents. The glass transition temperature of pure novolak-type phe-



(c)



(d)

**Figure 4** (Continued from the previous page)

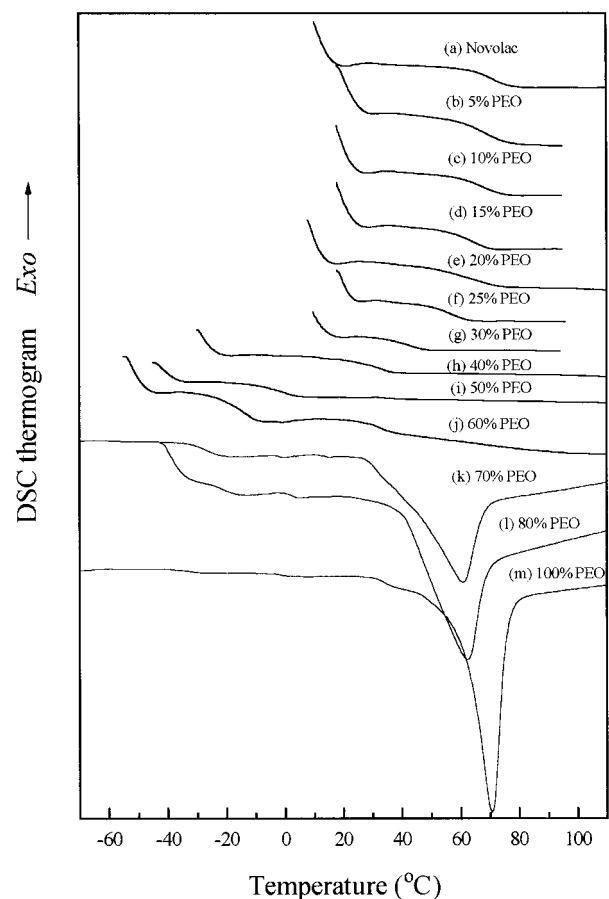
nolic is  $70 \pm 1^\circ\text{C}$ , and that of amorphous PEO,  $-65 \pm 1^\circ\text{C}$ , obtained from the literature.<sup>15</sup> After quenching from the melt state, a rescanning (second run) shows that a single  $T_g$  behavior is observed throughout the whole blend range at various compositions of the phenolic blends, suggesting that the phenolic/PEO blend system in this study is directly miscible. The phenolic shows an unusually high  $T_g$  compared to other similar low molecular weight polymers due to the high density of the intramolecular hydrogen bonding. PEO resin is a highly crystalline polymer, while the phenolic resin is completely amorphous and relatively rigid. It is the essence of PEO that it has a high density of ether groups and a simple molecular structure. The flexible PEO chain intersects into the free volume of a phenolic matrix and provides more opportunity to form intermolecular hydrogen bonding and also increases the average strength of the hydrogen bonding in this blend system.

When intermolecular hydrogen bonding is decreased by increasing the PEO content, the hydro-

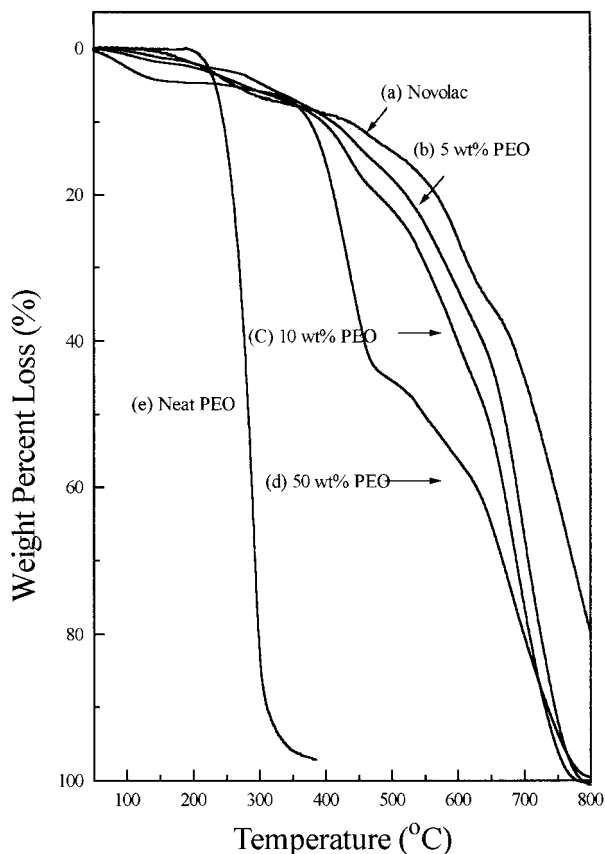
gen bonding no longer plays a key role in affecting the molecular motion of the phenolic/PEO blend. An endothermic peak in the DSC curve is obvious when the PEO exceeds 70 wt % in the blend family. The hydrogen bonding is gradually replaced by a dispersion force (randomly) in the phenolic-poor region. The crystal of PEO is exhibited in the DSC curve in the phenolic-poor region, causing the phenolic not to have enough hydroxyl groups to destroy the crystalline lattice of PEO.

### Thermogravimetric Analysis

Figure 6 illustrates the thermogravimetric analysis (TGA) of the PEO-modified phenolic resin. The decomposition temperature (the temperature of



**Figure 5** DSC thermogravimetric curves of PEO/phenolic resin blends with various compositions (wt %): (a) 0/100; (b) 5/95; (c) 10/90; (d) 15/85; (e) 20/80; (f) 25/75; (g) 30/70; (h) 40/60; (i) 50/50; (j) 60/40; (k) 70/30; (l) 80/20; (m) 100/0.



**Figure 6** Thermogravimetric analysis of phenolic/PEO polymer blend at various PEO contents: (a) 0 wt %; (b) 5 wt %; (c) 10 wt %; (d) 50 wt %; (e) 100 wt %.

10 % weight loss) of pure PEO is somewhat lower than that of pure phenolic resin. From the derivative weight-loss curve, the decomposition temperature of the modified phenolic is decrease with increase of the PEO content, as summarized in Table IV. However, the decomposition temperature of the modified phenolic resin is always above 370°C, indicating that the modified phenolic resin possesses good thermal stability.

## Flame Retardance

The flame retardance of the pultruded glass fiber-reinforced modified phenolic resin shows an extremely high LOI value (>55) and has the property of UL-94 V-0. These values are maintained to 8 wt % PEO added. The effect of a minor PEO content on the flame retardance was insignificant because the phenolic resin and the glass fiber are char-yielded materials.

## CONCLUSIONS

1. The mechanical properties (including flexural modulus, notched Izod impact strength) of modified novolak-type phenolic resin show the highest value at 6 wt % PEO content composition. The postcured specimen shows higher mechanical properties than that of the uncured one since its reaction is more complete.
2. The interface between the matrix and the glass fiber of the PEO-modified novolak-type phenolic resin is improved; consequently, the mechanical properties of the composites increased significantly.
3. The phenolic/PEO blend is a completely miscible system in which the flexible ether chain of the PEO backbone penetrates the rigid phenolic matrix. PEO is a good reagent for toughening the phenolic resin.
4. The decomposition temperature of the phenolic/PEO blend was always higher than 370°C for all specimens in this study, although its temperature decreased with increasing PEO content.
5. The flame retardance to 8 wt % PEO in modified novolak-type phenolic resin composites shows values of UL-94 at V-0 with the LOI at more than 55, showing excellent fire-resistance properties.

**Table IV** Temperature of the 10% Weight Loss of Phenolic/PEO Blend with Various PEO Contents

Measurement	PEO Content (wt %)						
	0	5	10	15	20	50	100
Temperature of 10 wt % weight loss of phenolic/PEO blends (°C)	438.1	426.1	415.2	406.5	395.7	370.9	250.8

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