

Blocked Diisocyanate Polyester-Toughened Novolak-Type Phenolic Resin: Synthesis, Characterization, and Properties of Composites

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Received 19 August 1996; accepted 3 September 1997

ABSTRACT: A blocked diisocyanate polyester was synthesized to copolymerize with novolak-type phenolic resin. From the results of IR and NMR spectra, it was found that the blocked diisocyanate polyester reacts with the hydroxyl group of the novolak-type phenolic resin at high temperature. The deblocking temperature for the novolak-type phenolic resin is 120°C. The blocking agent, ϵ -caprolactam, is convenient for this system. The copolymer exhibited a single glass transition temperature and a negative deviation of the glass transition temperature. The results showed that the copolymer system is miscible and the molecular motion of the copolymer is increased with the addition of a modifier. The interface between the modified phenolic resin and the glass fiber is improved and the tensile strength of pultruded composite is increased with the modifier content. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1119–1127, 1998

Key words: blocked diisocyanate polyester; phenolic resin; toughen; composites

INTRODUCTION

Phenolic resin is used widely as an industrial material because of its good heat resistance, electrical insulation, dimensional stability, and flame and chemical resistance.^{1–5} However, phenolic resin is brittle and not very tough, like many other thermosetting resins. To be able to modify phenolic is an important subject for its further application. Recently, much research has been done to investigate improving the toughness of phenolic resin.^{6–9} In previous studies,^{10–13} we used a novolak-type phenolic resin blended with thermoplastic to improve the toughness of the phenolic resin. The results suggested that the phenolic resin was

linked by a hydrogen bond to a thermoplastic, because the glass transition temperatures (T_g s) of the mixture were shifted from the T_g of the phenolic resin. The miscibility of a polymer blend depends on the strength of specific intermolecular interaction. Phase separation would occur when specific interactions (such as dipolar interaction and hydrogen bonding) are absent within the polymer blend. Copolymerization is another route to toughen phenolic resin to avoid phase separation.⁷

Blocked diisocyanate polymer is the most favored agent to copolymerize with other polymers.⁸ The copolymerization of phenolic resin and a blocked diisocyanate polymer depends on the reactivity between the hydroxyl group of the novolak-type phenolic resin and the isocyanate group. In this study, a blocked diisocyanate ester-type polyol was used to copolymerize with the novolak-type phenolic resin. The improvement of the mechanical properties of the composite and fiber wet-out are also discussed.

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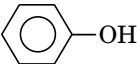
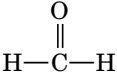
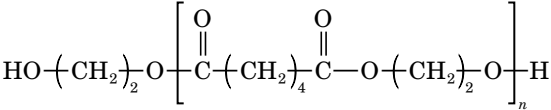
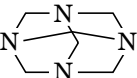
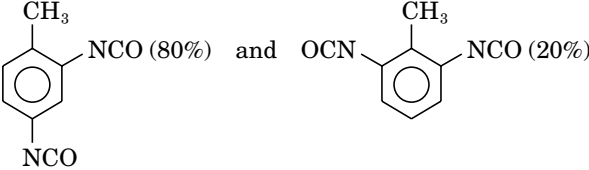
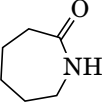

Contract grant sponsor: National Science Council, Republic of China; contract grant number: NCS 84-2216-E007-007.

Journal of Applied Polymer Science, Vol. 69, 1119–1127 (1998)

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CCC 0021-8995/98/061119-09

Table I Materials Used in This Study

Reagent	Structure	Supplier
Phenol	 $M_w = 94.11$ purity > 98.0%	The Union Chemical Works Ltd., Taiwan
Formaline	 37 wt % water solution	The Union Chemical Works Ltd., Taiwan
Poly (ethylene adipate) glycol (PEAG)	 $M_w = 2000$	Yong Shun Chemical Co., Taiwan
Hexamine	 Purified industry grade	Chu-Chung Resin Co., Taiwan
E-glass fiber	764-NT-218 Diameter = 13.1 μm	PPG Co., USA
TDI		Tokyo Chemical Industry Co., Japan
CPL		Janssen Chemical Co., Belgium
Tetrahydrofuran		Tokyo Kasei Kogyo Co., Ltd., Japan

EXPERIMENTAL

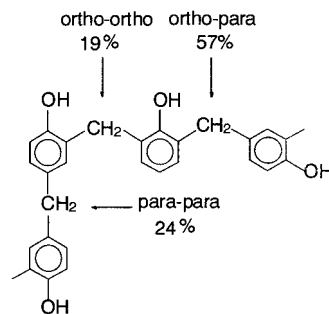
Materials

The materials used in this study are listed in Table I.

Synthesis

- The synthesis of our novolak-type phenolic resin was described in a previous paper.¹⁴ The novolak-type phenolic resin was heated under a vacuum at 160°C for 2 days to remove any volatile material. The T_g of the novolak-type phenolic resin is $65 \pm 1^\circ\text{C}$, and the M_n and the M_w were 500 and 1200, respectively. The molecular structure of the novolak-type phe-

nolic resin is described as follows¹¹:



- The synthesis of blocked diisocyanate polyester is as follows: The blocked diisocyanate polyester was synthesized in a resin flask with a thermometer, a reflex condenser, and

a stirrer. Toluene diisocyanate (TDI) and poly(ethylene adipate glycol) (PEAG) in a tetrahydrofuran solution with a mol ratio of 1 : 2 (PEAG : TDI) were fed into a flask with stirring under a nitrogen atmosphere at 60°C for 2 h. After the reaction was complete, the blocking agent [e.g., ϵ -caprolactam (CPL)] was added into the reflux flask. The reaction was catalyzed by the addition of 0.005 mol % of dibutyltin dilaurate at 60°C for 24 h. At the end of the reaction, the flask was connected to a vacuum system under a pressure of 100 mm H₂O at 80–90°C until the solvent was driven off completely. The product was cooled to room temperature and stored for further processing.

Pultruded Composite

Blocked diisocyanate ester and 10 wt % hexamine (based on phenolic resin) were added to the modified novolak-type phenolic resin synthesized for pultrusion¹⁴ (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.⁸ The dimensions of the 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 were treated by chrome plating. The pulling rate was 30 cm/min at the die temperatures of 200 and 220°C. The diameter of the E-glass-type glass fiber used was 13.1 μ m in the pultrusion system.

Testing Methods

Differential Scanning Calorimetry (DSC)

The T_g s of the polymer blends and copolymer were determined by a differential scanning calorimeter (DuPont, DSC Model 2900). The scan rate was 20°C/min within a temperature range of –80 to 100°C. The measurement was made with a 3–4-mg sample on the 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 and to remove the residual solvent and water in the specimen completely. The T_g values were determined at the midpoint of the transition point of the heat capacity (C_p) change, and the reproducibility of the T_g value was within $\pm 1^\circ\text{C}$. The 10 wt % hexamine (based on the pheno-

lic resin) was added into the phenolic resin for the curing process. The scan rate was 5°C/min within a temperature range of 20–350°C for curing the novolak-type phenolic resin.

Infrared Spectroscopy (IR)

The polymer blends were prepared by the solution-casting method. The phenolic resin and a toughening agent were mixed in THF [1% (w/v)] according to the designed composition at room temperature. The mixed solution was stirred for 6–8 h, and the solution was allowed to evaporate slowly at room temperature for 24 h. The blend films were then dried at 50°C for 2 days under a vacuum. IR measurements were carried out on a Perkin–Elmer infrared spectrometer by the conventional NaCl disk method. IR spectra recorded at elevated temperature were obtained by using a heating cell mounted inside the sample compartment of the spectrometer. Temperature was controlled within $\pm 0.1^\circ\text{C}$.

Solution ¹³C-NMR

A ¹³C-NMR solution of the phenolic resin/blocked diisocyanate polyester copolymer was measured by using a Bruker AM 400 spectrometer operated at 100 MHz for ¹³C. Deuterated acetone was used as a lock solvent and tetramethylsilane was used as an internal standard. The measurement provides information which confirms that a chemical reaction occurred between the novolak-type phenolic resin and the blocked diisocyanate polyester at 140°C for 2 h.

Tensile Strength

Tensile strength was measured with an Instron 4201 according to 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.

SEM

A scanning electron microscope (Model JSM-5300 from JEOL) was used for the morphology study.

RESULTS AND DISCUSSION

Reaction of Poly(ethylene adipate glycol) and Blocking Agent

Figure 1 shows the IR spectra of PEAG, PEAG reacted with TDI, and a blocked reaction with the

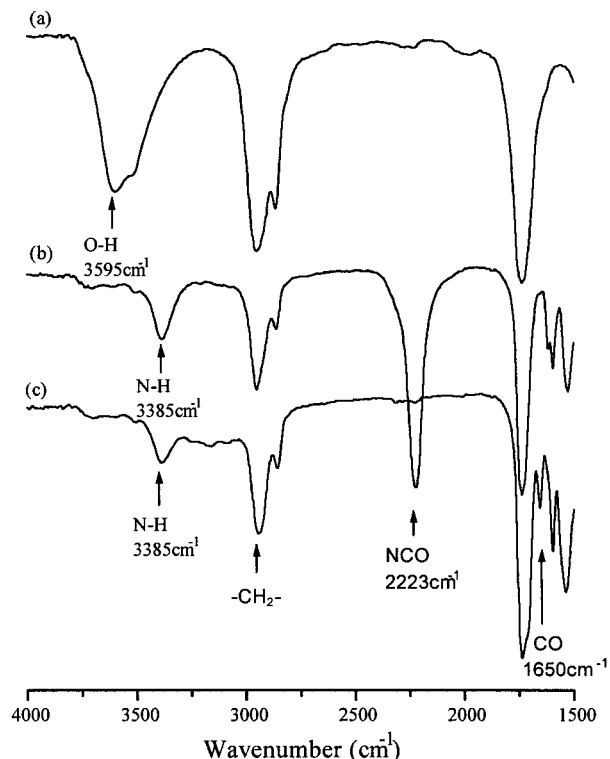


Figure 1 (a) IR spectrum of PEAG at room temperature; (b) IR spectrum of PEAG reacted with TDI at room temperature; (c) IR spectrum of the blocked reaction: The NCO group of the PEAG is capped by blocking agent of CPL at room temperature.

blocking agent, CPL, at 25°C, which could be identified from the main absorption peaks as follows:

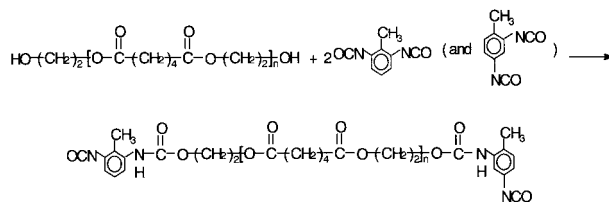
1. 3385 cm^{-1} : N—H stretch
2. 2850–3000 cm^{-1} : C—H (alkaline) stretch
3. 2223 cm^{-1} : NCO stretch
4. 1640–1670 cm^{-1} : C=O stretch

The reaction between PEAG and TDI and between blocked diisocyanate polyester (TDI-PEAG-TDI) and CPL are described as follows: The PEAG has three main functional groups, e.g., methylene, carbonyl, and the hydroxyl group, as shown in Figure 1(a). The broad absorption of 3595 cm^{-1} was assigned to the hydroxyl group of PEAG. The reaction that occurred when the PEAG was mixed with TDI, generated a new amide group at 3385 cm^{-1} , as shown in Figure 1(b). Figure 1(c) suggests that the NCO group of the reaction product between PEAG and TDI is protected by the blocking agent (CPL). A band at 1650 cm^{-1} is assigned to the newly formed carbonyl group, which implies that the reaction of isocyanate and the blocking agent occurred. This

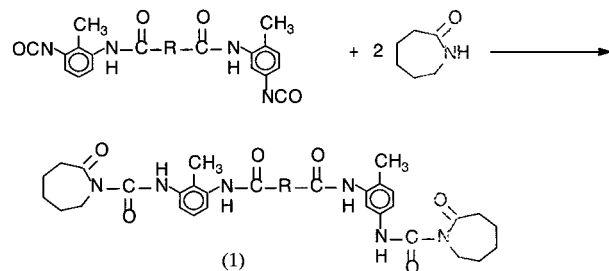
suggests that the isocyanate group of the blocked diisocyanate polyester reacts with CPL.

The above reactions can be illustrated as follows:

Reaction between PEAG and TDI:



The blocking reaction:



where R is

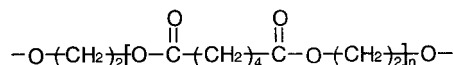
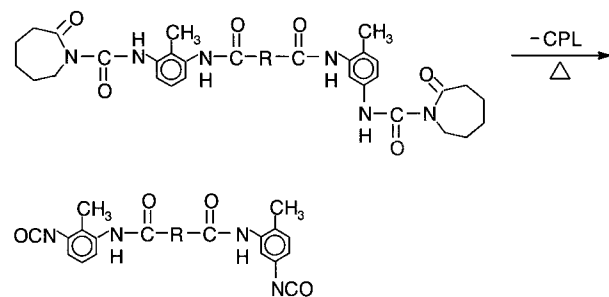


Figure 2 shows the IR spectra of the deblocked compound (1) at various temperatures (the blocking agent was CPL). The intensity of the IR absorption of the isocyanate group gradually increased with increase of temperature, suggesting that the blocking agent CPL was eliminated from compound (1) at higher temperature. The deblocking temperature is defined as the breaking point of increasing intensity, and that of CPL is 120°C in this system.

The deblocking reactions can be described as follows:



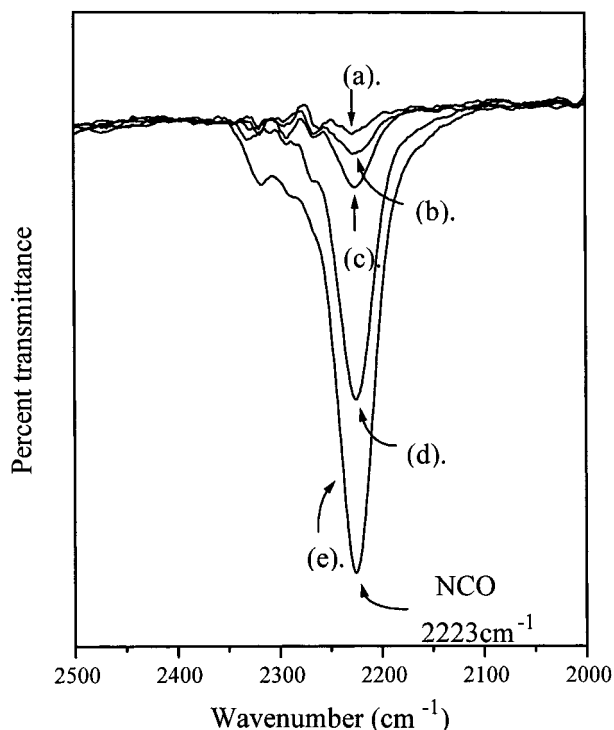
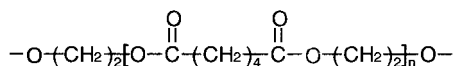


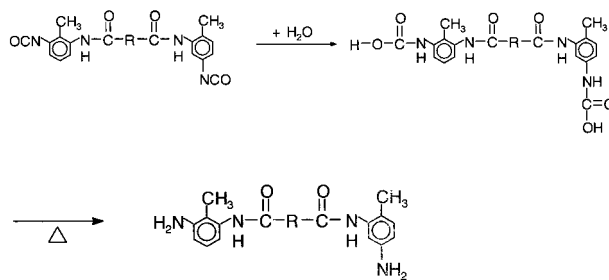
Figure 2 IR spectrum of the deblocked reaction of the blocked diisocyanate polyester at various temperatures (the blocking agent is CPL): (a) 80°C; (b) 110°C; (c) 120°C; (d) 140°C; (e) 160°C for 10 min.

where *R* is

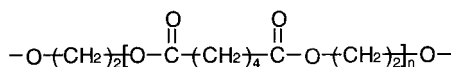


Reaction of Blocked Diisocyanate Polyester and Novolak-Type Phenolic Resin

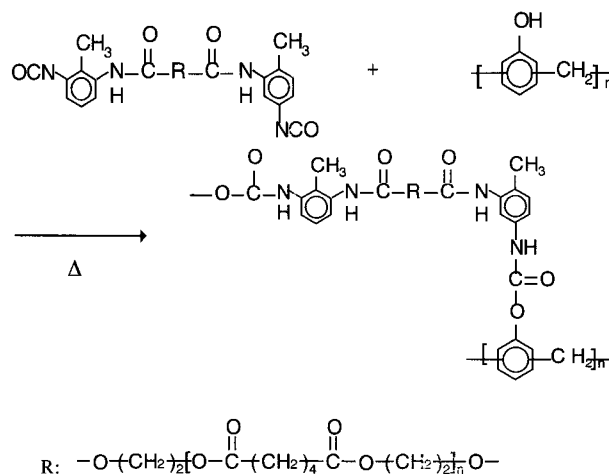
The reactivity of the blocked diisocyanate polyester with the hydroxyl group of the novolak-type phenolic resin was investigated. The following step will distinguish whether the blocked diisocyanate group reacts with the moiety or with the hydroxyl group of the novolak-type phenolic resin at the deblocking temperature. At first, the blocked diisocyanate polyester was heated at 140°C in air for 2 h. Next, the mixture of the blocked diisocyanate polyester and the novolak-type phenolic resin was also heated in air at 140°C for 2 h. Figure 3 shows the ¹H-NMR spectrum of the blocked diisocyanate polyester heated at 140°C in air for 2 h. The chemical shift of 3.7 ppm is assigned to the hydrogen resonance of —N—H₂. The reaction equation can be inferred as follows:



where *R* is



However, the hydrogen resonance of —N—H₂ in the ¹H-NMR spectrum is not present in the mixture of the blocked diisocyanate polyester and the novolak-type phenolic resin that was heated at 140°C in air for 2 h, as shown in Figure 4. The novolak-type phenolic resin does not contain a reactive methylol group which may be crosslinked by heating or reacted with another functional group. It is reasonable to infer that the NCO group of the deblocked diisocyanate polyester would react with a hydroxyl of novolak-type phenolic resin. Those NMR spectra confirm the following reaction:



The Miscibility of the Copolymer

The glass transition temperature (*T_g*) is usually used to study the miscibility of a copolymer. When a copolymer is homogeneous, it has only one *T_g* that shifts with the composition. On the other hand, when a copolymer is not homogeneous, it shows multi-*T_g*s that depend on each component. The glass transition temperatures of the pure novolak-type phenolic resin and the PEAG were 70

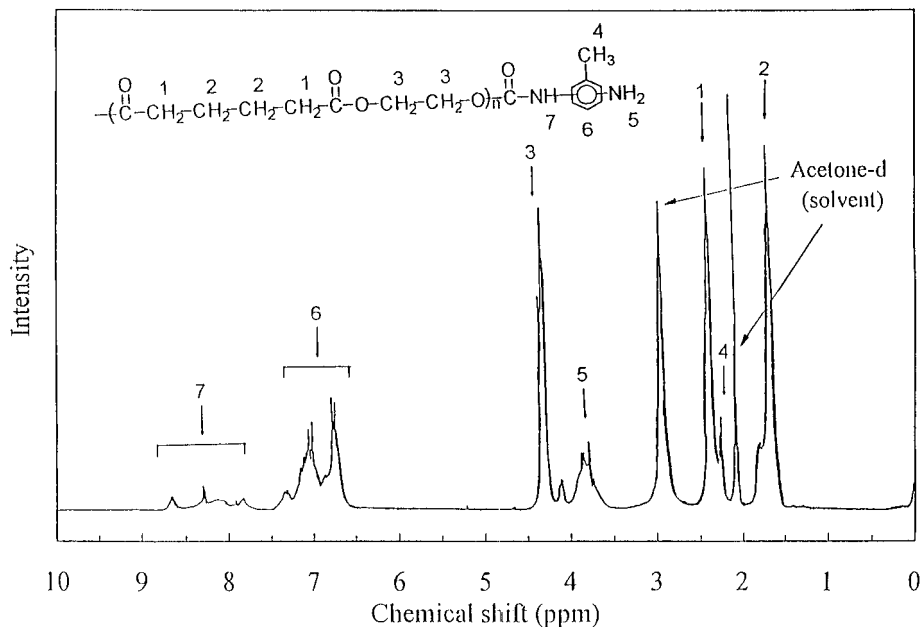


Figure 3 $^1\text{H-NMR}$ spectrum of the blocked diisocyanate polyester heated at at 140°C in air for 2 h.

and -58°C , respectively. Figure 5(a) shows the glass transition temperature of the phenolic/PEAG blend with various compositions that were heated at 140°C in air for 2 h. Those blends show

a single T_g through the whole blend composition range, indicating that the polymer blends are completely miscible. Figure 5(b) and Table II show the glass transition temperatures of the copolymer

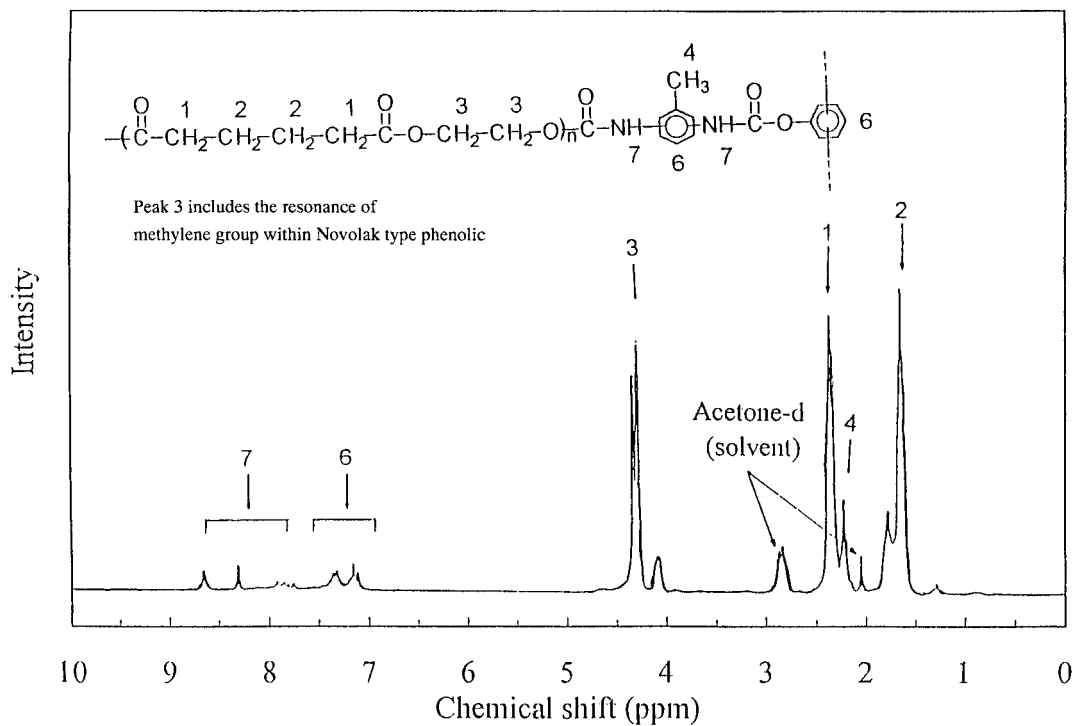


Figure 4 $^1\text{H-NMR}$ spectrum of the blocked isocyanate polyester heated with the novolak-type phenolic resin at 140°C in air for 2 h.

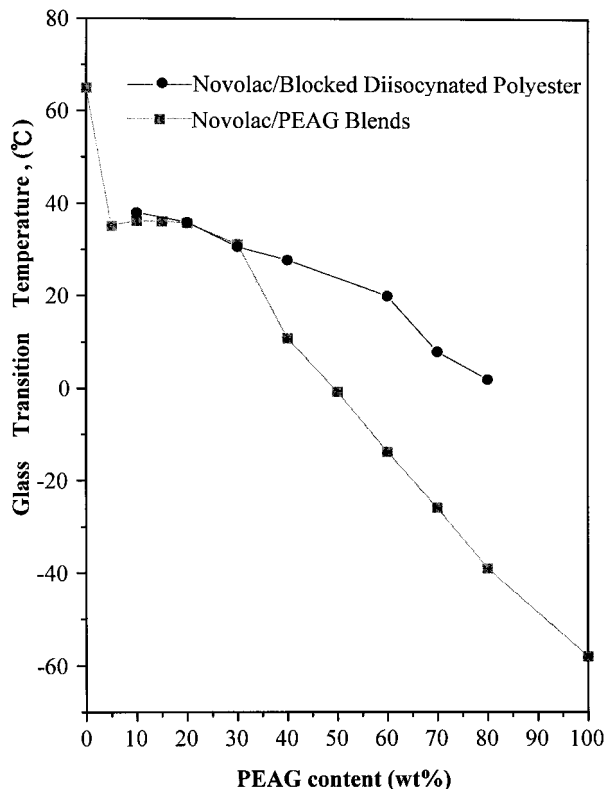


Figure 5 (a) Glass transition temperature of phenolic/PEAG blends with various compositions heated at 140°C in air for 2 h. (b) Glass transition temperature of phenolic/blocked isocyanate polyester blends with various compositions heated at 140°C in air for 2 h.

with various compositions that were heated at 140°C in air for 2 h. The glass transition temperature of the blocked diisocyanate polyester (TDI-PEAG-TDI) is -10°C. Those copolymers, as well as the phenolic/PEAG, show a single T_g value through the compositions, suggesting that the copolymer was a miscible system. Both the polymer blend and the copolymer showed a negative T_g de-

Table II Glass Transition Temperatures of Phenolic/Blocked Diisocyanate Polyester Blends with Various Compositions

Compositions	T_g (°C)
Phenolic/blocked diisocyanate polyester = 100/0	65.0
90/10	38.0
80/20	36.0
70/30	30.6
60/40	27.7
40/60	20.0
30/70	8.0
20/80	2.0

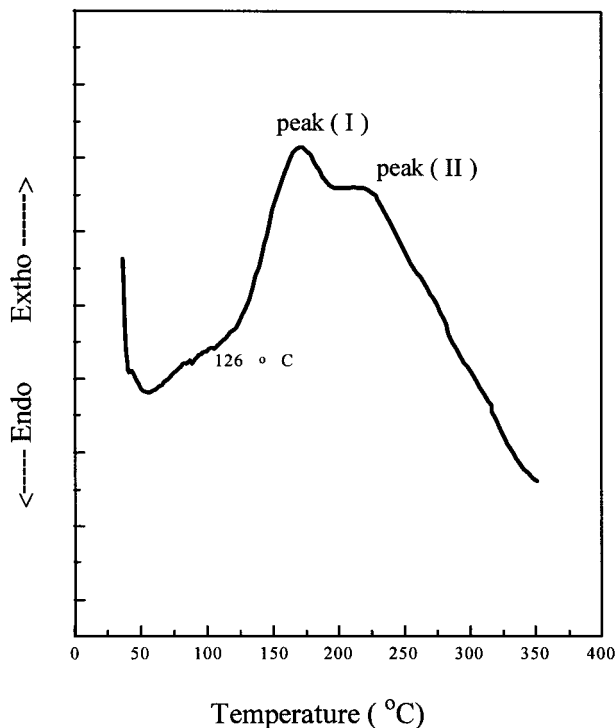


Figure 6 Differential scanning calorimetric analysis of the curing process of pure novolak-type phenolic resin with 10 wt % hexamine under ambient pressure.

viation in the phenolic-rich region. Based on our previous study,¹⁰⁻¹² it indicates the newly built intermolecular hydrogen bonding between the phenolic resin and the polyester, which cannot afford the loss of self-association of the phenolic resin. Hence, the strength of the hydrogen bonding of the copolymer (and blend) decreases with the addition of a modifier and allows a significant increase in the molecular motion of the phenolic resin.

Crosslinking Temperature of Novolak-Type Phenolic Resin

When the deblocking temperature is higher than the curing temperature of the phenolic resin, the phenolic resin does not react with the blocked diisocyanate group from the copolymer. On the other hand, the blocked polyester may react with moisture when the deblocking temperature is below the boiling point of water and the copolymer cannot be synthesized. The curing temperature of the novolak-type phenolic resin with the hexamine curing agent was analyzed by differential scanning calorimetry, as shown in Figure 6. There are two peaks on the DSC curve and the first onset point is 126°C. The first peak is a large exothermic peak, which is related to the methylene and di-

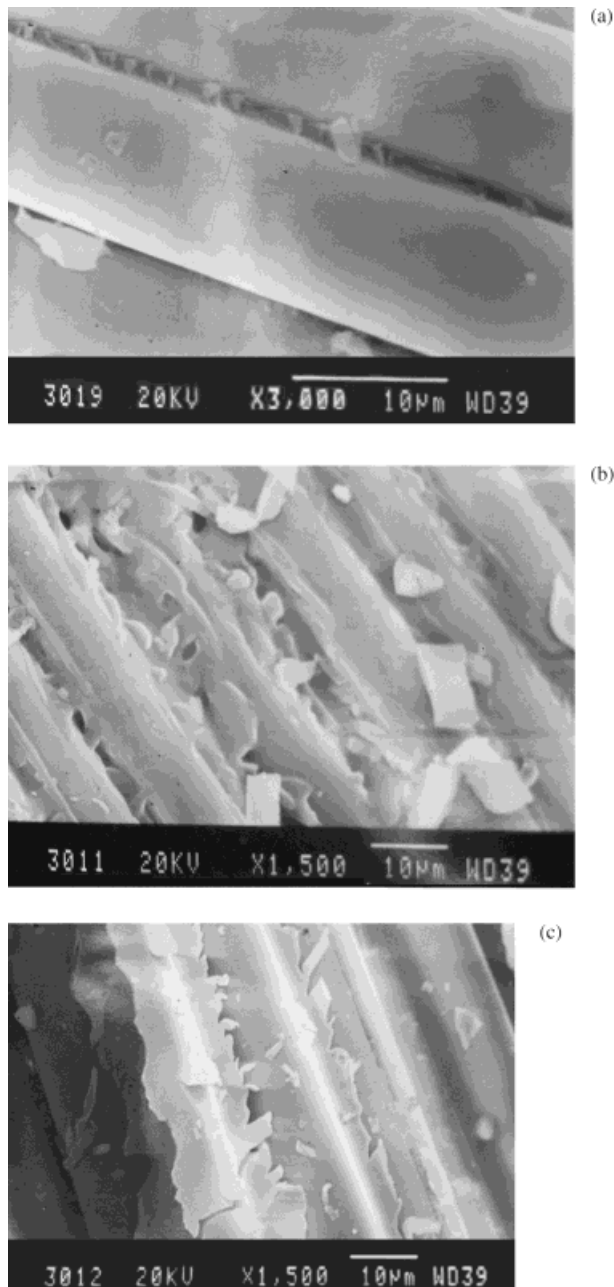


Figure 7 SEM photographs of the pultruded fiber-reinforced blocked diisocyanate polyester-modified phenolic resin composite with various modifier contents: (a) 0 wt %; (b) 5 wt %; (c) 15 wt %.

methylene ether bridge in the temperature range of 130–185°C. The second peak is a small exothermic peak that indicates that the reaction may occur at higher temperature (185–230°C). The deblocking temperature of CPL for the blocked diisocyanate polyester is 120°C, which is slightly lower than the curing temperature of the phenolic resin and is suitable for the phenolic resin. Since the deblocking temperature is still higher than the

boiling point of water, the effect of water on the reaction can be avoided.

Morphology and Tensile Strength of Pultruded Composites

Figure 7 shows SEM photographs of the pultruded glass fiber-reinforced phenolic resin copolymerized with various polyester contents. From Figure 7(a), it is observed that the fiber bundles are distributed evenly in the pure phenolic matrix; however, the wet-out of the fiber is poor. Figure 7(b,c) 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)]. The flexible ester group of the copolymer enhances the wet-out of the glass fiber.

Figure 8 shows the tensile strength of the modified phenolic composite with various poly(ethylene oxide) (PEO) contents. The tensile strength of the composite depends on both the polymer matrix property and the wet-out of polymer matrix and the fiber. The tensile strength of the pultruded composition is increased with the modifier

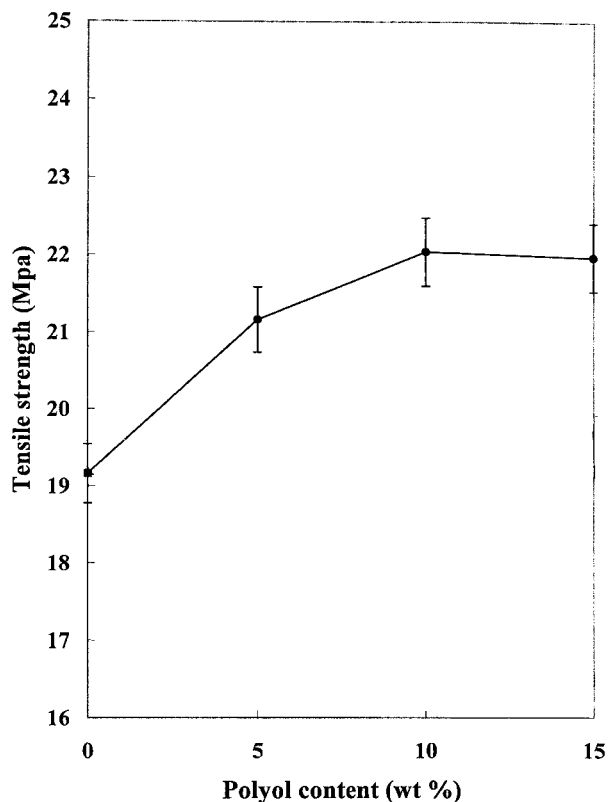


Figure 8 Tensile strength versus pultruded fiber-reinforced blocked diisocyanate polyester-modified phenolic resin composite with various modifier contents.

Table III Mechanical Properties of Poly(ethylene oxide)-Modified Phenolic Composite

Specimen	Property	Poly(ethylene oxide) Contents (wt %)				
		0	2	4	6	8
Uncured specimen	Flexural strength (GPa)	31.0	32.0	33.0	33.5	32.1
	Tensile strength (MPa)	559	562	562	566	564
	Notched Izod impacted 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 (MPa)	570	572	574	580	576
	Notched Izod impacted strength (kJ/m)	1.61	1.76	1.99	2.18	2.03

content. In this system, the presence of the ester group improves the tensile strength of the composite due to its flexible property. Table III shows the mechanical properties of the PEO-modified phenolic resin composite.

CONCLUSIONS

1. The CPL-blocked diisocyanate polyester could react with the hydroxyl group of the novolak-type phenolic resin at a higher temperature to form a copolymer.
2. The synthesized copolymer is a homogeneous system, and the deviation of the glass transition temperature is negative, implying that the molecular motion of the phenolic resin was increased.
3. The modified phenolic resin enhances the interface between the polymer matrix and glass fiber since the flexible ester group of the copolymer improves the interaction of the matrix with the glass fiber.
4. The tensile strength of the modified phenolic resin is increased with the modifier content due to the improvement of both the toughened phenolic resin and the wet-out of the fiber.

This research was financially supported by the National Science Council, Republic of China, under Contract No. NCS 87-2216-E007-025.

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