

# Pultruded Fiber Reinforced Blocked Polyurethane (PU) Composites. I. Processability and Mechanical Properties

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## SYNOPSIS

This paper presents a proprietary process developed to manufacture polyurethane (PU) pultruded composites. The blocked isocyanate (NCO)-terminated PU prepolymer synthesized in this study was prepared from  $\epsilon$ -caprolactam blocked blends of toluene diisocyanate (TDI) and branched polyester. The processability and mechanical properties of various fibers (glass, carbon, and Kevlar 49 aramid fiber) reinforced PU composites have been studied. From the investigation of the pot life of resins, the reactivity of resins, and fiber wet-out, it was found that the blocked PU prepolymers with chain extender showed excellent processability for pultrusion. Results show that the mechanical properties (i.e., tensile strength, specific tensile strength, flexural strength, specific flexural strength, flexural modulus, and impact strength) increase with fiber content. Kevlar fiber/PU composites possess the highest impact strength and specific tensile strength, whereas carbon fiber/PU composites show the highest tensile strength, flexural strength, specific flexural strength, and flexural modulus. Experimental results of tensile strength of all composites except carbon fiber/PU composites follow the rule of mixtures. The deviation of property of carbon fiber/PU composite is due to fiber breakage during processing. Pultruded fiber reinforced PU composites showed excellent tensile and impact strength compared to other pultruded composites studied.

## INTRODUCTION

In recent years, the pultrusion process has emerged as one of the most cost-effective processing techniques for composite materials. Pultruded composites exhibit all of the features produced by other composite processes, such as high strength-to-weight ratio, corrosion resistance, electrical insulation, and dimensional stability.<sup>1-5</sup> A number of resins have been used for the pultrusion process, including the thermoset resins (unsaturated polyester, epoxy, phenolic, methacrylate, etc.)<sup>6-13</sup> and thermoplastic resins (PPS, ABS, nylon 6, etc.).<sup>14-17</sup> Generally, the most suitable resin for a pultrusion process must possess the following characters: (1) a suitable viscosity (500–2000 cps) in the impregnation tank, (2) a long pot life in the impregnation tank, (3) a high reactivity, and (4) good wetting ability between fiber

and resin.<sup>18</sup> Long pot life in the impregnation tank means the viscosity of resin only increases slightly for a long processing time; hence, the fibers have adequate time to be wetted out and the pultrusion process can be operated for a long time. However, the resin should have high reactivity, in order to fabricate the composite in a short time in the pultrusion die. Furthermore, good fiber wet-out should be obtained to reach the optimum mechanical properties for the composite.

The objective of utilizing polyurethane (PU) for the pultrusion process is to take advantage of the unique properties of polyurethane including high abrasion resistance, excellent solvent and oil resistance, high tear and tensile strength, etc. Polyurethanes have been used widely in adhesion, coating, synthetic leather, construction, automobile and shoe soles, etc.<sup>19,20</sup>

In this study, the pultrusion of fiber reinforced PU composites has been conducted using a proprietary process and a blocked PU prepolymer system.<sup>21-23</sup> A suitable viscosity range (500–2000 cps)

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**Table I** Material Used in This Study

Material	Specification	Supplier
Polyol	Desmophen 1100 (branched polyester), mol wt = 786, equiv wt = 262	Bayer Co., Germany
Isocyanate	TDI-80, toluene diisocyanate of 80% 2.4 TDI blend 20% 2.6 TDI	BASF Chemical Co., Germany
Chain extender	Laromin C-260, cycloaliphatic diamine, cure epoxy at room temp, mol wt = 240	Shell Chemical Co., USA
Blocking agent	$\epsilon$ -Caprolactam, mol wt = 113.2	China Protroleum Co., Taiwan, ROC
Fiber	Glass fiber (E-glass), 764-NT-218, diameter = 13.1 $\mu\text{m}$ Carbon fiber (HT-12000), diameter = 7.0 $\mu\text{m}$ Kevlar fiber (K-49), diameter = 11.9 $\mu\text{m}$	PPG Co., USA Toho Co., Japan DuPont Co., USA

of isocyanate (NCO)-terminated PU prepolymer was provided by blocking agent to block the blends of the isocyanate and polyol at a suitable temperature. The prepolymer with chain extender was used directly and polymerized in the die. This study investigates the processability of PU pultrusion processes and evaluates the mechanical properties of pultruded glass fiber, carbon fiber, and Kevlar fiber reinforced PU composites.

## EXPERIMENTAL

### Materials

The materials used in this study are listed in Table I, which include polyol, diisocyanate, diamine, blocking agent, fiber reinforcements, and blocked PU prepolymer synthesized in this research.

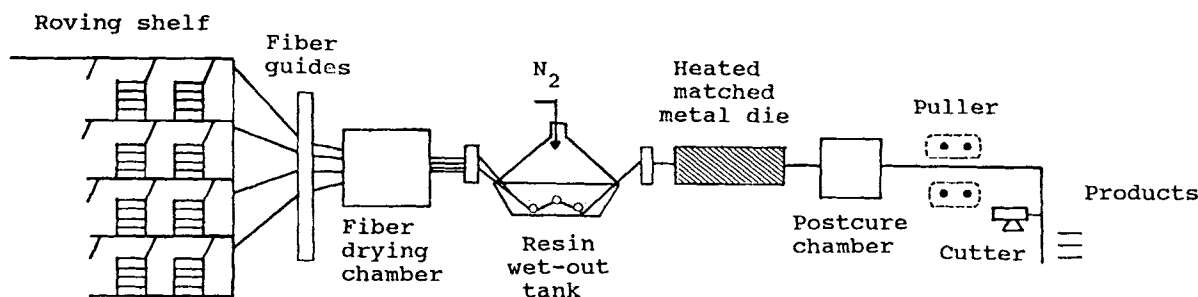
### Apparatus

The pultrusion machine used was custom designed and consisted of a pultrusion die and multiple heating zones, as shown in Figure 1. The internal dimensions of the die were 0.210  $\times$  1.27  $\times$  82.0 cm

(thickness  $\times$  width  $\times$  length). The surfaces of the stainless steel die were treated by chrome plating. Viscosities were measured with a Brookfield RVF model viscometer. The GPC (Gel Permeation Chromatography) used was a Unical 3-02 (Viscotek Co., USA). The IR (infrared) spectrophotometer used was a Model 842 (Perkin Elmer Co., USA). The SEM (scanning electron microscope) used was a S-570 (Hitachi Co., Japan). The NMR (nuclear magnetic resonance) used was a Jun-Fx 100 (Jeol Co., USA). A universal material testing machine was used for mechanical property tests, namely, an Instron 4201 (Instron Co., USA). The impact strength testing machine utilized was a TMI-43-1 (Testing Machine Inc., USA). The heat deflection temperature tester used was a DTUL/UICAT CS-107 (Custom Scientific Instrument Inc., USA).

### Property Measurements

Tensile strength was measured following the specification of ASTM D-3039. The sample dimensions were 22.9  $\times$  1.25  $\times$  0.2 cm and the crosshead speed was 2.5 mm/min. Flexural strength and flexural modulus were measured following ASTM D-790.



**Figure 1** Flow chart of pultrusion machine.

The sample dimensions were  $12.7 \times 1.25 \times 0.2$  cm, the span was 9 cm, and crosshead speed was 2 mm/min. Notched Izod impact strength was measured following ASTM D-256. The sample dimensions were  $6.35 \times 1.25 \times 0.2$  cm. Heat deflection temperature was measured following ASTM D-648. The sample dimensions were  $12.7 \times 1.25 \times 0.2$  cm.

### Preparation of the Blocked NCO-Terminated PU Prepolymer

**Synthesis of the NCO-Terminated PU Prepolymer.** The NCO-terminated PU prepolymers used in this study were prepared from toluene diisocyanate (TDI-80, 80/20 blend of 2,4 and 2,6 isomers) and from polyol (branched polyester) at an NCO/OH equivalent ratio of 2/1.

The polyols were degassed at  $70^\circ\text{C}$  and 5 mm Hg pressure before charging into the reactor. The reaction was exothermic upon stirring and under a nitrogen blanket. The reaction temperature was maintained at  $70^\circ\text{C}$  until the theoretical isocyanate content was reached. The NCO-terminated PU prepolymer used in this study was a low viscosity liquid.

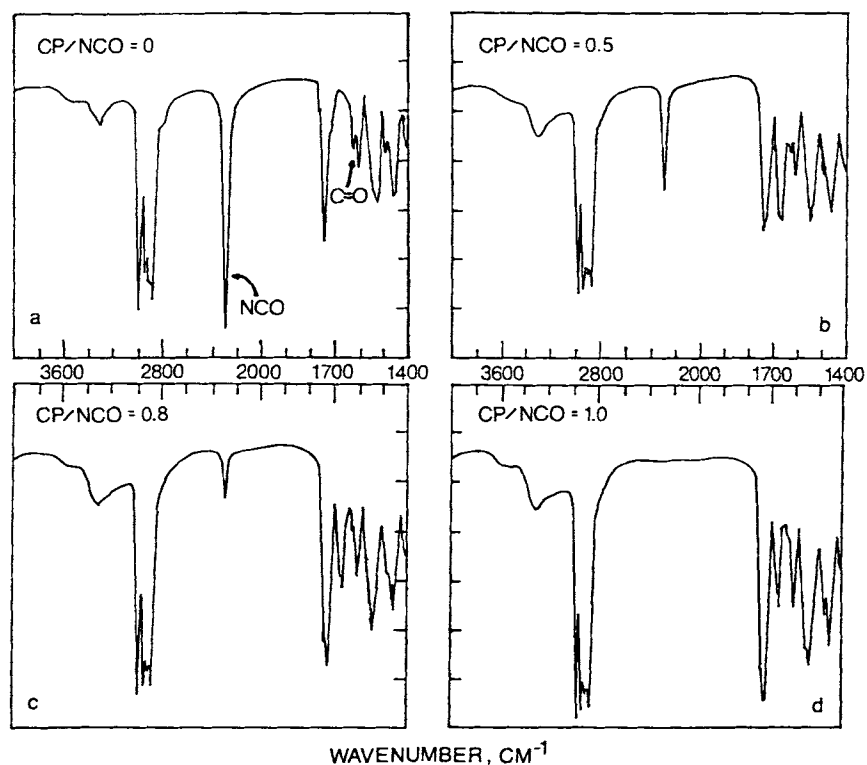
**Blocking of the NCO-Terminated PU Prepolymer.** Since NCO-terminated PU prepolymer

was a viscous liquid at room temperature, it was heated at  $80^\circ\text{C}$  (higher than the melt point of  $\epsilon$ -caprolactam,  $69^\circ\text{C}$ ) before blocking to reduce its viscosity to 400–500 cps. Dissolved or molten blocking agent  $\epsilon$ -caprolactam was added to the NCO-terminated PU prepolymer in the amount of 1 eq/eq NCO. The blend of the prepolymer with the blocking agent was maintained at  $80^\circ\text{C}$  and stirred to ensure the completion of the reaction of the blocking agent with the free NCO groups (the absorption peak of NCO disappears completely). The reactants were then cooled to room temperature and stored for further process.

## RESULTS AND DISCUSSION

### Characterization of the Blocked NCO-Terminated PU Prepolymer by Infrared and Nuclear Magnetic Resonance Spectra

In order to investigate the blocking mechanism, two sets of test specimens were examined by IR for the reaction of blocking NCO-terminated PU prepolymer at  $80^\circ\text{C}$ . The first set of specimens is the NCO-terminated PU prepolymer which was blended with



**Figure 2** IR spectra of NCO-terminated PU prepolymer blocked with  $\epsilon$ -caprolactam (CP) at various CP/NCO ratios: (a) 0; (b) 0.5; (c) 0.8; (d) 1.0.

various amounts of  $\epsilon$ -caprolactam at 0, 0.5, 0.8, and 1.0 eq/eq NCO. The second set of specimens is the same prepolymer which was blended with 1 eq  $\epsilon$ -caprolactam/eq NCO group and was measured as a function of time.

Figure 2 shows four infrared spectra of NCO-terminated PU prepolymer blocked with  $\epsilon$ -caprolactam at various CP/NCO ratios at (a) 0, (b) 0.5, (c) 0.8, and (d) 1.0. The spectrum (a) in Figure 2 shows the NCO-terminated PU prepolymer at the ratio of CP/NCO equals to 0, which exhibited a strong single absorption peak at  $2270\text{ cm}^{-1}$  and a double peak at  $1600\text{ cm}^{-1}$  corresponding to the NCO and  $\text{C}=\text{O}$  and a single peak at  $1740\text{ cm}^{-1}$ . With the increasing of  $\epsilon$ -caprolactam equivalent amount CP/NCO = 0.5, 0.8, and 1.0 as shown in Figures 2(b), (c), and (d), respectively, the double peak at  $1600\text{ cm}^{-1}$  transformed into a single absorption peak and the absorption peak intensity at  $2270\text{ cm}^{-1}$  (NCO) decreased gradually. The spectrum in Figure 2(d) indicated that the residual NCO of NCO-terminated PU prepolymer could be easily blocked with  $\epsilon$ -caprolactam.

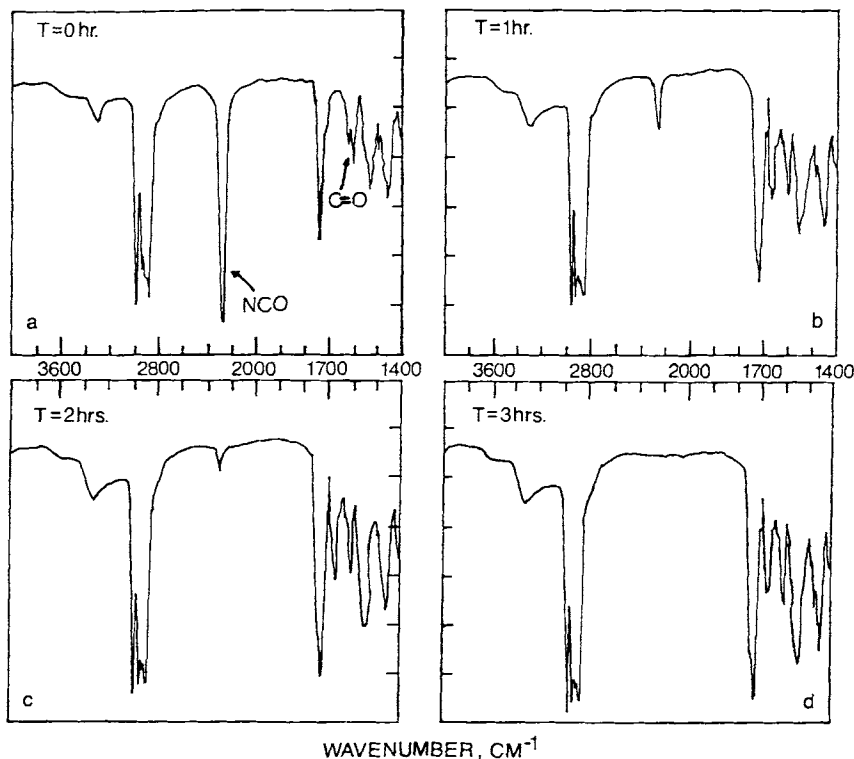
Figure 3 shows the IR spectra of the NCO-terminated PU prepolymer blocked with 1 eq  $\epsilon$ -caprolactam versus time at 0, 1, 2, and 3 h at  $80^\circ\text{C}$ .

From the figure, one can observe that the absorption peak at  $2270\text{ cm}^{-1}$  (NCO) disappears gradually with the reaction time. The resulting absorption spectrum indicated that the majority of the free NCO groups was blocked in the first 1 hour and blocking was almost complete in the third hour.

The  $^1\text{H-NMR}$  evaluation was performed on a compound obtained by the reaction of 1 eq NCO-terminated PU prepolymer with 1 eq  $\epsilon$ -caprolactam. This compound was dissolved in *d*-chloroform and analyzed by  $^1\text{H-NMR}$ .

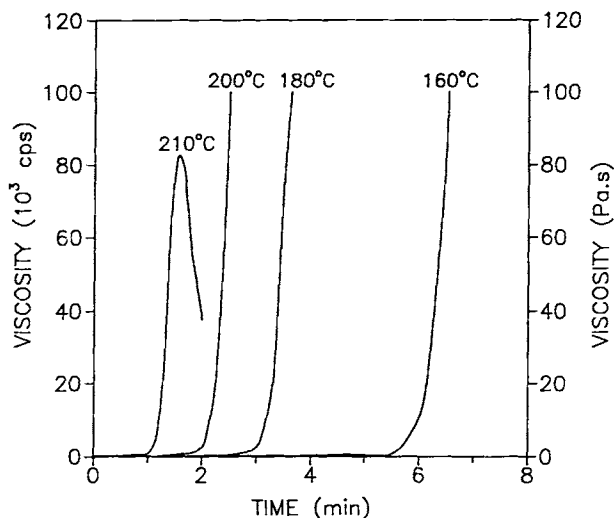
Figure 4 shows the  $^1\text{H-NMR}$  spectra of (a)  $\epsilon$ -caprolactam and (a) blocked NCO-terminated PU prepolymer. The spectrum (a) of Figure 4 shows the unreacted cycloamide hydrogen peak of  $\epsilon$ -caprolactam at  $\delta = 6.14$ . The equivalent mixture of NCO-terminated PU prepolymer and  $\epsilon$ -caprolactam exhibited a peak at  $\delta = 7.15$  when the blocking reaction was complete as shown in Figure 4(a). When the blocked NCO-terminated PU prepolymer was complete, the peak at  $\delta = 6.14$  disappears, and a new peak appears at  $\delta = 7.15$  which corresponds to the amide hydrogen peak of blocked NCO-terminated PU prepolymer.

The IR and  $^1\text{H-NMR}$  spectra show evidence that a chemical reaction between free NCO and  $\epsilon$ -cap-



**Figure 3** IR spectra of NCO-terminated PU prepolymer blocked with one equivalent of  $\epsilon$ -caprolactam versus time at (h): (a) 0; (b) 1; (c) 2; (c) 3.





**Figure 5** Viscosity of blocked NCO-terminated PU prepolymer with cycloaliphatic diamine (Laromin C260) versus time at various temperatures.

885, 655, and 505 cps, respectively. These results indicate that suitable viscosities (500–2000 cps) for good fiber wetting out can be obtained. The optimum process temperature in the impregnation tank was 50–70°C.

**Pot Life.** In order to provide a sufficient time for fiber wet-out and subsequent pultrusion processing, the pot life of resin must be prolonged. Table IV summarizes the pot life of blocked NCO-terminated PU prepolymer with cycloaliphatic diamine. One can observe when the temperatures were set at 50, 55, 60, 65, and 70°C, increases of the viscosities of blocked NCO-terminated PU prepolymer with

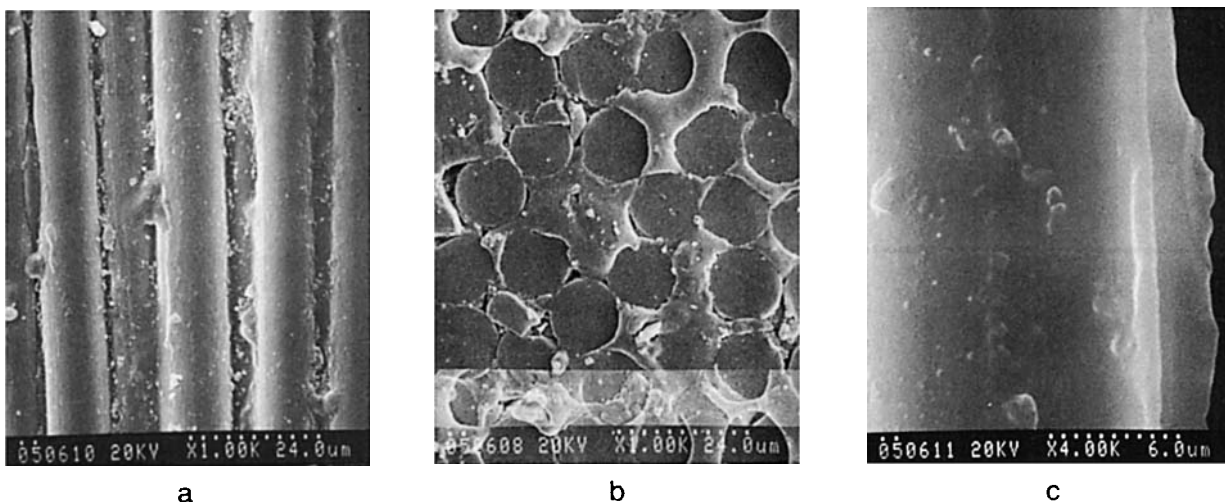
**Table IV** The Pot Life (Viscosity Change) of the Blocked NCO-Terminated PU Prepolymer with Cycloaliphatic Diamine

Temperature (°C)	Viscosity (cps) <sup>a</sup>		
	A	B	C
50	1780	1796	16
55	1240	1282	42
60	885	968	83
65	655	813	158
70	505	780	275

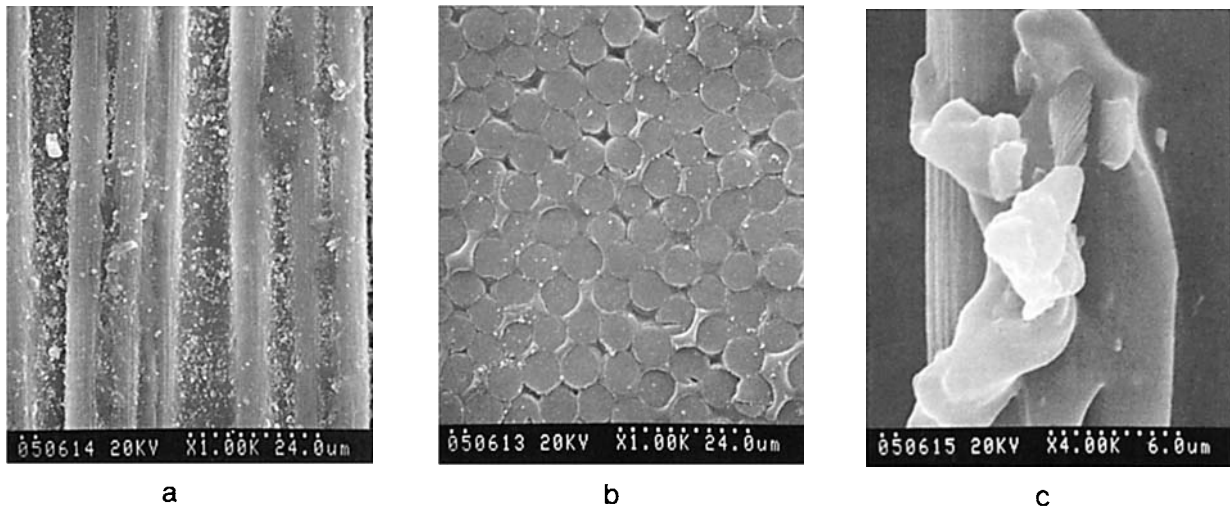
<sup>a</sup> A = virgin viscosity of resin; B = viscosity of resin after 2 days; C = viscosity change of resin after 2 days.

cycloaliphatic diamines are 16, 42, 83, 158, and 275 cps, respectively, after 2 days. These results indicate that the pot life of resins are longer than 2 days, which provides a sufficient time for subsequent processing.

**Reactivity** In the pultrusion process, the resin must have high reactivity, otherwise, they cannot be fabricated in a short time in the die. Figure 5 showed the viscosity of blocked NCO-terminated PU prepolymer with cycloaliphatic diamine changes with time. From the figure, it was found that the prepolymer with cycloaliphatic diamine has high reactivity at elevated temperature; thus the composites can be fabricated in a short time in the die. However, from the figure, one can also observe that the viscosity of blocked NCO-terminated PU prepolymer with cycloaliphatic diamine reached 82,500



**Figure 6** Scanning electron micrograph (SEM) of pultruded glass fiber reinforced PU composites: (a) longitudinal; (b) cross section; (c) fracture surface.



**Figure 7** Scanning electron micrograph (SEM) of pultruded carbon fiber reinforced PU composites: (a) longitudinal; (b) cross section; (c) fracture surface.

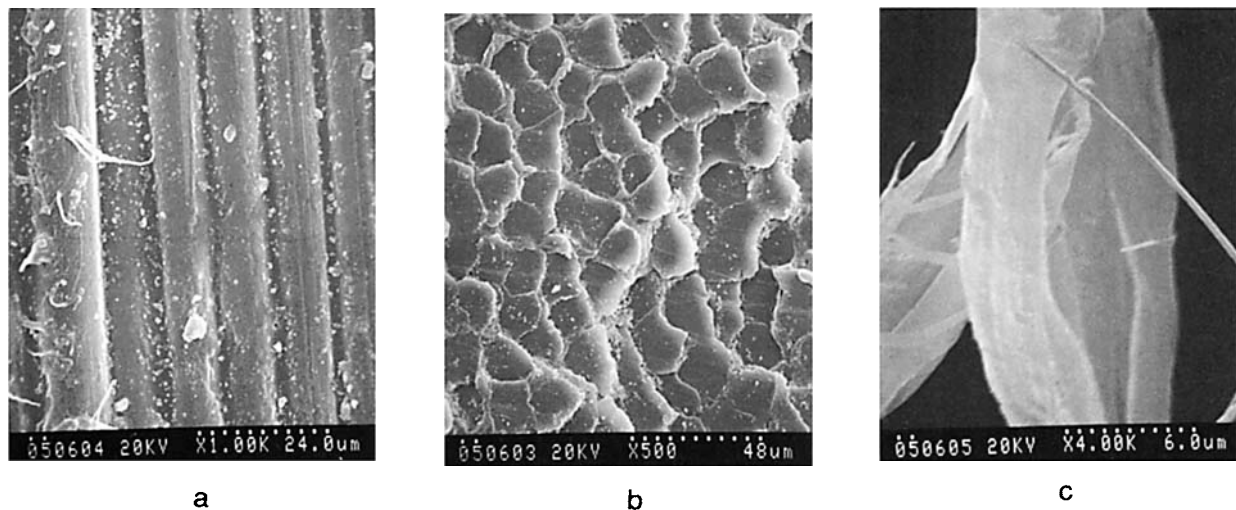
cps at reaction temperature of 210°C, and then descended sharply. The result indicates that the blocked NCO-terminated PU prepolymer with cycloaliphatic diamine degraded at 210°C. Thus the highest reaction temperature of blocked NCO-terminated PU prepolymer with cycloaliphatic diamine shall be kept below 210°C.

**Wetting Ability of Fiber.** In order to obtain composites with the best mechanical and thermal properties, adequate fiber wet-out is very important. The morphology phenomena can be observed by SEM photographs. The longitudinal, cross-section, and fracture surfaces of pultruded glass fiber, carbon fiber, and aramid fiber (Kevlar 49 fiber) reinforced

PU composites were investigated by scanning electron micrography as shown in Figures 6–8. From (a) and (b) of these figures one can observe that the fiber bundles are distributed evenly in the PU matrices. Photomicrographs (c) of Figures 6–8 show the wet-out of fiber by PU resin is excellent.

#### Effect of Type and Content of Fiber Reinforcements on the Mechanical Properties

In order to investigate the effect of type and content of fiber reinforcements on the properties of pultruded PU composites, glass fiber (GF), carbon fiber (CF), and Kevlar 49 fiber (KF) reinforced PU com-



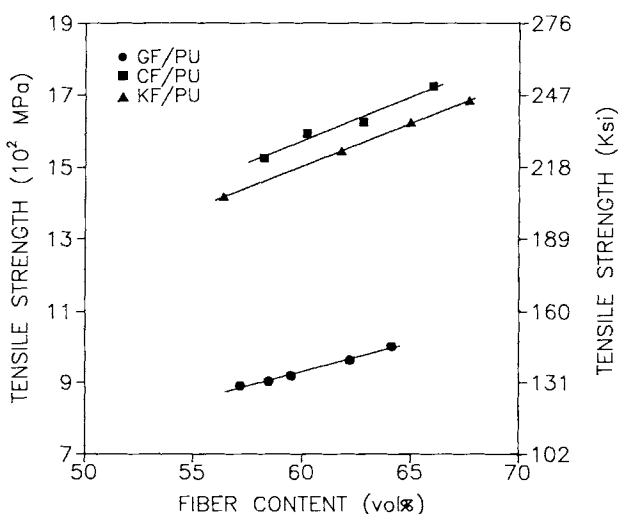
**Figure 8** Scanning electron micrograph (SEM) of pultruded Kevlar fiber reinforced PU composites: (a) longitudinal; (b) cross section; (c) fracture surface.

posites (GF/PU, CF/PU, and KF/PU) with various fiber contents were fabricated at the die temperature of 180°C and the pulling rate of 40 cm/min in this study. Tensile strength, specific tensile strength, flexural strength and modulus, and notched Izod impact strength of composites were measured.

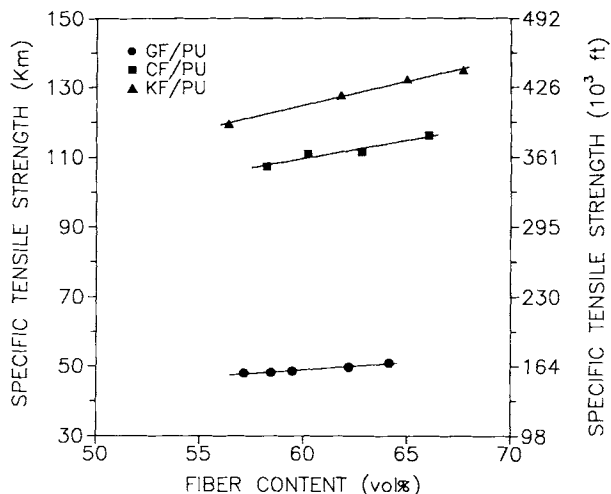
**Tensile Strength and Specific Tensile Strength** Figure 9 illustrates the tensile strength of pultruded glass fiber, carbon fiber, and Kevlar fiber reinforced PU composites with various fiber contents. Results indicate that the tensile strength increased with fiber volume content and a linear relationship exists. CF/PU composites possess the highest tensile strength, whereas that of the GF/PU composite is the lowest.

The effect of fiber volume content on specific tensile strength is shown in Figure 10. The specific tensile strength of KF/PU composite is the highest, whereas that of GF/PU composite is the lowest among the composites studied. The specific tensile strength of KF/PU composite is higher than that of CF/PU composite, because the density of KF/PU composite is lower than that of CF/PU composite. The density of the KF/PU composite is 1.210–1.274 g cm<sup>-3</sup>; CF/PU composite is 1.450–1.515 g cm<sup>-3</sup>, and GF/PU composite is 1.892–2.010 g cm<sup>-3</sup>.

Experimental results of tensile strength of all composites, except the CF/PU composites, followed the rule of mixtures. The carbon fiber/PU composites deviated from this rule due to the fiber breakage during processing.



**Figure 9** Tensile strength vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PU composites.



**Figure 10** Specific tensile strength vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PU composites.

**Flexural Strength, Flexural Modulus, and Specific Flexural Strength.** The effect of fiber volume content on flexural strength and flexural modulus are shown in Figures 11 and 12. The higher the fiber volume content, the higher the flexural strength and the flexural modulus. CF/PU composite showed the highest flexural strength and flexural modulus followed by GF/PU and then KF/PU.

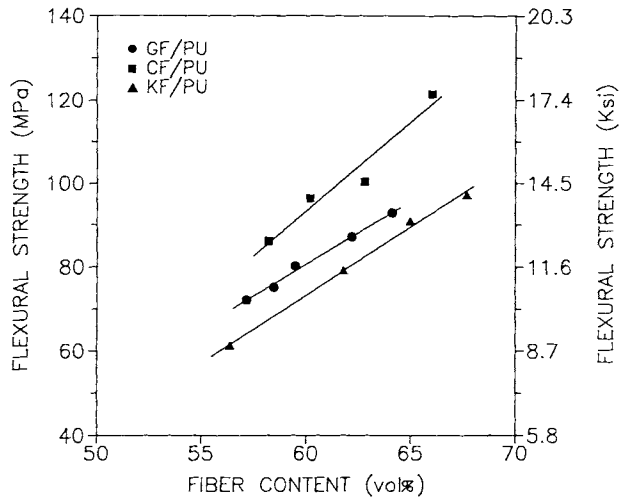
The effect of fiber volume content on the specific flexural strength is shown in Figure 13. It was found that the higher the fiber volume content, the higher the specific flexural strength. CF/PU shows the highest specific flexural strength followed by KF/PU and then GF/PU. The specific flexural strength of KF/PU composite is higher than that of GF/PU composite, because the density of KF/PU composite is lower than that of GF/PU composite.

**Notched Izod Impact Strength.** The effect of fiber volume content on notched Izod impact strength is shown in Figure 14. The notched Izod impact strength increased linearly with fiber volume content. The Kevlar 49 fiber reinforced composites had the least toughness. KF/PU showed the highest notched Izod impact strength followed by GF/PU and then CF/PU.

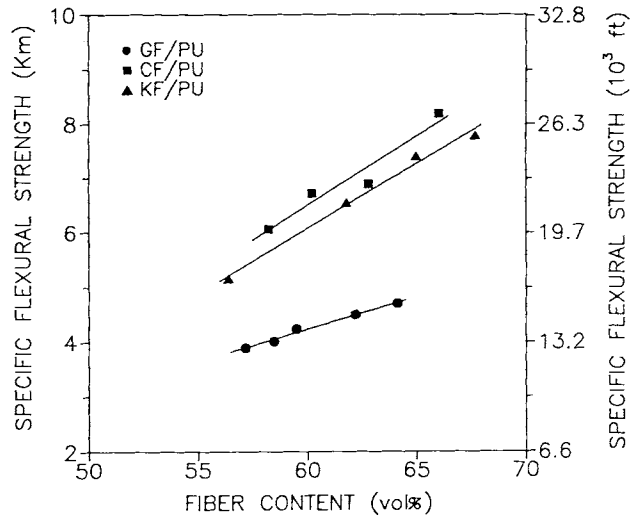
#### Properties Comparison of Pultruded Glass and Carbon Fiber Reinforced PU Composites with Other Pultruded Composites

Tables V and VI show the properties of pultruded glass fiber and carbon fiber reinforced PU compos-





**Figure 11** Flexural strength vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PU composites.



**Figure 13** Specific flexural strength vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PU composites.

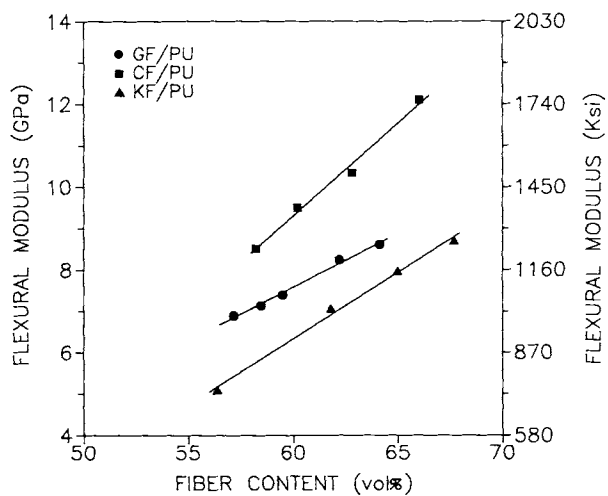
ites and other pultruded thermoplastic composites (PPS, ABS, nylon 6)<sup>14,15,17</sup> and thermoset composites (epoxy, unsaturated polyester, phenolic).<sup>6,14,25</sup>

**Tensile Strength** The pultruded GF/PU composites possess the highest tensile strength among the six pultruded glass fiber reinforced composites. CF/PU shows the highest tensile strength apart from CF/epoxy among the five pultruded carbon fiber reinforced composites.

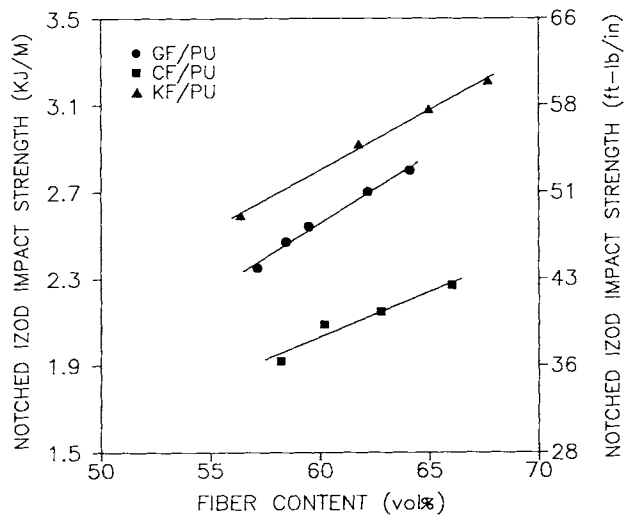
**Flexural Strength.** Both GF/PPS and CF/PPS show the highest flexural strength of all the pultruded composites studied. However, both GF/

PU and CF/PU are somewhat lower in flexural strength.

**Notched Izod Impact Strength.** Since polyurethane (PU) is an elastomer, which is usually described as a material characterized by the property of high elasticity. This means it has high toughness and has the ability to be stretched to a great extent under load and to recover almost completely when the load is released. Therefore, both GF/PU and CF/PU show the highest impact strength of all the pultruded composites studied. The pultruded fiber



**Figure 12** Flexural modulus vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PU composites.



**Figure 14** Notched Izod impact strength vs. fiber volume content of pultruded glass fiber (●), carbon fiber (■), and Kevlar fiber (▲) reinforced PU composites.

**Table V Properties Comparison Among Pultruded Glass Fiber (GF) Reinforced PU, Nylon 6 (NY6), PPS, Unsaturated Polyester (UP), Phenolic (PH), and ABS Resin Composites**

Properties	GF/PU	GF/NY6	GF/PPS	GF/UP	GF/PH	GF/ABS
Fiber content (wt %)	75	75	72	75	73	75
Tensile strength MPa (ksi)	890 (129)	869 (126)	793 (115)	828 (120)	448 (65)	710 (103)
Flexural strength MPa (ksi)	72 (11)	469 (68)	965 (140)	828 (120)	483 (70)	538 (78)
Notched Izod impact [kJ/m (ft-lb/in.)]	Unbroken	2.4 (44)	3.1 (58)	2.1 (40)	2.1 <sup>a</sup> (40)	2.5 <sup>a</sup> (47)
HDT [°C (°F)]	76 (169)	184 (363)	>260 (>500)	260 (500)	>280 (>536)	100 (212)
References	This study	17	14	14	25	15

<sup>a</sup> Notched Charpy impact strength.

reinforced PU composites do not break under impact at room temperature.

**Heat Deflection Temperature (HDT).** In general, plastic composites show much higher HDT than elastomeric composites. Therefore, both GF/PU and CF/PU are somewhat lower in HDT.

## CONCLUSIONS

In this study, a suitable blocking PU resin system was developed for the pultrusion process. The blocked NCO-terminated PU prepolymer was synthesized by  $\epsilon$ -caprolactam blocked TDI/branched polyester. It was found from GPC, and viscometer that the weight average molecular weight and viscosity of blocked NCO-terminated PU prepolymer were 4230 ( $M_w$ ) and 31,000 cps (25°C). From the mono-*n*-butylamine back-titration (wet) method, the equivalent weight and NCO content of un-

blocked NCO-terminated PU prepolymer were measured as 1400 and 3%. From IR and <sup>1</sup>H-NMR spectra the degree of blocking reaction can be observed.

The feasibility of the pultrusion of glass fiber, carbon fiber, and Kevlar fiber reinforced blocked PU composite has been demonstrated in this study. From viscosity study that the optimum temperature of blocked PU prepolymer in the impregnation tank was 50–70°C, and long pot life of blocked PU prepolymer with chain extenders (cycloaliphatic diamine) can be confirmed at 50–70°C. The high reactivity of prepolymer was observed from viscometer at elevated temperature. From the morphological study of SEM photographs that good fiber impregnation by the blocked PU resin was observed. The blocked NCO-terminated PU prepolymer with chain extender was suitable for a PU pultrusion process.

**Table VI Properties Comparison Among Pultruded Carbon Fiber (CF) Reinforced PU, Nylon 6 (NY6), PPS, Phenolic (PH), and Epoxy Resin Composites**

Properties	CF/PU	CF/NY6	CF/PPS	CF/PH	CF/epoxy
Fiber content (vol %)	58	57	56	58	54.4
Tensile strength [MPa (ksi)]	1525 (221)	1496 (217)	1172 (170)	1103 (160)	1917 (278)
Flexural strength [MPa (ksi)]	86 (13)	498 (72.3)	1365 (198)	827 (120)	1213 (176)
Notched Izod impact [J/m (ft-lb/in.)]	Unbroken	1708 (32)	1601 (30)	2562 <sup>a</sup> (48)	2364 <sup>a</sup> (44.3)
HDT [°C (°F)]	78 (173)	195 (383)	280 (536)	280 (536)	—
References	This study	17	14	25	6

<sup>a</sup> Notched Charpy impact strength.

The mechanical properties (i.e., tensile strength, specific tensile strength, flexural strength, specific flexural strength, flexural modulus, and impact strength) increase with fiber content. Kevlar fiber/PU composites possess the highest impact strength and specific tensile strength, whereas carbon fiber/PU composites show the highest tensile strength, flexural strength, specific flexural strength, and flexural modulus. Experimental results of tensile strength of all composites except carbon fiber/PU composites follow the rule of mixtures. The deviation of the property of carbon fiber/PU composite is due to the fiber breakage during processing. Pultruded fiber reinforced PU composites showed excellent tensile and impact strength compared to other pultruded composites studied.

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## REFERENCES

1. J. D. Martin, *15th National SAMPE Tech. Conf.*, 60-71 (1983).
2. K. Fuse and Y. Shirasaka, *40th Annu. Conf., RP/C, SPI, 2-C* (1985).
3. K. Arakawa, S. Iijima, E. Iwami, and K. Nomaguchi, *43rd Annu. Conf., RP/C, SPI, 19-D* (1988).
4. K. J. Elias and D. K. Watkins, *42nd Annual. Conf., RP/C, SPI, 12-A* (1987).
5. J. D. Martin and J. E. Sumerak, *38th Annu. Conf., RP/C, SPI, 6-F* (1983).
6. J. S. Hwang, Master thesis, National Tsing Hua University, Taiwan, ROC, 1986.
7. J. O. Outwater, *J. Compos. Mater.* **20**, 253 (1986).
8. Y. A. Jajima and D. G. Crozier, *Polym. Eng. Sci.*, **28**, 491 (1988).
9. S. M. Jessen and A. Plumtree, *Composites*, **20**, 559 (1989).
10. J. A. Kershaw, *38th Annu. Conf., RP/C, SPI, 6-C* (1983).
11. R. R. Hindersinn, U.S. Pat. 4,419,400 (1983).
12. D. R. Howard and D. R. Sayers, *40th Annu. Conf., RP/C, SPI, 2-A* (1985).
13. D. R. Howard and D. R. Sayers, *41st Annu. Conf., RP/C, SPI, 1-D* (1986).
14. J. E. O'Connor and W. H. Beever, *42nd Annu. Conf., RP/C, SPI, 1-D* (1987).
15. J. S. Hwang, S. N. Tong, S. J. Tasi, Paul H. H. Hsu, and Peter T. K. Wu, *43rd Annu. Conf., RP/C, SPI, 6-E* (1988).
16. S. N. Tong, D. S. Chen, and P. L. C. Hao, *SPE AN-TEC '83*, 438-439 (1983).
17. C. C. M. Ma and M. S. Yn, Taiwan, R.O.C. Pat. 35,969 (1989).
18. C. C. M. Ma, National Science Council Report No. NSC 79-0405-E007-08, Republic of China, 1980.
19. C. Hepburn, *Polyurethane Elastomer*, Applied Science, New York, 1982, p. 1-2.
20. C. E. Schildknecht, *Polymerization Processes*, Wiley, New York, 1978.
21. R. L. Jacobs and J. W. Long, *J. Elastomers Plast.*, **11**, 15 (1979).
22. A. Damusis, U.S. Pat. 3,267,078 (to Wyandotte Chemicals Co.) (1966).
23. Z. W. Wicks, Jr., *Blocked Isocyanates*, *Prog. Coatings*, **3**, 73 (1975).
24. J. A. Rolston, *Polym. Plast. Tech. Eng.*, **13**(1), 65 (1979).
25. C. C. M. Ma and W. C. Shih, U.S. Pat. 4,873,128 (1989).

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