

In Situ Pultrusion of Urea–Formaldehyde Matrix Composites. I. Processability, Kinetic Analysis, and Dynamic Mechanical Properties

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ABSTRACT: We conducted a feasibility study on the pultrusion of a glass-fiber-reinforced urea–formaldehyde (UF) composite using a proprietary method. The UF prepolymer synthesized in this study was prepared from blends of UF monomer and a curing agent (NH₄Cl). The process feasibility, kinetic analysis, and dynamic mechanical properties of the glass-fiber-reinforced UF composites by pultrusion were investigated. From investigations of the long pot life of the UF prepolymer, the high reactivity of the UF prepolymer, and excellent fiber wet-out, we found that the UF resin showed excellent process feasibility for pultrusion. A kinetic model, $d\alpha/dt = A \exp(-E/RT)\alpha^m(1 - \alpha)^n$, is proposed to describe the curing behavior of a UF resin. Kinetic parameters for the model were obtained from dynamic differential scanning calorimetry scans with a multiple-regression technique. The dynamic storage modulus of the pultruded-glass-fiber-reinforced UF composites increased with increasing die temperature, filler content and glass-fiber content and with decreasing pulling rate. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1242–1251, 2002

Key words: pultrusion; urea–formaldehyde (UF); prepolymer; glass fiber; process feasibility; kinetics; dynamic mechanical properties; composites

INTRODUCTION

Pultrusion is a continuous process for the production of composite materials.¹ This process has emerged as one of the most cost-effective processing techniques for composites. The use of the pultrusion process to manufacture continuous profiles of composite materials is expanding rapidly.² Figure 1 is a schematic representation of the pul-

trusion process. A typical pultrusion machine in general consists of eight inline parts: (1) a fiber roving shelf, (2) fiber guides, (3) a fiber drying chamber, (4) a resin wet-out tank, (5) a heated matched metal die, (6) a postcure chamber, (7) a puller, and (8) a cutter.³

The methods of manufacturing pultruded products include emulsion,⁴ hot melt,⁵ fluidized bed,⁶ slurry,⁷ *in situ* polymerization,⁸ reaction injection molding,⁹ and matrix fiber interweaving with reinforced fiber prepregs.¹⁰ Except for *in situ* polymerization, these other methods create poor fiber wet-out and cause serious shrinkage of pultruded products. Therefore, *in situ* polymerization for pultrusion is the best method to manufacture pultruded composites. Generally, the processability

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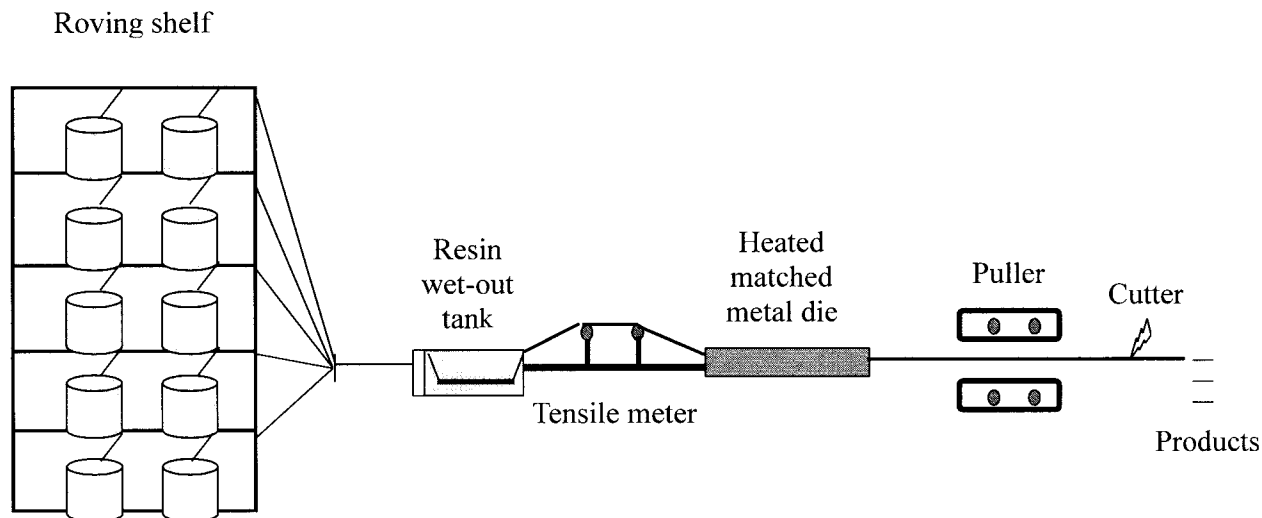


Figure 1 Flow chart of pultrusion machine.

of resin for an *in situ* pultrusion process must have the following: (1) a suitable viscosity (500–2000 mPa · s) in the impregnation tank, (2) a long pot life in the impregnation tank, (3) high reactivity, and (4) good wetting ability between fiber and resin.^{11–12} The fiber will exhibit excellent wet-out when the resin has a suitable viscosity in the impregnation tank. Long pot life in the impregnation tank means the viscosity of resin should only increase slightly over a long processing time so that the fibers have adequate time to be wetted out and the pultrusion process can be operated for a long time. To fabricate the composites in a short time in the pultrusion die, the resin should have high reactivity. Furthermore, good fiber wet-out is necessary to obtain optimum mechanical properties for the composites.

To study the curing reaction of resins for the pultrusion process, a variety of experimental techniques have been developed to study the curing reaction of resins. The technique of dynamic differential scanning calorimetry (DSC) is a useful method to monitor the course of exothermic cure reactions.^{13,14} From this method, the kinetic model and kinetic parameters of resin can be obtained from a simulation under nonisothermal conditions. To investigate the best structural application of pultruded composites, the dynamic mechanical properties of composites should be studied.¹⁵ The objective of the use of urea–formaldehyde (UF) for the pultrusion process is to take advantage of the unique properties of UF, including its excellent mechanical properties, thermal properties, abrasion resistance, hardness, and

low cost.^{16,17} Furthermore, because the UF resin shows the characteristics of long pot life, high reactivity, and good glass-fiber wet-out, it is suitable for the pultrusion process.

The aim of this work was to study the glass-fiber-reinforced UF composites for pultrusion. A suitable viscosity range (500–2000 mPa · s) of UF prepolymer was synthesized from blends of UF resin and a curing agent (NH_4Cl) at a suitable temperature. The prepolymers were used directly and polymerized in the die. This provides a new concept for *in situ* pultrusion. This article presents the process feasibility, the kinetic analysis of the resin, and the dynamic mechanical properties of the fiber-reinforced UF composites by pultrusion.

EXPERIMENTAL

Materials

The materials used in this study are listed in Table I. They include resin, curing agent (NH_4Cl), glass fiber, one filler, and the UF prepolymer synthesized in this study.

Synthesis of UF Prepolymer

We synthesized the UF prepolymer by heating the UF resin with a small amount of curing agent (NH_4Cl). The procedure was as follows:

1. Curing agent (0.15 phr) curing agent (NH_4Cl) was added to the UF resin and

Table I Materials Used in this Study

Material	Specification	Supplier
Monomer	UF Viscosity = 80–100 mPa · s at 25°C Solid content = 47 ± 2% (UF resin = 47 wt %, water = 53 wt %) pH = 6.6–7.2	Chang Chun Resin Co., Hsin Chu, Taiwan, Republic of China
Curing agent	NH ₄ Cl	Chang Chun Resin, Hsin Chu, Taiwan, Republic of China
Fiber	Molecular weight = 53.5 Glass fiber (E-glass) TGFR-P2200 Specific gravity = 2.54 Diameter = 23 μm Tensile strength = 3500 N/mm ²	Taiwan Glass Co., Taipei, Taiwan, Republic of China
Filler	Kaolin Specific gravity = 2.6	Yin Chin Co., Taiwan, Taipei, Republic of China

was stirred continuously for 30 min to ensure mixing was complete.

- The reaction was then carried out in a water bath, and the temperature was maintained at 70°C until a suitable prepolymer viscosity (1000 mPa · s at 25°C) was reached.
- To prevent further polymerization, the synthesized prepolymer was quenched in an ice bath for 30 min and was then stored at a low temperature (< 5°C).

Apparatus and Measurement

The pultrusion machine was custom designed. It consisted of multiple heating zones and a pultrusion die with dimensions of 820 × 12.7 × 3.19 mm and 820 × 12.7 × 2.08 mm (length × width × thickness). The surfaces of the stainless steel die were treated by chrome plating.

Viscosities of prepolymer were measured with a Brookfield RVF model viscometer.

IR measurements were carried out with a PerkinElmer model IR-983 (USA). The sample was directly dabbed onto a KBr pellet for IR tests.

The gel time was measured following the specifications of ASTM 3532-76. The hot plate was set a precise temperature. With 1–2 g of resin on the hot plate, the tip of a needle was used to pick the resin three times per second until the resin was too sticky to be picked.

Scanning electron microscopy (SEM) photographs were obtained on a S-570 Hitachi (Japan) scanning electron microscope. The microphotographs were taken on the surface obtained by

fracturing the specimen in liquid nitrogen and then coating it with gold powder.

A model 2000 differential scanning calorimeter from DuPont Co. (USA) was used.

We used a DuPont 9900 dynamic mechanical analyzer (DMA) from 0 to 300°C. The DMA system was a resonance frequency type, and the sample dimensions were 50 × 12.5 × 2.0 mm (length × width × thickness). The heating rate was 5°C/min, and the amplitude of oscillation was 1 Hz. Poisson's ratio was 1:2.

The void content was determined with the following equation according to ASTM D2734:

$$\text{Void content} = \frac{D_b - D_a}{D_b} \times 100\%$$

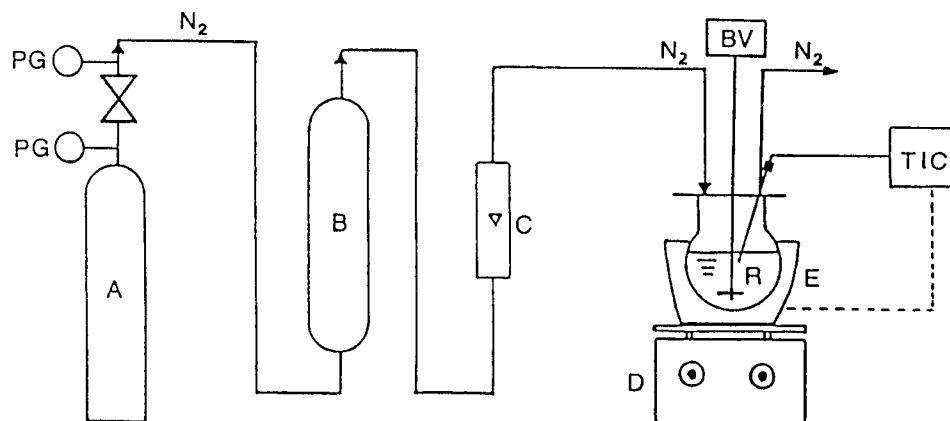
where D_a is the actual density of the composite and D_b is the theoretical density of the composite as calculated by the following equation:

$$D_b = \frac{100}{\frac{W_m}{\rho_m} + \frac{W_f}{\rho_f}}$$

where W_m is the weight fraction of the resin, W_f is the weight fraction of the fiber, ρ_m is the density of the resin, and ρ_f is the density of the fiber.

The swelling ratio (q) was determined with the following equation:¹⁹

$$q = \frac{V}{V_0} = 1 + \frac{(W - W_0)D_0}{W_0D_s}$$



A. Nitrogen Supply D. Hot Plate
 B. Silica Gel E. Heating Mantle
 C. Flowmeter R. Reactor
 TIC : Temperature Indicator and Controller
 PG : Pressure Gauge
 BV : Agitator

Figure 2 Apparatus for the polymerization of the UF prepolymer.

where V_0 is the volume of the unswollen pultruded composite, V is the volume of the swollen pultruded composite, W_0 is the weight of the unswollen pultruded composite, W is the weight of the swollen pultruded composite, D_0 is the density of pultruded composite, and D_s is the density of solvent (chloroform).

RESULTS AND DISCUSSION

Synthesis of UF Prepolymer

The UF prepolymer was synthesized by heating 0.15 phr of curing-agent-free UF resin in a water bath. The reaction was permitted to exotherm on stirring and under a nitrogen blanket until a suitable prepolymer viscosity was reached. Figure 2 shows the apparatus for the polymerization of the UF prepolymer. To remove the reaction heat (exothermic), the synthesized prepolymer was quenched in an ice bath for 30 min and was then stored at a temperature below 5°C.

The viscosity of the synthesized UF prepolymer was measured with a Brookfield viscometer as shown in Figure 3. The polymerized temperature was set at 60–75°C. When the prepolymer viscosity reached 160–200 mPa · s, the synthesized

prepolymer was quenched in an ice bath for 30 min. When the temperature returned to room temperature (25°C), the synthesized prepolymer viscosity was about 1000 mPa · s. From Figure 3, one can observe that the optimum synthesis temperature of the UF prepolymer was 70°C. When the temperature was lower than 70°C, the pro-

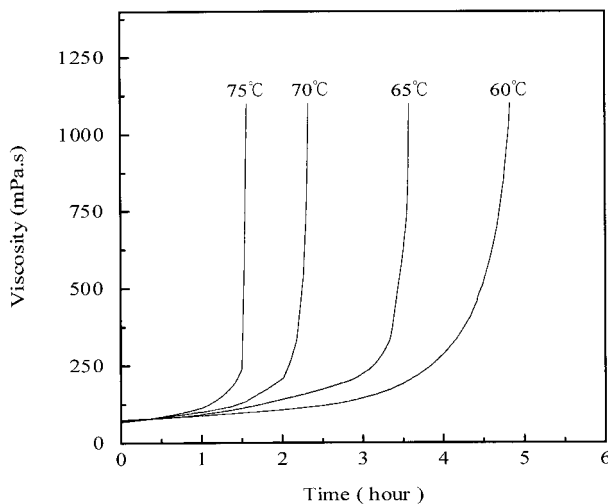


Figure 3 Viscosity of the synthesized UF prepolymer versus time at various temperatures.

Table II Viscosity of UF Prepolymer at Various Temperatures

	Temperature (°C)			
	25	30	40	50
Viscosity (mPa · s)	1050	900	750	600

cessing time was too long to process; however, when the temperature was higher than 70°C, the viscosity of the UF prepolymer could not be easily controlled.

Processability Study

The resin used for *in situ* pultrusion processes must possess the following characteristics as well as a suitable viscosity (500–2000 mPa · s) in the impregnation tank: (1) a long pot life, (2) high reactivity, and (3) good wet-out between fiber and resin.

Viscosity Versus Temperature in the Impregnation Tank

Because the suitable viscosity of prepolymer in the impregnation for pultrusion processes had to be set at 500–2000 mPa · s, we had to measure the prepolymer viscosity. Table II shows the relationship between the viscosity of the UF prepolymer and temperature. When the temperatures were set at 25, 30, 40, and 50°C, the viscosities of prepolymer were 1050, 900, 750, and 600 mPa · s, respectively, a suitable range for good fiber wetting out. The optimum process temperature in the impregnation tank was 25–50°C.

Pot Life

To provide a sufficient time for pultrusion processing, the pot life of the UF prepolymer had to be prolonged. Figure 4 shows the viscosity versus reaction time of the UF prepolymer at various temperatures. The viscosity of UF prepolymer rose only 400 mPa · s (from 1100 to 1500 mPa · s) after 8 h at 20°C and rose 1100 mPa · s (from 900 to 2000 mPa · s) after 7 h at 30°C. All viscosity increases were not more than 2000 mPa · s after 7 h. These results indicate that the pot life of the UF prepolymer was longer than 7 h when the impregnation tank was set at 20–30°C, which provided sufficient time for subsequent processing.

Reactivity

In the pultrusion process, the UF prepolymer has to have a high reactivity; otherwise, it cannot be

fabricated in a short time in the die. Generally, when UF is polymerized, the IR spectra absorption peaks for OH; the first grade amide of C=O, C—N, and N—H; the second grade amide of C—N and N—H; and the third grade amide of C—N and N—H disappear at 3345, 1650, 1550, and 1250 cm^{-1} , respectively. Figure 5 shows the IR spectra of UF and the UF prepolymer. From the figure, one can observe that when the UF prepolymer was polymerized at 180°C for 60 sec, all these peaks clearly disappeared. Figure 6 shows the gel time (see Apparatus and Measurement) of the UF prepolymer at various temperatures. As shown in the figure, the UF prepolymer had short gel times (< 60 sec) when the temperature was above 180°C. As shown in Figures 5 and 6, the UF resin had a high reactivity at elevated temperatures; thus, the composites could be fabricated in a short time in the pultrusion die.

Wetting Ability of Fiber

To obtain composites with the best mechanical properties, adequate fiber wet-out is very important. The morphology phenomena can be observed by SEM photographs. The cross-section and fracture surfaces of pultruded-glass-fiber-reinforced UF composites, investigated by SEM micrography, are shown in Figure 7. From Figure 7(a), one can observe that the fiber bundles were distributed evenly in the UF matrices. From Figure 7(b), it can be seen that the glass-fiber surface still retained a lot of UF resin after fracture tests; therefore, excellent wet-out of glass fiber by UF resin was observed.

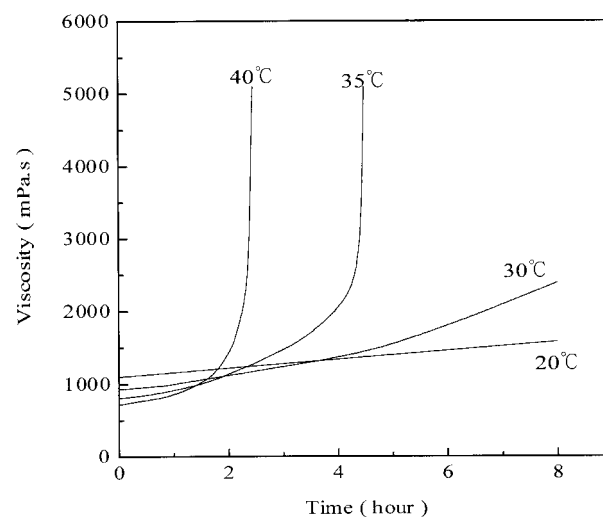


Figure 4 Viscosity of the UF prepolymer versus time at various temperatures.

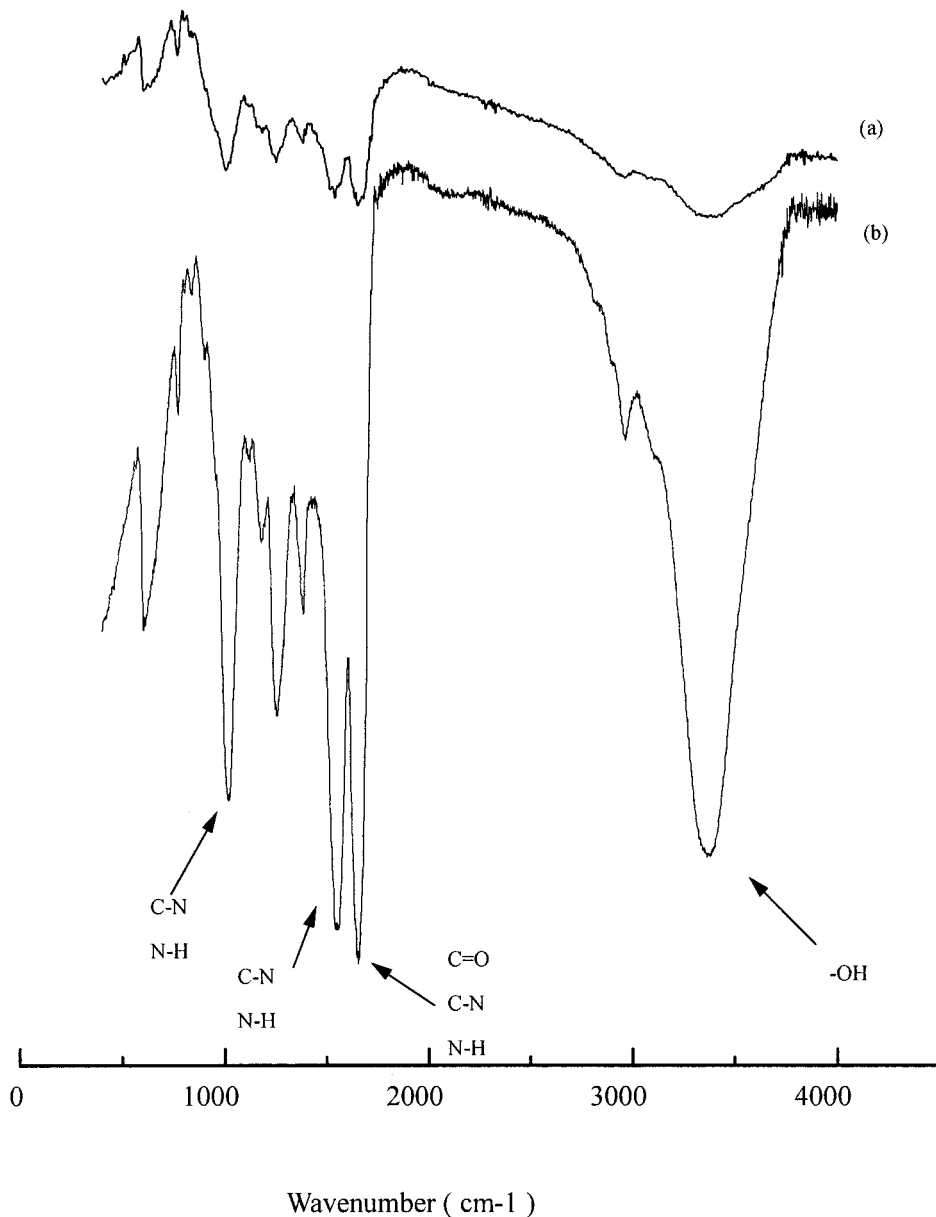


Figure 5 IR spectra of (a) UF and (b)UF prepolymer.

Kinetic Analysis

The mechanistic kinetic model used in this study to describe the curing behavior of UF/glass fiber was based on an autocatalytic reaction. Details of the derivation were discussed elsewhere.¹⁸ The rate equation is given by

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) \alpha^m (1 - \alpha)^n \quad (1)$$

where α is the conversion (i.e., degree of curing), A is the preexponential factor, E is the activation

energy, R is the universal gas constant, T is the absolute temperature, and m and n are the orders of reaction.

The heat evolved during the curing reaction and measured by the dynamic DSC thermogram can be related to the α and $d\alpha/dt$ rate by

$$\Delta H = \int_0^t \frac{dQ_t}{dt} dt \quad (2)$$

$$\alpha = \frac{Q_t}{\Delta H} \quad (3)$$

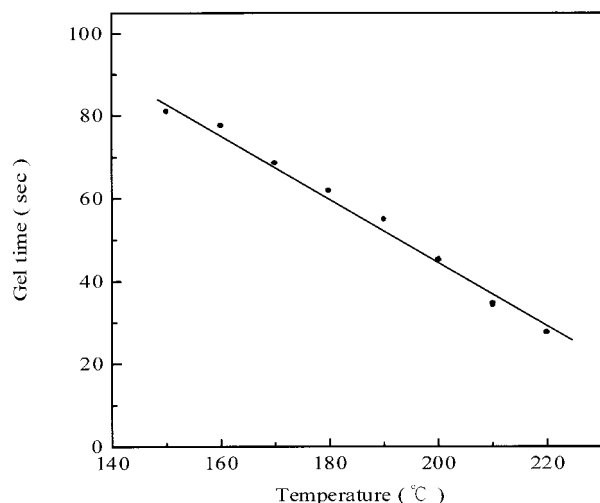


Figure 6 Effect of temperature on the gel time of the UF prepolymer.

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H} \frac{dQ_t}{dt} \quad (4)$$

where α is the conversion at time t , Q_t is the reaction heat up to time t or temperature T , and ΔH is the total heat of reaction for 100% α . Equation (1) can be expressed in logarithmic form as follows:

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E}{RT} + m \ln \alpha + n \ln(1 - \alpha) \quad (5)$$

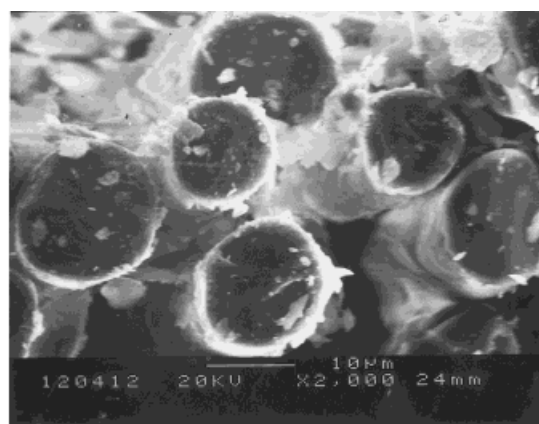
By integrating the DSC curve, we obtained a ΔH of 670.7 J/g. Using a multiple regression technique to solve eq. (5), one can obtain the following kinetic parameters: $A = 7.19 \times 10^{11} \text{ min}^{-1}$, $E = 23.37 \text{ kcal/mol}$, $m = 0.472$, and $n = 0.637$. Figures 8 and 9 illustrate α and $d\alpha/dt$ versus temperature of the UF prepolymer for the curing reaction at a scan speed of 10°C/min. The solid lines represented the calculated values obtained from eq. (1) with the aforementioned kinetic parameters, whereas the dashed lines are data obtained directly from the DSC thermogram with eqs. (3) and (4). From Figures 8 and 9, one can observe that the experimental data agree very well with the theoretical prediction.

Dynamic Mechanical Properties

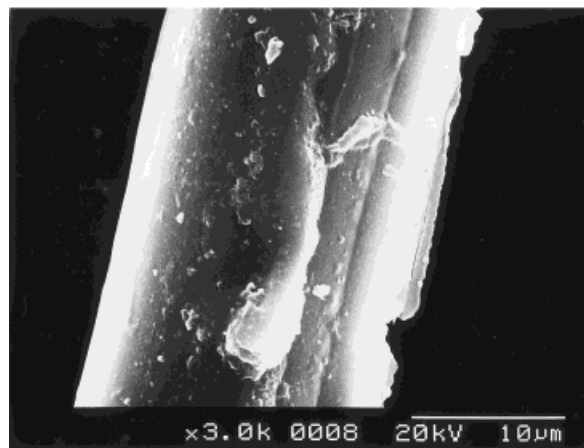
The dynamic mechanical behavior of the composite was of great interest and importance for struc-

tural applications, and it was very sensitive to the processing conditions. Unreinforced polymer and incompletely polymerized composites still would show good appearance and reasonable integrity, but the dynamic mechanical behavior would be quite different from those of reinforced polymers and well-polymerized composites.

Figure 10 shows the dynamic storage modulus (E') versus temperature of pultruded-glass-fiber-reinforced UF composites at various glass-fiber contents. From the figure, we see that the E' increased with increasing glass-fiber content. At low temperatures, E' of the pultruded UF composites was 10^9 – 10^{10} Pa (typical glassy state).



(a) Cross-section



(b) Fracture surface

Figure 7 SEM micrographs of pultruded-glass-fiber-reinforced UF composites: (a) cross-section and (b) fracture surface.

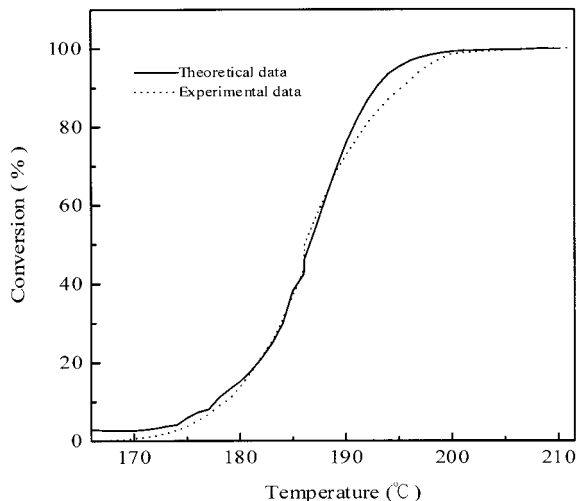


Figure 8 α versus temperature of the UF prepolymer from (—) experimental data and (—) theoretical data by dynamic DSC at 10°C/min.

When the temperature was near the glass transition temperature (160–180°C), the E' decreased sharply and finally leveled off at 10^7 – 10^8 Pa (typical rubbery state).

The effect of the filler (kaolin) contents on the E' of the pultruded-glass-fiber-reinforced UF composites is shown in Figure 11. As shown in this figure, the E' increased with increasing kaolin content. The reasons for this increase were that the composite structure became more tightly constrained (close bond) and void contents de-

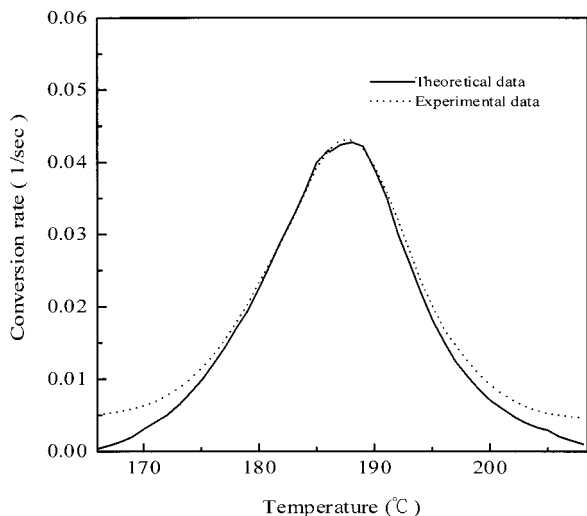


Figure 9 da/dt versus temperature of the UF prepolymer from (—) experimental data and (—) theoretical data by dynamic DSC at 10°C/min.

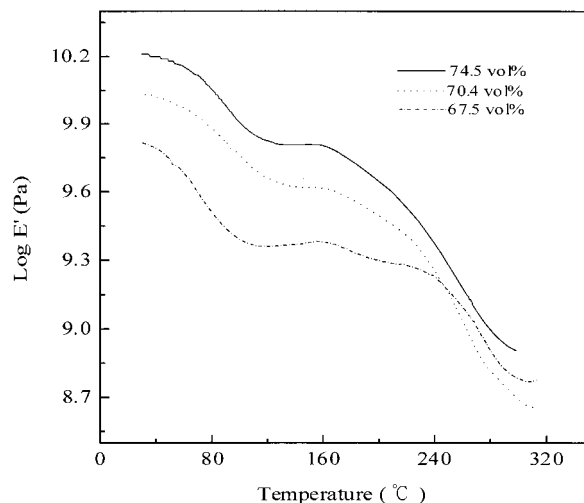


Figure 10 E' versus temperature of pultruded-glass-fiber-reinforced UF composites at various glass-fiber contents.

creased when the filler was added.¹² Table III summarizes the void content of the pultruded-glass-fiber-reinforced UF composites at various filler (kaolin) contents. The void contents decreased with increasing kaolin content.

Other important factors for the determination of the dynamic mechanical properties of the pultruded composites are the die temperature and pulling rate. Figures 12 and 13 show the E' versus temperature of the pultruded-glass-fiber-reinforced UF composites at various die temperatures and pulling rates, respectively. As can be

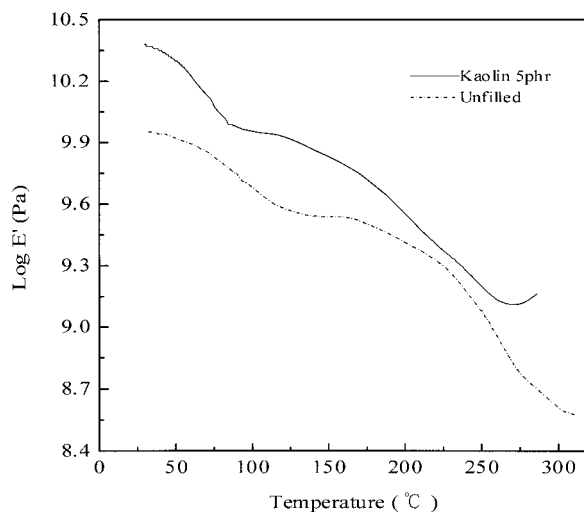


Figure 11 E' versus temperature of pultruded-glass-fiber-reinforced UF composites at various filler (kaolin) contents.

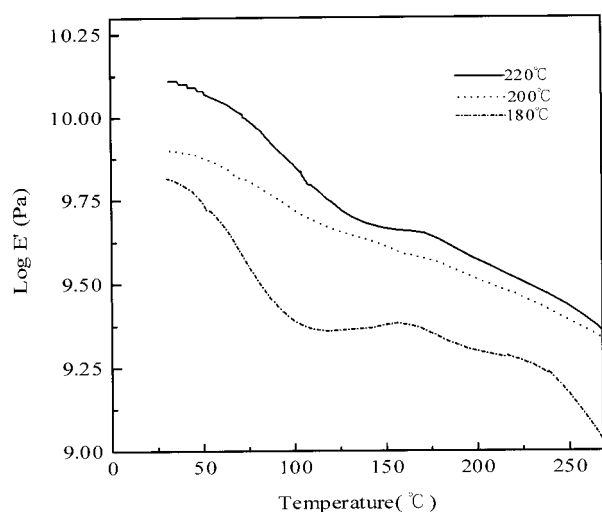
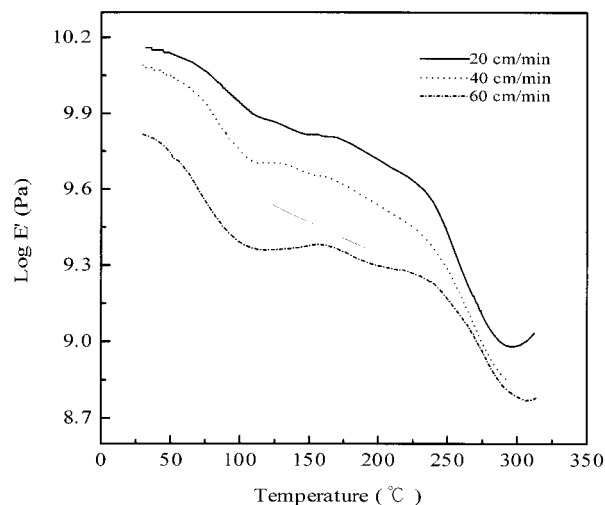
Table III Void Content of Pultruded-Glass-Fiber-Reinforced UF Composites at Various Filler (Kaolin) Contents

Filler (Kaolin) Content (phr)	Void Content (%)
0	5.53
5	3.12

seen in the figures, the E' increased with increasing die temperature and decreasing pulling rate. The increasing modulus was a consequence of the increase in degree of α (crosslinking). The higher degree of α caused the polymer chains to become more tightly crosslinked and, therefore, less mobile. The degree of crosslinking of the composites could be explained from their q_s .¹⁹ The degree of crosslinking of composites increased with decreasing q . Tables IV and V show the effect of die temperatures and pulling rates on the q of the pultruded-glass-fiber-reinforced UF composites. As shown in these tables, the q of composites decreased with increasing die temperatures and with decreasing pulling rates.

CONCLUSIONS

In this study, a suitable UF resin system was developed for the pultrusion process. The UF prepolymer was synthesized by a UF monomer with

**Figure 12** E' versus temperature of pultruded-glass-fiber-reinforced UF composites at various die temperatures.**Figure 13** E' versus temperature of pultruded-glass-fiber-reinforced UF composites at various pulling rates.

a curing agent (NH_4Cl), and the polymerized temperature was set at 70°C .

The feasibility of the pultrusion of glass-fiber-reinforced UF composites was demonstrated. From the viscosity study, the optimum temperature of the UF prepolymer in the impregnation tank was determined to be $25\text{--}50^\circ\text{C}$, and the long pot life of the UF prepolymer was confirmed at $20\text{--}30^\circ\text{C}$. The high reactivity of the UF prepolymer was observed from IR spectra and gel time at elevated temperature. From the morphological study of SEM photographs, good fiber impregnation by the UF resin was observed. This demonstrates that the UF resin was suitable for a pultrusion process.

The experimental results agree very well with the theoretical prediction and indicate that the autocatalytic model $d\alpha/dt = A \exp(-E/RT)\alpha^m(1 - \alpha)^n$ is suitable for reinforced UF resin. The following kinetic parameters were obtained: $A = 7.19 \times 10^{11} \text{ min}^{-1}$, $E = 23.37 \text{ kcal/mol}$, $m = 0.472$, and $n = 0.637$. The dynamic mechanical behavior of the composite was of great interest

Table IV Swelling Ratio of Pultruded-Glass-Fiber-Reinforced UF Composites at Various Die Temperatures

Die Temperature ($^\circ\text{C}$)	Swelling Ratio
180	1.51
200	1.46
220	1.42

Table V Swelling Ratio of Pultruded-Glass-Fiber-Reinforced UF Composites at Various Pulling Rates

Pulling Rates (cm/min)	Swelling Ratio
20	1.40
40	1.48
60	1.58

and importance for structural applications, and it was very sensitive to the processing conditions. The E' of pultruded-glass-fiber-reinforced UF composites increased with increasing die temperature, filler content, and glass-fiber content and with decreasing pulling rate.

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