Mathematical Model for the Pultrusion of Blocked PU–UP Matrix Composites

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Received 25 October 2002; accepted 21 January 2003

ABSTRACT: The thermokinetic behavior of blocked polyurethane (PU)–unsaturated polyester (UP)–based composites during the pultrusion of glass-fiber-reinforced composites was investigated utilizing a mathematical model that accounted for the heat transfer and heat generation during curing. The equations of continuity and energy balance, coupled with a kinetic expression for the curing system, were solved using a finite difference method to calculate the temperature profiles and conversion profiles in the thickness direction in a rectangular pultrusion die. A kinetic model, $dP/dt = A \exp(-E/RT)P^m(1 - P)^n$, was proposed to describe the curing behavior of a blocked PU–UP resin. Kinetic parameters for the model were obtained from dynamic differential scanning calorimetry scans using a multiple regression technique, which was able to predict the effects of processing parameters on the pultrusion. The effects of processing parameters including pulling speed, die wall temperature, and die thickness on the performance of the pultrusion also were evaluated. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1996–2002, 2003

Key words: pultrusion; blocked PU–UP; mathematical model; kinetic; processing parameters; composites

INTRODUCTION

Pultrusion is a continuous process of producing composite materials. Figure 1 shows a schematic representation of the pultrusion process.[1] The pultruder consists of a fiber delivery system, resin bath, preform fixtures, heated die, synchronized pullers and cutoff saw.[2] This technology offers the advantages of continuous production and integration of fiber impregnation and composite consolidation in the same process. The simplicity, efficiency, and flexibility of this process make it one of the most interesting methods for the fabrication of continuous fiber composite products with constant cross-section.[3] Most of the published articles on pultrusion in the literature[4–10] have discussed its applications, some aspects of pultruded composites, and the pultrusion process itself from the vantage point of monitoring the quality of incoming resins. Several works[11–14] have reported on the fundamental aspects of the process, which is difficult to control unless it is known how to handle the exothermic chemical reactions taking place inside a pultrusion die.

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Contract grant sponsor: National Science Council, Taiwan, Republic of China; contract grant number: NSC 84-2216-E-034-002.

Journal of Applied Polymer Science, Vol. 90, 1996–2002 (2003)

Recently, a variety of experimental techniques have been developed to study the curing reaction of resins. Among them, the dynamic differential scanning calorimetry (DSC) technique has been found to be a convenient and useful method for monitoring the course of exothermic cure reactions.[15–17] The method is based on the measurement of the rate at which heat is generated in an exothermic chemical reaction. With the assumption that the heat generated by a chemical reaction is proportional to the extent of the reaction, the kinetic parameters can be obtained from a simulation under nonisothermal conditions.

To manufacture pultruded composites of consistent quality, a fundamental investigation to develop a strategy for controlling the pultrusion process is essential. The most important condition for achieving a uniform degree of cure in the cross-sections of pultruded composites is the temperature profile in the pultrusion die. The temperature model predicts the temperature of the pultruded composites as a function of the distance from the composite centerline and the location in the pultrusion die. The composite is treated as a long, transversely isotropic slab of constant height with either a prescribed boundary temperature or prescribed heat flux from the surfaces. Hence, heat transfer is considered through the thickness only, and issues of axial heat transfer of viscous dissipation are avoided.[18] Note that it is important to have control of the temperature and conversion profiles in the thin direction in a rectangular pultrusion die and in the radial direction in a

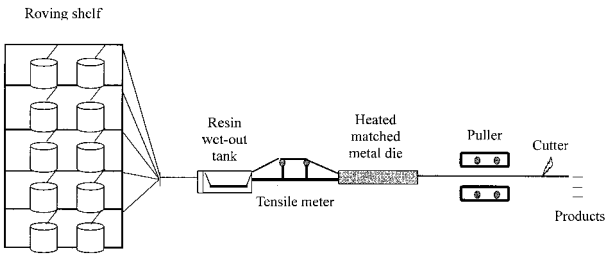

Figure 1 Flow chart of pultrusion machine.

cylindrical pultrusion die. Therefore, it is also important to develop a mathematical model for simulating and ultimately for controlling the pultrusion process and the process.[19–21]

The purpose of this study was to develop a mathematical model to accurately predict the temperature and conversion in a rectangular pultrusion die by introducing a kinetic expression using dynamic DSC scanning and heat transfer, which are relevant for the pultrusion of blocked PU–UP resin. The predictions of the model were compared with experimental results. The effects of processing parameters on the pulling rate, die wall temperature, and die thickness also were investigated.

EXPERIMENTAL

Materials

The materials used in this study are listed in Table I. They include unsaturated polyester (UP) prepolymer, initiator, blocked polyurethane (PU) prepolymer, chain extender, and glass fiber.

Procedures

To prepare the blocked PU–UP (50:50 wt %) prepolymer, one equivalent of blocked NCO-terminated PU prepolymer was heated to 50°C and then mixed homogeneously with one equivalent of aromatic diamine (ACR H-3486). The PU prepolymer was heated to 50°C and then mixed homogeneously with 0.5 phr (parts per hundred parts of resin) of initiator. Then, the two mixtures were blended in 50:50 weight ratios at 50°C and mixed completely using a high torque stirrer.

Between 5 and 10 mg of blocked PU–UP prepolymer with a 50 wt % glass fiber content was placed in the DSC cell. The aluminum sample pan was tightly sealed, and a DSC scan at a heating rate of 10°C/min was performed.

Apparatus and measurement

The pultrusion machine was custom-designed. It consisted of multiple heating zones and a pultrusion die whose dimensions were 82 × 1.27 × 0.319 cm and 82 × 1.27 × 0.208 cm (length × width × thickness), respectively. The surfaces of the stainless-steel die were treated by chrome plating.

The calorimetric measurements were conducted using a DuPont 2000 differential scanning calorimeter (DSC) with nitrogen as the flushing gas. The temperature and power calibration of the DSC were optimized within the temperature range of 30°C–300°C, using indium as the DSC calibration standard.

The flexural properties were measured on an Instron 1123 universal testing machine (Instron Co., USA) following the specification of ASTM Standard D 790. The sample dimensions were 127 × 12.5 × 3.0

TABLE I
Raw Materials

Material	Specification	Supplier
UP prepolymer	Ortho-type unsaturated polyester (UP) Viscosity = 200 mPas at 25°C Viscosity = 200 mPas at 25°C	Eternal Co., Taiwan, ROC
Initiator	C-type curing agent (high-temperature type) (blend of 80% cumene hydroperoxide and 20% plasticizer) Viscosity = 500 mPas at 25°C	Swancor Co., Taiwan, ROC
PU prepolymer	Blocked NCO-terminated PU prepolymer Viscosity = 31,000 mPas M_w = 4230 Equivalent weight = 1410	Bayer, Germany
Chain extender	Aromatic diamine (ACR H-3486) (blend of 60% 4,4-methylene diamine and 40% *m*-phenylene diamine) Molecular weight = 266 Viscosity = 20,000 mPas at 25°C Specific gravity = 1.11 at 25°C	Shell Chemical Co., USA
Fiber	Glass fiber (E-glass) 764-NT-218 Specific gravity = 2.54 Diameter = 13.1 μm	PPG Co., USA

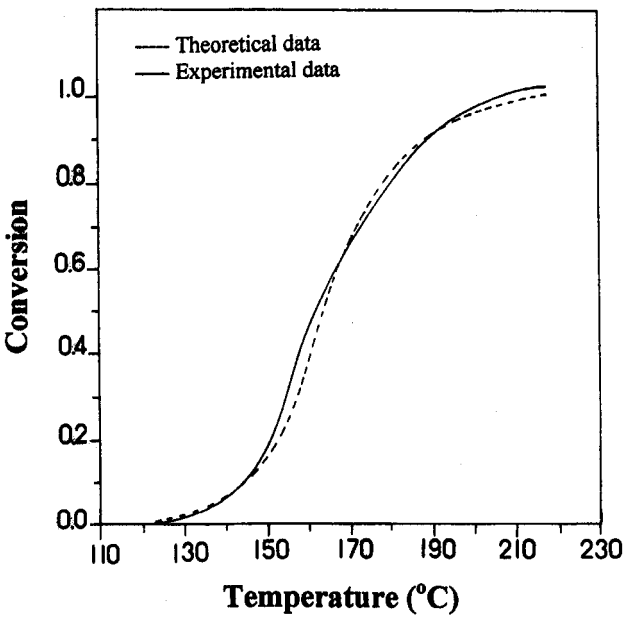

Figure 2 Conversion (P) versus temperatures of blocked PU–UP (50:50 wt %) prepolymer from (–) theoretical data and (—) from experimental data by dynamic DSC at 10°C/min.

mm (length × width × thickness), the span was 90 mm, and the crosshead speed was 2 mm/min.

RESULTS AND DISCUSSION

Kinetic analysis

The mechanistic kinetic model used in this study to describe the curing behavior of a blocked PU–UP/glass fiber is based on an autocatalytic reaction. Details of the derivation are discussed elsewhere. The rate equation is given by

$$\frac{dP}{dt} = A \exp\left(-\frac{E}{RT}\right)P^m(1-P)^n \tag{1}$$

where P 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 conversion and conversion rate by

$$\Delta H = \int_0^t \frac{dQ_t}{dt}dt \tag{2}$$

$$P = \frac{Q_t}{\Delta H} \tag{3}$$

$$\frac{dP}{dt} = \frac{1}{\Delta H}\frac{dQ_t}{dt} \tag{4}$$

where P is the conversion at time t, Q_t is the reaction heat up to time t or temperature T, dP/dt is the conversion rate, and ΔH is the total heat of reaction for 100% conversion. It is possible to express eq. (1) in logarithmic form, as follows:

$$\ln\frac{dP}{dt} = \ln A - \frac{E}{RT} + m\ln P + n\ln(1-P) \tag{5}$$

By integrating the DSC curve, the total reaction heat, ΔH = 205 J/g, can be obtained. Using multiple regression technique to solve eq. (5), it is possible to obtain the kinetic parameters $A = 6.45 \times 10^6$ min^{-1}, E = 18.95 kcal/mol, m = 0.764, and n = 0.628. Figures 2 and 3 show the conversion (P) and conversion rate (dP/dt), respectively, versus the temperature of blocked PU–UP (50:50 wt %) resin for the curing reaction at a scan speed of 10°C/min. The dashed lines in Figures 2 and 3 represent the calculated values obtained from eq. (1) with the aforementioned kinetic parameters, and the solid lines represent the values obtained directly from the DSC thermogram data by using eqs. (3) and (4). It can be observed from the results shown in Figures 2 and 3 that the experimental data agreed very well with the theoretical predictions.

Simulation results for a pultrusion process

The results obtained from the kinetic investigations were used to simulate the influence of system compo-

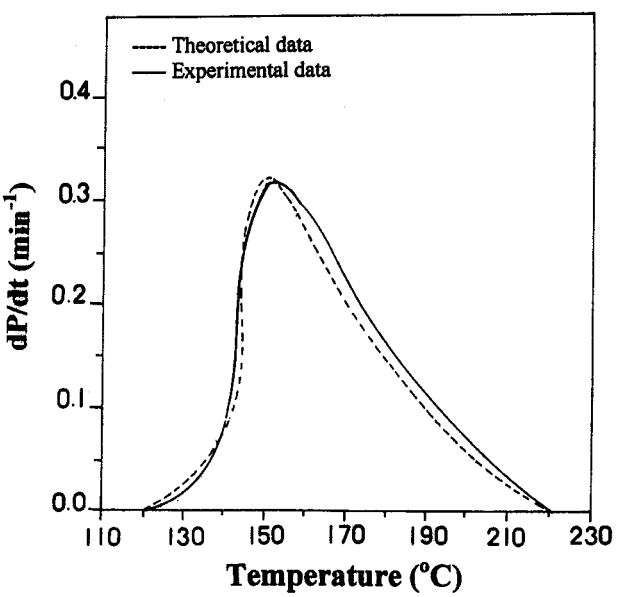

Figure 3 Conversion rate (dP/dt) versus temperatures of blocked PU–UP (50:50 wt %) prepolymer from (–) theoretical data and (—) experimental data by dynamic DSC at 10°C/min.

TABLE II
Physical Properties of Blocked PU–UP (50:50 wt %) Resin and Glass Fiber

Materials	Density (g/cm^3)	Specific heat (cal/g-K)	Thermal conductivity
Uncured resin	1.13	$-0.352+0.00251T$	5.35×10^{-5}
Cure resin	1.25	$-0.264+0.00176T$	2.32×10^{-4}
Glass fiber	2.54	0.197	2.08×10^{-3}

sition on temperature and conversion profiles inside a rectangular pultrusion die whose dimensions were 80 $\times$ 1.25 $\times$ 0.319 cm and 80 $\times$ 1.25 $\times$ 0.208 cm, respectively. To simplify the system, the following assumptions have been proposed: (1) the heat conduction is only in the thickness direction; (2) the process is in a steady state; (3) the diffusion of resin during curing is negligible; (4) the velocity profile is flat; and (5) the local motion of resin during curing is negligible.

From the above assumptions, the working equation of the model can be combined with the kinetic expression and heat-transfer equations. They can be written as

$$-R_a = C_{ao}\frac{dP}{dt} = A\exp\left(-\frac{E}{RT}\right)P^m(1-P)^n \qquad (6)$$

$$\rho C_p v_z \frac{\partial T}{\partial z} = K_t\left(\frac{\partial^2 T}{\partial x^2}\right) + \Delta H \cdot R_a \cdot W_m \qquad (7)$$

where x is the position in the thickness direction; C_{ao} is the initial concentration of the reactant (i.e., functional group in the resin) at the die entrance of $z = 0$, ρ is the bulk density, C_p is the bulk specific heat, K_t is the bulk thermal conductivity, R_a is the rate of formation of the cured resin, ΔH is the total heat, W_m is the weight fraction of the uncured resin; T is the temperature, v_z is the pulling speed; and z is in the axial (length) direction.

Note that the material being cured consists of three components: uncured resin, fiber, and cured resin. Therefore, the bulk physical properties of the composite system are calculated from the following equations:

$$\frac{1}{\rho} = \frac{W_m^0}{\rho_m}(1-P) + \frac{W_m^0}{\rho_p}P + \frac{W_f}{\rho_f} \qquad (8)$$

$$C_p = W_m C_{pm} + W_p C_{pp} + W_f C_{pf} \qquad (9)$$

$$\frac{1}{K_t} = \frac{\phi_m}{K_{tm}} + \frac{\phi_p}{K_{tp}} + \frac{\phi_f}{K_{tf}} \qquad (10)$$

where W is the weight fraction, ϕ is the volume fraction, and the subscripts m^0, m, p, and f refer to resin, uncured resin, cured resin, and glass fiber, respectively. The boundary conditions for the model are given by

$$\begin{aligned}
&\text{(a) } x = x_0 \text{ and } 0 \le z \le L,\ T = T(z) \\
&\qquad\qquad \text{(die wall temperature profile)} \\
&\text{(b) } z = 0 \text{ and } 0 \le x \le x_0,\ T = T_i \\
&\qquad\qquad \text{(initial temperature of the system)} \\
&\text{(c) } x = 0 \text{ and } 0 \le z \le L,\ (\partial T/\partial x) = 0 \\
&\qquad\qquad \text{(symmetry condition)}
\end{aligned} \qquad (11)$$

The solving of eqs. (6) and (7) was done in a numerically dimensionless way using a finite difference method. For numerical computation of the blocked PU–UP/glass fiber system, the experimentally determined values of the kinetic parameters were used, which were described in the kinetic analysis section. The physical properties of the materials are given in Table II. The dimensions of the pultrusion die, the temperature of the material entering the die, and the weight percent of glass fiber in the material are summarized in Table III.

Figure 4 shows the temperature versus die position z (along the die length) for blocked PU–UP (50:50 wt %) composites at various X values (die thickness direction/half of die thickness). In Figure 4 the dotted line represents the profile of the die wall temperature that was employed as the boundary [see eq. 11(a)] to solve eqs. (6) and (7).

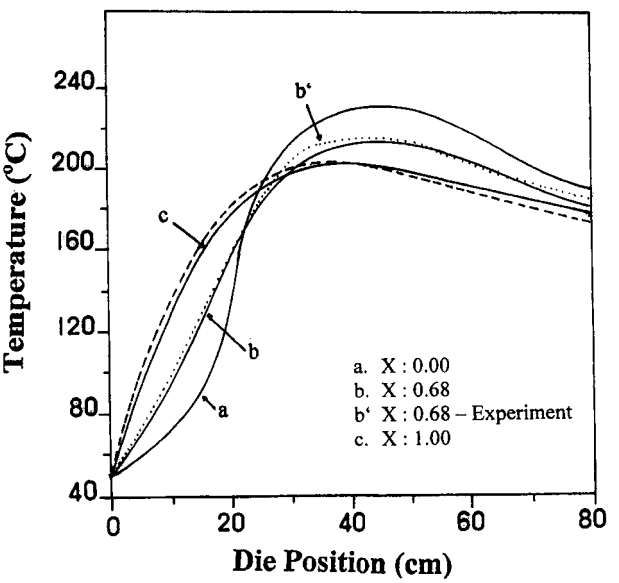

Figure 4 Temperature versus die position for glass-fiber pultruded blocked PU–UP (50:50 wt %) composite at various values of X: (a) 0 (at center); (b) 0.68; (b′) 0.68 (experiment); (c) 1.0 (at surface). The dotted line is the temperature profile at the die wall imposed as the boundary condition; pulling speed of 20 cm/min; die wall temperature of 180°C; die thickness of 0.319 cm.

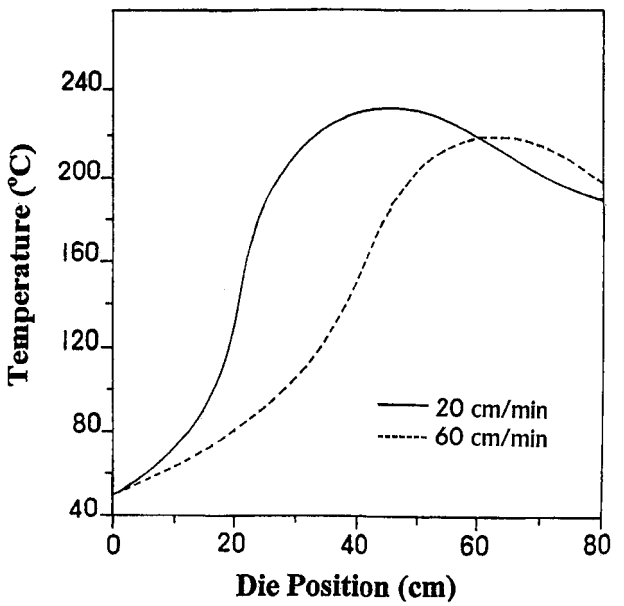

Figure 5 Temperature profiles versus die position of the die center at pulling speeds of 20 and 60 cm/min for glass-fiber pultruded blocked PU–UP (50:50 wt %) composite.

It can be observed from Figure 4 that:

(1) the thermal conductivity of both the resin and glass fiber (especially the resin) was very low (also seen in Table II) and the rate of heat transfer in the thickness direction (i.e., from the wall to the center of the die) also was very low; hence, a large temperature difference between the die wall and the center of the pultrusion die existed.
(2) The curing reaction was exothermic, the temperature increasing more as the curing reaction continued. Consequently, the temperature at the center of the die (i.e., at $x = 0$) continued to increase even in the region where the die wall temperature was kept constant.
(3) As the die wall temperature decreased near the end of the die, the temperature at the center of the die became higher than the die wall temperature.
(4) A comparison of curve b′ (the experimental curve that was measured by using thermocouples imbedded in the die) and curve b (the theoretical predictions from the mathematical model) shows that the two curves are in very close agreement, indicating the mathematical model is in good agreement with the temperature profile predicted along the die length.

TABLE III
Dimensions of Die and Feed Temperature Used for Simulation

Die thickness (cm)	Die length (cm)	Feed temperature (°C)	Fiber content (vol %)
0.208	80	50	56.5
0.319	80	50	56.5

Effect of pulling speed

One of the most important processing parameters that affect the properties of pultruded composites is the pulling speed. Therefore, the effect of the pulling speed on the temperature and conversion profiles was studied. Figures 5 and 6 show the theoretically predicted temperature and conversion profiles, respectively, of the die center at pulling speeds of 20 and 60 cm/min It can be seen from Figures 5 and 6 that when the pulling speed was decreased from 60 to 20 cm/min, the position at which the center temperature of the die went through a maximum was decreased from $Z = 62$ cm to $Z = 45$ cm. This implied that when the pulling speed decreased, the maximum temperature curve of the die was moved to the entrance, and the conversion profile curve was moved to the entrance of the pultrusion die. The conversion increase with a decrease in pulling speed was explicit.

Effect of die wall temperature

Figures 7 and 8 show the theoretically predicted temperature and conversion profiles, respectively, of the die center at die wall temperatures of 180°C–200°C. It can be observed from Figures 7 and 8 that the higher the die temperature, the steeper were the temperature

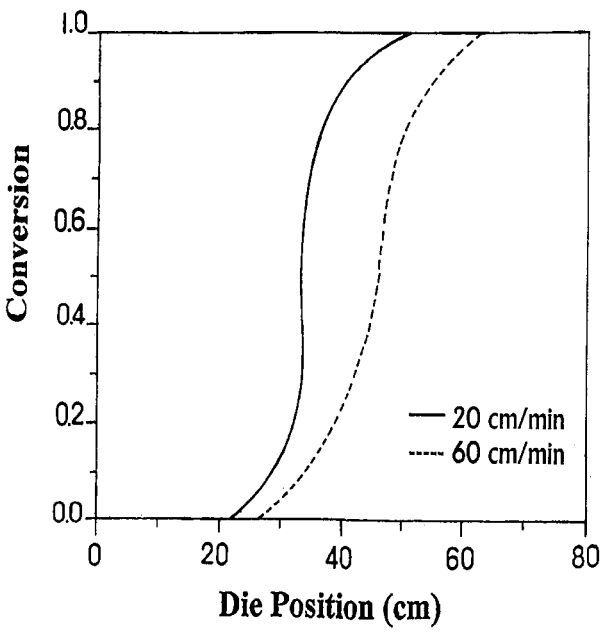

Figure 6 Conversion profiles versus die position of the die center at pulling speeds of 20 and 60 cm/min for glass-fiber pultruded blocked PU–UP (50:50 wt %) composite.

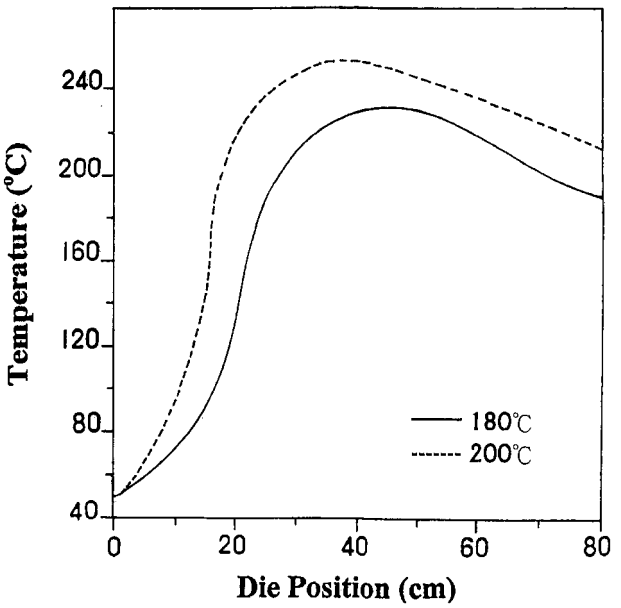

Figure 7 Temperature profiles versus die position of the die center at die wall temperatures of 180°C and 200°C for glass-fiber pultruded blocked PU–UP (50:50 wt %) composite.

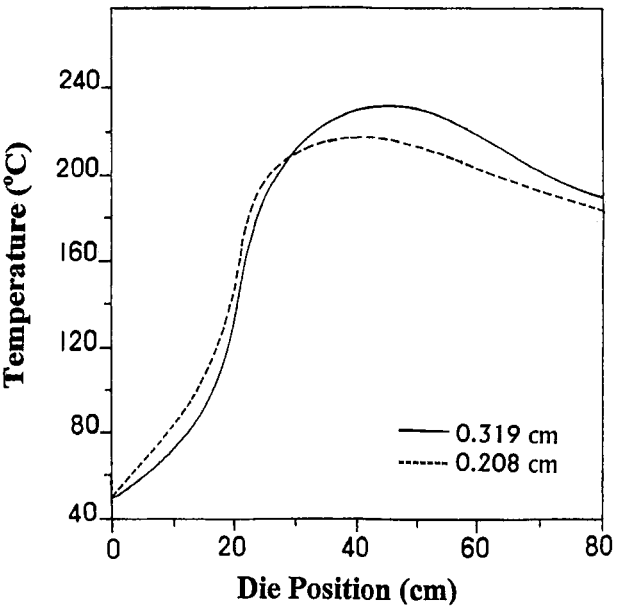

Figure 9 Temperature profiles versus die position of the die center at die thickness of 0.319 and 0.208 cm for glass-fiber pultruded blocked PU–UP (50:50 wt %) composite.

and conversion profile curves. The maximum temperature and conversion profile curves along the die length were moved to the die exit as the die wall temperature decreased. This implied that the reaction rate and conversion increased with an increasing die wall temperature.

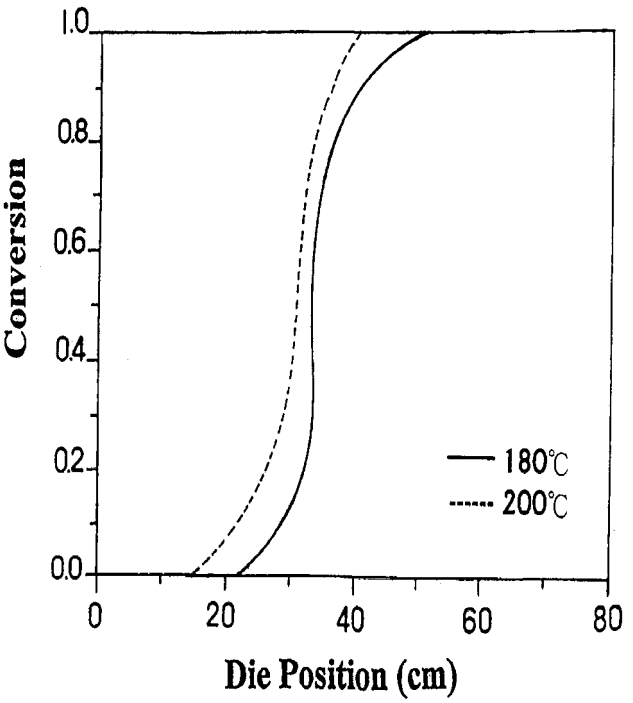

Figure 8 Conversion profiles versus die position of the die center at die wall temperatures of 180°C and 200°C for glass-fiber pultruded blocked PU–UP (50:50 wt %) composite.

Effect of die thickness

Figures 9 and 10 show the theoretically predicted temperature and conversion profiles, respectively, of the

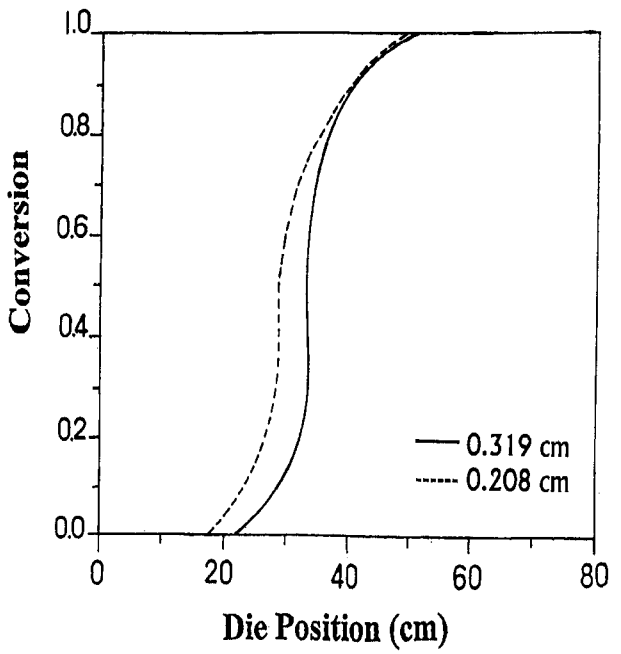

Figure 10 Conversion profiles versus die position of the die center at die thickness of 0.319 and 0.208 cm for glass fiber pultruded blocked PU–UP (50:50 wt %) composite.

TABLE IV
Mechanical Properties of Pultruded Glass-Fiber-Reinforced Blocked PU–UP (50:50 wt %) Composites Measured at Various Die Thickness

Die thickness (cm)	Die length (cm)	Flexural strength (MPa)	Flexural modulus (MPa)
0.208	80	206	29100
0.319	80	180	26500

die center at die thicknesses of 0.319 and 0.208 cm. It can be seen from Figures 9 and 10 that the greater the die thickness, the higher was the temperature gradient because temperature could not easily transfer to the center of die when die thickness increased. The conversion profile curves along the die length were moved to the die entrance as the die thickness decreased because conversion at the die center increased with decreasing die thickness. Table IV shows the flexural strength and flexural modulus values of pultruded composites measured at various die thicknesses. It can be seen from Table IV that the mechanical properties of pultruded composites increased with decreasing die thickness—that is, the smaller the die thickness, the greater was the degree of conversion of composites.

CONCLUSIONS

A mathematical model with an autocatalytic kinetic model and heat-transfer equation was developed to predict the temperature and conversion profiles in a rectangular pultrusion die.

The experimental results agree very well with the theoretical prediction and indicate that the autocatalytic model, $dP/dt = A \exp(-E/RT)P^m(1 - P)^n$, is suitable for reinforced blocked PU–UP resin. The kinetic parameters $A = 6.45 \times 10^6$ min^{-1}, $E = 18.95$ kcal/mol, $m = 0.764$, and $n = 0.628$ were obtained. It was found that the predicted values of the temperature profiles along the pultrusion die length were in good agreement with the experimental data, implying that the mathematical model was suitable for the pultrusion processes. The maximum temperature profile and conversion profile curves along the die length were moved to the entrance when the pulling speeds and die thickness decreased and the die wall temperatures increased. The degree of cure (conversion) increased with decreasing pulling speed and die thickness and increasing die wall temperatures. It can be seen that the mechanical properties of the pultruded composites increased with decreasing die thickness, that is, the thinner the die, the greater the degree of conversion of the composites.

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