The Development of a Mathematical Model for the Pultrusion of Blocked Polyurethane Composites

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SYNOPSIS

The thermokinetic behavior of blocked polyurethane-based composites during the pultrusion of glass-fiber reinforced composites is investigated utilizing a mathematical model accounting for the heat transfer and the heat generation during curing. The equations of continuity and energy balance, coupled with a kinetic expression for the curing system, are solved using a finite difference method to calculate the temperature and conversion profiles in the thickness direction in a rectangular pultrusion die. A kinetic model, $dP/dt = A \exp(-E/RT)(1 - P)^n P^m$, was proposed to describe the curing behavior of a blocked polyurethane resin. Kinetic parameters for the model were obtained from dynamic differential scanning calorimetry (DSC) scans using a multiple regression technique, which was able to predict the effects of processing variables on the pultrusion. The effects of process variables (e.g., pulling rate, die temperature, and die thickness) on the performance of the pultrusion are also evaluated. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The pultrusion process is a continuous process to fabricate composite profiles with a constant cross section. It can produce almost unlimited length composites with more flexible and higher tensile strength than that of any other reactive polymer process.[1-3] The process involves pulling resin-impregnated fiber filaments through a heated die to cure the resin and then cutting the reinforced materials to a desired length. A schematic of the process is given elsewhere.[16] Most of the literature published[4-7] discusses its applications, some aspects of pultruded products, and the pultrusion process from the point of view of monitoring the quality of incoming resins. However, little has been said about the fundamental aspects of the process. The process is difficult to control unless one knows how to handle the exothermic chemical reactions taking place inside a pultrusion die.

Very recently, a variety of experimental techniques have been developed to study the curing re-

action of resins. Among them, the technique of dynamic differential scanning calorimetry (DSC) has been found to provide a convenient and useful method to monitor the course of exothermic cure reactions.[8-10] 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 the chemical reaction is proportional to the extent of reaction, the kinetic parameters can be obtained from simulation under nonisothermal conditions.

To produce pultruded products with consistent quality, it is essential to develop a strategy for controlling the pultrusion process on the basis of fundamental investigation. To achieve a uniform degree of cure in the cross section of a pultruded product, the temperature profile in the pultrusion die is the most important condition. It should be pointed out that control of the temperature and conversion profiles in the radial direction in a pultrusion die is very important. It is therefore important to develop a mathematical model for simulating the pultrusion process and ultimately for controlling the process. Today, most mathematical models used in the pultrusion process deal with unsaturated polyester and epoxy resins[11-15] instead of other resins. Very re-

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cently, Chen and Ma[16,17] reported the development of a blocked polyurethane resin system that can be used in the pultrusion process.

The purpose of this study is 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 polyurethane resin. The predictions of the model will be compared with experimental results. The effects of processing variables on the pulling rate, die temperature, and die thickness are also investigated.

EXPERIMENTAL

Materials

A blocked NCO-terminated polyurethane (PU) prepolymer synthesized in this study has been described previously.[16] The chain extender (i.e., curing agent) used was cycloaliphatic diamine (Laromin C260) and was supplied by the Shell Chemical Co., U.S.A., which has an equivalent weight of 60 with respect to active hydrogen. The continuous E-glass fiber roving reinforcement used in this research was 764-NT-218 and was supplied by the PPG Co., U.S.A., which has a filament diameter of 13.1 μm and a density of 2.54 g cm^{-3}.

Procedures

The calorimetric measurements were conducted using a DuPont 910 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 30–300°C using indium as the DSC calibration standard.

One equivalent of cycloaliphatic diamine (Laromin C260) was stirred into one of blocked NCO-terminated PU prepolymer until thoroughly mixed, keeping the sample container at 30°C. A 5–10 mg sample with 50 wt % glass fiber 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.

RESULTS AND DISCUSSION

Kinetic Parameters for the Curing Reaction of the Resin

The mechanistic kinetic model used in this work to describe the curing behavior of a blocked NCO-ter-

minated PU resin/glass fiber is based on an autocatalytic reaction. Details of the derivation are discussed elsewhere.[18,19] The rate equation is given by

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

where P is the conversion (i.e., degree of cure); A, a preexponential factor; E, the activation energy; R, the universal gas constant; T, the absolute temperature; and m and n, 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

$$Q_t = \int_0^t \frac{dH}{dt} dt = \frac{1}{\beta} \int_{T_z}^T \frac{dH}{dt} dT \qquad (2)$$

$$P = \frac{Q_t}{\Delta H} \qquad (3)$$

$$\frac{dP}{dt} = \frac{1}{\Delta H} \frac{dQ_t}{dt} \qquad (4)$$

where P is the conversion at time t; Q_t, the reaction heat up to time t or temperature T; dH/dt, the rate of heat evolution per unit mass of resin at time t (dt being related to the scan speed $\beta = dT/dt$); and ΔH, the total heat of reaction for 100% conversion. It should be noted that the polymerization starts after the complete depletion in the system ($t = 0$ correspond to $T = T_z$). Equation (1) can be expressed in the logarithmic form, as follows:

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

By integrating the DSC curve, the total reaction heat $\Delta H = 26.3$ J/g can be obtained. Using a multiple regression technique to solve eq. (5), one can obtain the kinetic parameters $A = 2.95 \times 10^7$ min^{-1}, $E = 15.36$ kcal/mol, $m = 0.447$, and $n = 0.568$. Figures 1 and 2 illustrate conversion and conversion rate (dP/dt) vs. temperature of blocked PU prepolymer with cycloaliphatic diamine for the curing reaction at a scan speed of 10°C/min. The dashed lines represented the calculated values obtained from eq. (1) with the forementioned kinetic parameters, whereas the solid lines are obtained directly from the DSC thermogram data by using eqs. (3) and (4). From these results, one can observe that the experimental data agree very well with the theoretical prediction.
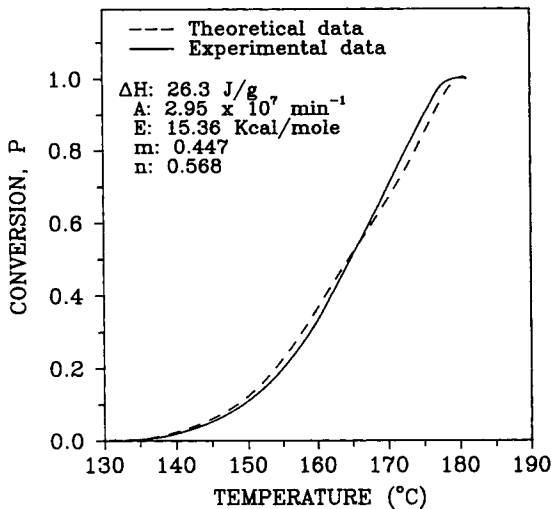
Figure 1 Conversion vs. temperature of blocked PU prepolymer with cycloaliphatic diamine: (-----) from theoretical data and (———) from experimental data by dynamic DSC study at 10°C/min.

Simulation Results for a Pultrusion Process

The results obtained from the kinetic studies were used to simulate the influence of system composition on temperature and conversion profiles inside the rectangular pultrusion die ($80 \times 1.25 \times 0.319$ cm and $80 \times 1.25 \times 0.208$ cm). To simplify the system, the following assumptions have been proposed: (1) the heat conduction is only in thickness direction; (2) the process is at 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 equations of the model can be combined with kinetic expression and heat-transfer equations. They can be written as

$$-R_a = C_{a0} \frac{dP}{dt} = A \exp\left(-\frac{E}{RT}\right) P^m (1 - P)^n \quad (6)$$

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

where x is position in the thickness direction; C_{a0}, the initial concentration of the reactant (i.e., functional group in the resin) at the die entrance, $z = 0$; ρ, the bulk density; C_p, the bulk specific heat; K_t, the bulk thermal conductivity; R_a, the rate of formation of cured resin (i.e., the rate of curing reaction); ΔH, the total heat; T, the temperature; and v_z, the pulling rate, and z is in the axial (length) direction.

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

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

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

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

where W is the weight fraction, ϕ is the volume fraction, and 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

(a) $x = x_0$ and $0 \le z \le L$,

$T = T(z)$ (die wall temperature profile)

(b) $z = 0$ and $0 \le x \le x_0$,
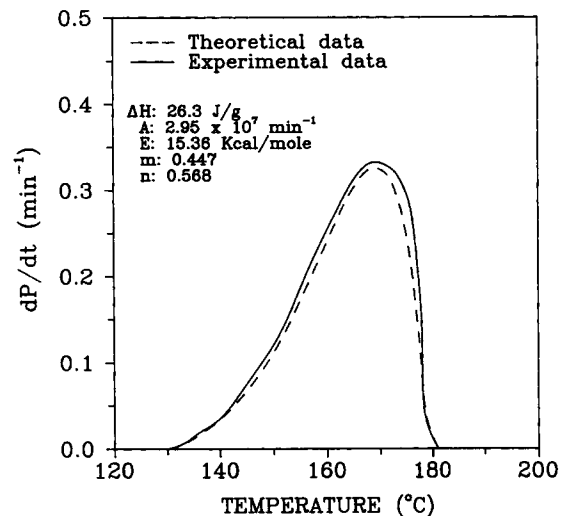
$T = T_i$ (initial temperature of the system)

(c) $x = 0$ and $0 \le z \le L$,

$(\partial T / \partial x) = 0$ (symmetry condition)   (11)

Equations (6) and (7) were solved in a numerically dimensionless way using a finite difference method. For numerical computation of the blocked

Figure 2 Conversion rate (dP/dt) vs. temperature of blocked PU prepolymer with cycloaliphatic diamine: (-----) from theoretical data and (———) from experimental data by dynamic DSC study at 10°C/min.

**Table I   Physical Properties of the Materials Investigated**

Material	Density $(g\ cm^{-3})$	Specific Heat $(cal/g\ K)$	Thermal Conductivity $(cal/cm\ s\ K)$
Uncured PU	1.04	$0.121 + 1.02 \times 10^{-3}\ T$	6.10×10^{-4}
Cured PU	1.05	$0.129 + 8.71 \times 10^{-4}\ T$	7.20×10^{-4}
Glass fiber	2.54	0.197	2.08×10^{-3}

Table II   Dimensions of Die and Feed Temperature Used for Simulation

Material	Die Thickness (cm)	Die Length (cm)	Feed Temperature (°C)	Fiber Content (Wt %)
PU/GF	0.319	80	50	78
PU/GF	0.208	80	50	78

polyurethane/glass fiber system, the experimentally determined values of the kinetic parameters were used that have been described in the previous sections. The physical properties of materials are given in Table I. The dimensions of the pultrusion die, the temperature of the material entering the die, and weight percent of fiber in the material are summarized in Table II.

Figure 3 shows the temperature vs. die position z (along the die length) for PU composites at various X values (die thickness direction/half of die thickness). As shown in Figure 3, the dotted line repre-
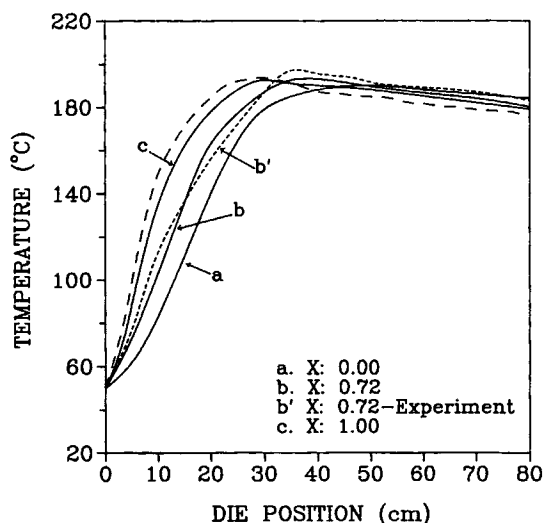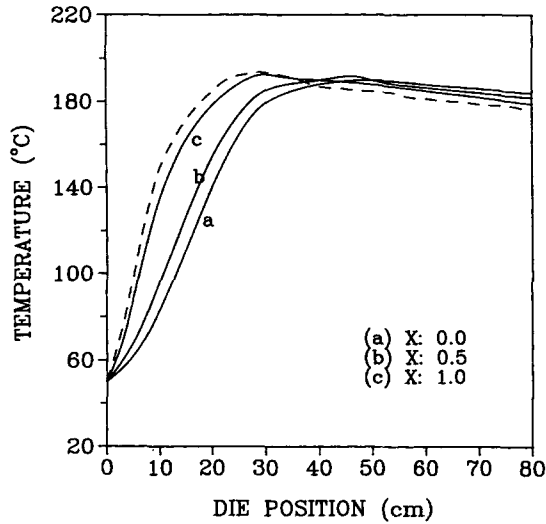

Figure 3   Temperature vs. die position for PU composites at various values of X: (a) 0.00 (at center); (b) 0.72; (b') 0.72 (experiment); (c) 1.00 (at surface). The dotted line is the temperature profile at the die wall imposed as boundary condition, and the pulling rate is 30 cm/min; die thickness, 0.319 cm; and die temperature, 180°C.

sents the profile of the die wall temperature that was employed as the boundary [see eq. 11(a)] to solve eqs. (6) and (7).

From Figure 3, one can observe the following: (1) the thermal conductivity of both the resin and glass fiber (especially the resin) is very low (also seen in Table I) and the rate of heat transfer in the thickness direction (i.e., from the wall to the center of the die) is also very low; hence, a large temperature difference between the die wall and the center of the pultrusion die existed. (2) The curing reaction is exothermic, the temperature increasing further as the curing reaction continues. Consequently, the temperature at the center of the die (i.e., at $x = 0$) continues to increase even in the region where the die wall temperature is kept constant. (3) As the die wall temperature decreases near the end of the die, the temperature at the center of the die becomes higher than the die wall temperature. (4) From a comparison of curve b' (the experimental curve that was measured by using thermocouples imbedded in the die) and curve b (the theoretical predicted from mathematical model), one can observe that the two curves agree very closely. This indicates that the mathematical model is in good agreement with the temperature profile predicted along the die length.

One of the most important processing variables that affects the properties of pultruded products is the pulling rate. Therefore, the effect of pulling rate on the temperature and conversion profiles was studied. Figures 4 and 5 depict the theoretically predicted temperature profile at pulling rates of 30 and 60 cm/min, respectively. It can be seen from these figures that when the pulling rates is decreased from 60 to 30 cm/min, the position at which the center temperature of the die goes through a maximum is
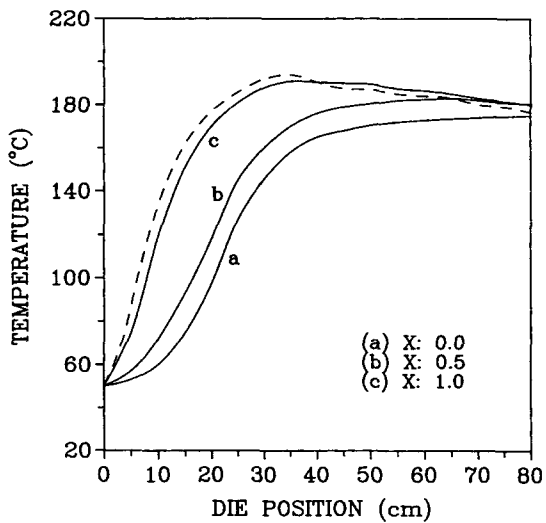
Figure 4 Temperature vs. die position for PU composites at various values of X: (a) 0.00 (at center); (b) 0.50; (c) 1.00 (at surface). The dotted line is the temperature profile at the die wall imposed as boundary condition, and the pulling rate is 30 cm/min; die thickness, 0.319 cm; and die temperature, 180°C.
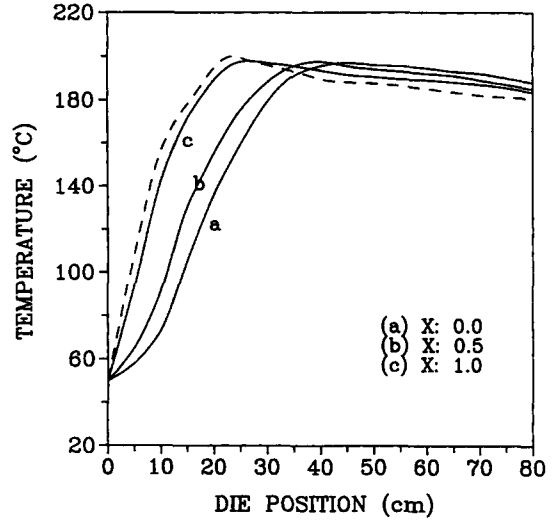
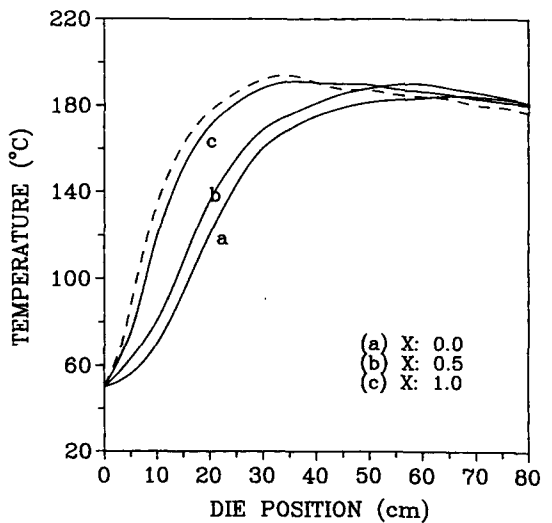
Figure 6 Temperature vs. die position for PU composites at various values of X: (a) 0.00 (at center); (b) 0.50; (c) 1.00 (at surface). The dotted line is the temperature profile at the die wall imposed as the boundary condition, and the pulling rate is 60 cm/min; die thickness, 0.319 cm; and die temperature, 190°C.

decreased from $Z > 80$ cm to $Z = 50$ cm. This implies that when the pulling rates decrease the maximum temperature curve of the die were moved to the entrance. The conversion profile curves was moved to the entrance of the pultrusion die. The conversion increases with the decrease in pulling rate is explicit.

Figures 5 and 6 show the theoretically predicted temperature profile at die temperatures of 180 and 190°C. From these figures, one can see that the higher the die wall temperature the steeper the temperature profile curves. The maximum temperature and conversion profile curves along the die length

Figure 5 Temperature vs. die position for PU composites at various values of X: (a) 0.00 (at center); (b) 0.50; (c) 1.00 (at surface). The dotted line is the temperature profile at the die wall imposed as boundary condition, and the pulling rate is 60 cm/min; die thickness, 0.319 cm; and die temperature, 180°C.

Figure 7 Temperature vs. die position for PU composites at various values of X: (a) 0.00 (at center); (b) 0.50; (c) 1.00 (at surface). The dotted line is the temperature profile at the die wall imposed as boundary condition, and the pulling rate is 60 cm/min; die thickness, 0.208 cm; and die temperature, 180°C.

Table III Mechanical Properties of Pultruded Glass-fiber (GF)-Reinforced PU Composites Measured at Various Die Thicknesses

Material	Die Thickness (cm)	Flexural Strength (MPa)	Flexural Modulus (MPa)
PU/GF	0.319	72.6	6920
PU/GF	0.208	80.2	7393

were moved to the die entrance as the die wall temperature increased. It is implied that the reaction rate and conversion increase with the increasing of die wall temperature.

Figures 5 and 7 show the theoretically predicted temperature profiles at die thicknesses of 0.319 and 0.208 cm. From these figures, one can see that the greater the die thickness the higher the temperature gradient, because the temperature cannot easily transfer to the center of die when the die thickness increases. The maximum conversion profile curves along the die length were moved to the die entrance as the die thickness increased, because conversion at the die center increased with decreasing die thickness. Table III shows the mechanical properties of pultruded composites measured at various die thicknesses. From this table, one can observe that the mechanical properties of composites increased with decreasing die thickness, i.e., the less the die thickness, the greater the degree of conversion of composites.

CONCLUSIONS

A mathematical model with an autocatalytic kinetic model and heat-transfer equation has been 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 auto-catalytic model is suitable for reinforced blocked polyurethane resin. The kinetic parameters $A = 2.95 \times 10^7$ min^{-1}, $E = 15.36$ kcal/mol, $m = 0.447$, and $n = 0.568$ were obtained. It was found that the predicted values of temperature profile along the pultrusion die length were in good agreement with experimental data, which implies that the mathematical model is suitable for this pultrusion process. The maximum temperature and conversion profile curves along the die length were moved to the entrance as the pulling rate and die thickness decreased and die wall temperature increased. The degree of cure increased with decreasing pulling rate and die thick-

ness and the predicted increasing die wall temperature is as expected.

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