Process Monitoring and Kinetics of Rigid Poly(urethane–isocyanurate) Foams

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ABSTRACT: Process temperature profiles of a two-component rigid poly(urethane–isocyanurate) foam system were studied and compared with the predictions of a one-dimensional numerical simulation. This model is based on experimentally determined thermophysical properties including thermal diffusivity, enthalpy of reaction, and rate of reaction. Temperature profiles were measured at three positions within the foam and at the foam surface for mold temperatures of 25°C and 55°C. A high rate of reaction and heat of reaction, along with low thermal diffusivity, cause temperatures near the foam center to be insensitive to mold temperatures for thick samples. Thermal analysis was used for determination of thermophysical properties. Temperature-dependent heat capacity, reaction kinetics, and heat of reaction were evaluated using temperature-scanning DSC. Thermal conductivity was analyzed from steady-state heat profiles. The system reaction kinetics indicated much faster kinetics than reflected by process cure temperature profiles made using thermocouples. The simulations accurately predict experimental results, allowing determination of demold time dependence on process conditions, including feed temperature, mold temperature programming, and sample thickness. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 374–380, 2000

Key words: poly(urethane–isocyanurate); kinetics; process monitoring; thermophysical properties

INTRODUCTION

The use of polyurethane foam composites for industrial applications is dictated by demolding cycle times and control of their dimensional stability (green strength). A variety of methods have been used for process monitoring of polymers.[1–3]

In order to substantially reduce cycle time, an understanding of the heat transfer processes that occur within the foam during curing is required. This involves measurement and analysis of the temperature profiles within the foam under appropriate molding conditions.

Two rigid foam systems were studied. One of them is a two-component commercial poly(urethane–isocyanurate) foam system. The other is a rigid isocyanurate foam system that was formulated in the laboratory. The systems have a demolding time of approximately 10–12 min. It is desirable to substantially reduce this cycle time through use of an optimized molding cycle. This work included establishment of the cure temperature profile of the foam system as a function of the molding conditions using single-system chemistry.

A numerical model was developed for use with the commercial system. This model allowed pre-

diction of the temperature profiles under a variety of operating conditions. The model is based on experimentally determined thermophysical properties of the system. Temperature-scanning DSC was employed to evaluate the kinetics and thermophysical properties of the laboratory system.

Poly(urethane–isocyanurate) Foam Cure Monitoring

In these studies the cure temperature profiles were investigated and compared with the predictions of a numerical simulation in order to provide insight into the optimum cure cycle. Molding experiments were carried out using a two-component rigid poly(urethane–isocyanurate) foam, and temperature profiles were determined at mold temperatures of 25°C and 55°C. A one-dimensional numerical model was used to demonstrate the capability of predicting the temperature profiles.

In order to optimize the cure time of a polyurethane foam system, the components require rapid mixing and injection, and the polymer cure reaction must take place quickly and uniformly and be followed by rapid cooling throughout the part. This would result in optimal mechanical properties of the part and permit demolding without resulting in dimensional distortion.
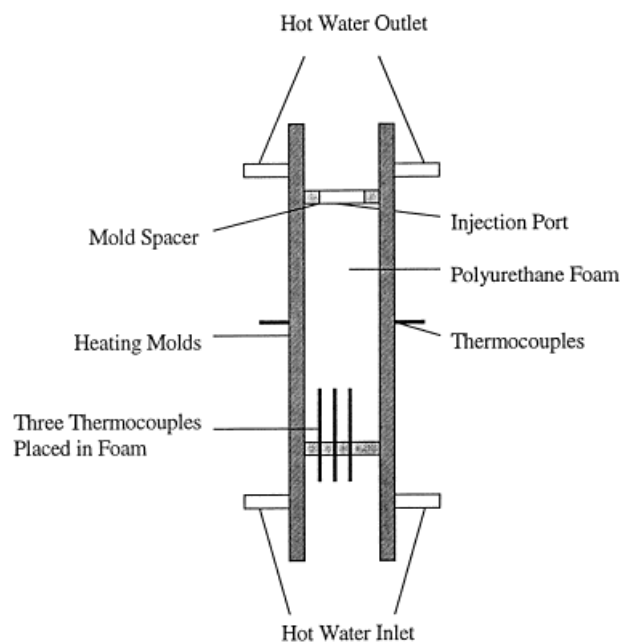
EXPERIMENTAL

Materials

The experimental equipment used in these studies is shown in Figure 1. Molding temperatures were set by the water-cooled aluminum molds, which were electronically controlled. Temperature data were monitored inside the molds and at three positions within the foam using commercial data acquisition software. This approach allowed comparison between experimental values with predictions by the numerical simulation.

The commercial poly(urethane–isocyanurate) system included a Stepan (Northfield, Ill.) and a Bayer (Pittsburgh, PA) polymeric MDI system with a isocyanate index of 250. Water was a blowing agent (with CO_2 formation from reaction with isocyanate). The manufacturer's specifications indicate that the system has a cream time of 20 s, rise time of 45 s, and a tack-free time of 65 s.

Samples were prepared by mixing the components for 10 s at room temperature and then

Figure 1 Instrumentation used for molding experiments includes temperature-controlled mold and three thermocouples for temperature measurement in the poly(urethane–isocyanurate) foam.

injecting them into the mold. Each sample was injected into the mold cavity through a hole in the mold spacer. Data acquisition began immediately upon injection.

Early molding studies were carried out at 25°C, and poor surface quality foams resulted. Later studies were carried out at 55°C and 85°C, and much better surface quality resulted at 55°C. This behavior was anticipated because the manufacturer specifications recommend operation at 55°C.

The laboratory system included a Voranol 360 polyol (polyether polyol) and a PAPI 27 polymeric MDI [poly(methylene polyphenyl isocyanate)] system with an isocyanate index of 300. A Genetron 141b (dichlorofluoroethane) and water served as the two blowing agents, DABCO TMR (quaternary ammonium carboxylates) and DABCO 33LV (1,4–diazabicyclo[2,2,2]octane) were the two catalysts.

RESULTS AND DISCUSSION

Cure Temperature Profiles and One-Dimensional Numerical Simulations

The results of the molding tests are presented in Figures 2 and 3 for 25°C and 55°C, respectively.
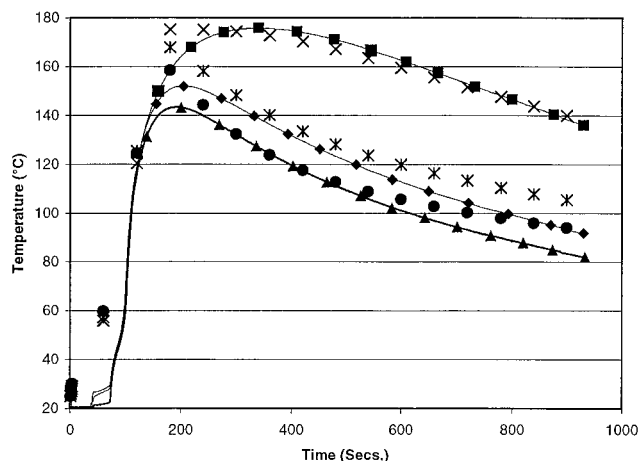
Figure 2 Time/temperature profiles within the foam at three locations in the mold are shown as lines. Simulations of these experiments are represented by discrete points. Mold temperatures and foam injection temperature were 25°C.

This system had a center-line peak exotherm that occurred in less than 350 s in a 50-mm sample. The peak temperature of 180°C was an acceptable exotherm temperature for this polymer system. The demold time, using a criterion of 170°C for demolding was 9 min at 25°C and 10 min at 55°C. The 170°C criteria is for dimensional stability and is an empirically determined value.

In addition to the centerline temperature shown in Figure 2 at 25°C, two other temperatures were measured in the foam, at 15 mm and 18 mm away from the centerline. The aluminum mold was initially at room temperature, and its temperature did not change significantly during the run. A thermocouple was also inserted at the interface of the foam and mold surface. The behavior of this thermocouple closely followed the behavior of the mold, indicating there is little resistance to heat transfer across this interface.

At 55°C, the peak exotherm at the centerline was nearly the same as at 25°C. Although this result, showing insensitivity of the cure temperature to the mold temperature, is in part due to the insulating properties of these foam materials, heat capacity also plays a role. It has been found that there is little dependence of the thermal conductivity[4,5] on temperature. However, the specific heat increases linearly with temperature.[5] This indicates that the thermal diffusivity ($k/\rho Cp$), where k is the thermal conductivity (J/m °C), ρ is the density (kg/m^3), and Cp is the heat capacity (J/kg K), will decrease accordingly, thus resulting

in similar centerline temperatures at both mold temperatures.

Numerical simulations were investigated using a one-dimensional unsteady-state model for heat flow in the foam system. This simulation involves the use of finite difference equations that are cast into forms suitable for iterative calculation with time steps and grid spacing that can be varied in each simulation.

Several features of this model are significant because they are well suited to polyurethane cure systems and are related to thermophysical properties that can be developed by experimental methods. The equations used in this model are presented in Table I. The one-dimensional heat conduction equation and boundary conditions are for the unsteady-state process. Use of a reaction rate in Arrhenius form is attainable by calorimetric or spectroscopic methods. The heat evolution term used is proportional to the reaction rate. This allows the use of an appropriate cure normalization factor, the period over which the reaction occurs and all the heat of reaction is released. State of cure for this model is determined by integration of the reaction rate expression over time. No adjustable parameters are used in these simulations, and all variables in the governing heat conduction equations are measurable thermophysical properties.

This model allows for temperature-dependent thermophysical properties and variable mold surface temperature. This permits simulation of both
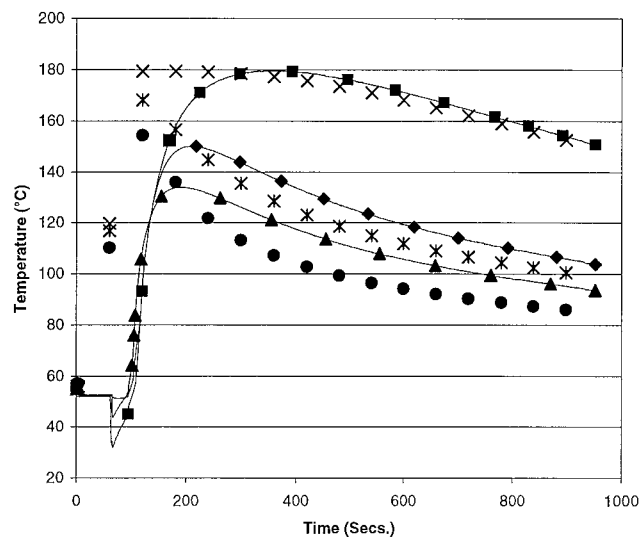
Figure 3 Time/temperature profiles within the foam at mold temperatures of 55°C and foam injection of 25°C.

Table I   Model Equations for Simulation of One-Dimensional Heat Transfer Including, Arrhenius Rate Term and Integrated State of Cure Expression
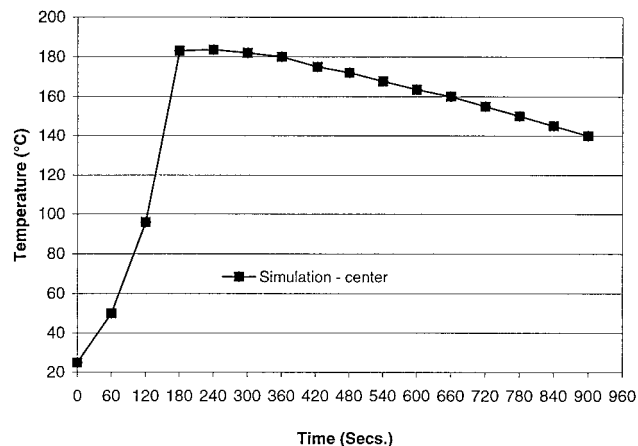
|	
One-dimensional heat conduction	$\dfrac{\partial}{\partial x}\left(k\dfrac{\partial T}{\partial x}\right) + Q = \rho C_p \dfrac{\partial T}{\partial t}$
Boundary conditions	$\left\|\begin{array}{l} T(x, t = 0) = T_0 \\ T(x = 0, t) = T_m(t) \\ \dfrac{dT}{dx} = 0 \quad \text{at} \quad x = h/2 \end{array}\right.$
Arrhenius rate expression	$\tau = A^{-E/RT}$
State of cure	$S = \int_0^t \tau dt$
Rate of heat generation	$Q = H\rho\tau(1 - S/C)/C$

Figure 4   Simulation of centerline temperature for process utilizing high-temperature (100°C) initial condition to initiate reaction, followed by rapid cooling (1°C) to suppress exotherm.

realistic operating conditions and hypothetical conditions that illustrate limiting characteristics not feasible in a manufacturing environment or even in a laboratory system. The finite difference method is easily applied to a Fortran program in a PC environment.

Numerical simulations were carried out using thermophysical data taken from preliminary experiments and several literature sources.[4–6] The results of these simulations are also shown in Figures 2 and 3. These data indicate that the one-dimensional model accurately predicts the temperature profiles of the curing foams. Differences between actual temperatures and the simulations on the cooling portion of the curves, especially at 55°C, may be caused by temperature dependence of thermophysical properties not yet fully accounted for.

The simulations carried out at limiting conditions also serve to illustrate limitations of the polyurethane foam system. For example, one condition of interest is rapid heating of the mold to initiate reaction, followed by rapid cooling of the mold to prevent excessive exotherm. Figure 4 is the result of a simulation with the mold surface temperature set at 100°C for 1 min followed by 1°C for 14 min. This simulation indicates that under these impractical conditions the demold time is only reduced to 9 min.

Increased polymer feed temperature is often an approach utilized to reduce cycle times. However, in this case this would not be a useful approach. The results of a simulation with the polyurethane foam preheated to 55°C prior to injection indicate that due to higher peak exotherms, the demold

time would be increased to 12 min because of limitations in heat removal by the foam after the reaction has taken place.
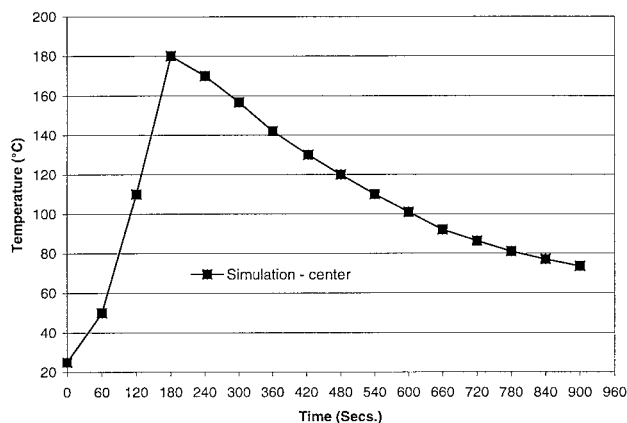
A substantial decrease in cycle times can be achieved through use of thinner samples. Figure 6 shows the results of a simulation done on a sample 25 mm thick. This simulation predicts that demolding is possible in as short a cycle as 4 min.

Thermophysical Properties

The thermophysical property evaluation was based on both the commercial and laboratory foam system. The thermophysical properties eval-
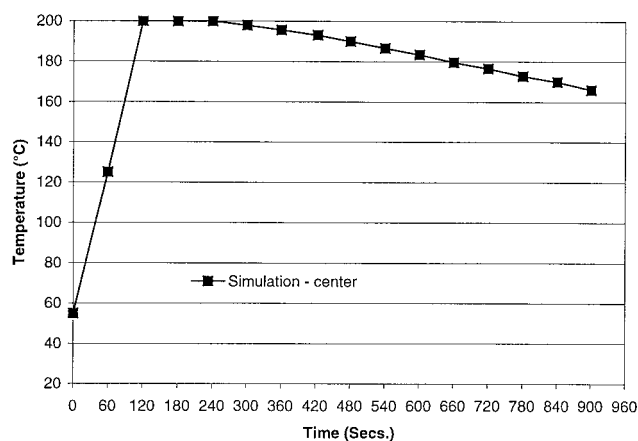
Figure 5   Simulation of temperature profile for injection of heated poly(urethane–isocyanurate) foam at 55°C.
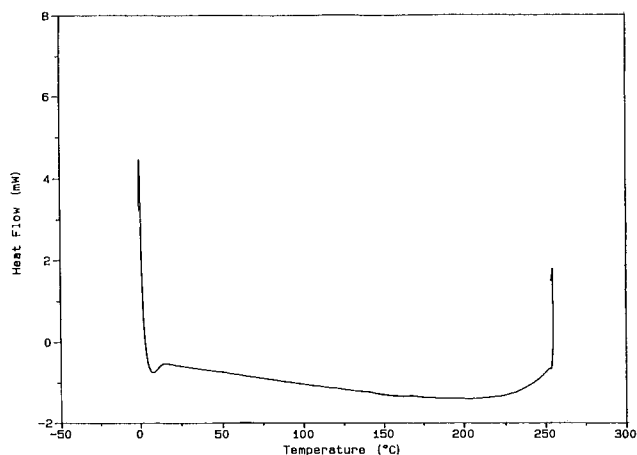
Figure 6 Simulation of centerline temperature of a sample 25 mm thick.

Figure 8 Heat capacity measurements are determined for the linear portion of the heat flow versus temperature curve given in

uated were heat capacity, heat of reaction, reaction kinetics, and thermal conductivity.
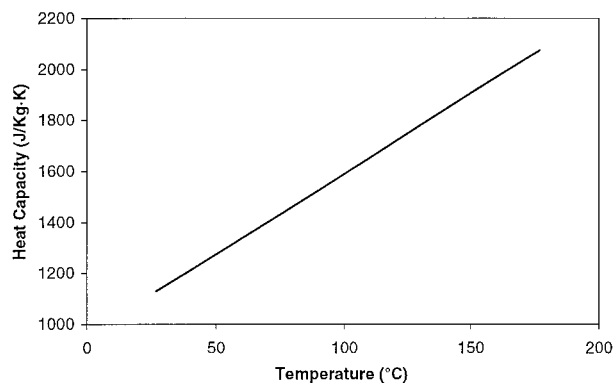
Heat Capacity

Heat capacity measurements were generated by a temperature-scanning DSC measurement. A typical sample thermogram is presented in Figure 7. Baselines were first established using empty pans in the sample cells. These baselines were subtracted from the sample thermograms in order to obtain absolute values for the heat capacities.

Samples of a dense film were prepared by mixing the system and pouring it onto a plate, followed by compression to remove the gases. The resulting film was then layered into the DSC pans. The results of this testing, shown in Figure

8, indicate that the heat capacity of the foam system is $Cp = 967 + 6.24 *T$ (°C) (J/kg K) in the region where heat flow and temperature are linear. This data compares with literature values of 780–1685 J/kg K, which are bulk polymer-specific heats. A rule of thumb used for dense polymer systems is 2100 J/kg K (0.5 cal/g°C).
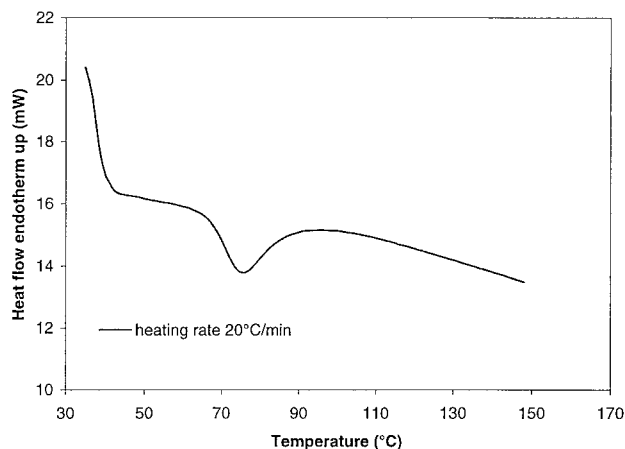
Heat of Reaction by DSC

The heat of reaction was obtained from temperature-scanning DSC thermograms. Samples were prepared by mixing the components for 2–3 s at room temperature. The samples were quenched in liquid nitrogen until they were placed in the DSC furnace, which was precooled to −70°C. Samples were then heated to 150°C under different heating rates from 10–20°C/min.

The DSC thermogram, which was run at 20°C/min, is presented in Figure 9. The heat of reaction of this system, measured by the integration under the heat flow curve, is 96,000 J/kg.

Reaction Kinetics by DSC

Kinetics constants were also evaluated using a temperature-scanning DSC. The thermogram is presented in Figure 9. It was observed that the curve exhibited two exothermic peaks, near 40°C and 70°C. Those peaks most likely correspond to the different foam formation reactions. Those reactions are:

$$RNCO + H_2O \rightarrow RNH_2 + CO_2 \qquad (1)$$

$$RNCO + R'OH \rightarrow R'OCONHR \qquad (2)$$

Figure 7 DSC thermogram of a cured sample poly-(urethane–isocyanurate) foam. Heat flow measurement was recorded using dynamic DSC from 0 to 250°C.

Figure 9 DSC thermogram of laboratory poly(urethane–isocyanurate) foam system indicates the presence of two exothermic reactions.

$$3RNCO \rightarrow \quad \text{[structure]} \quad (3)$$
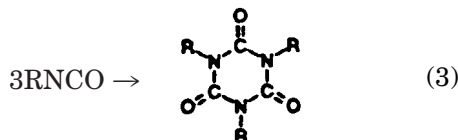
with eq. (1) known as the blowing reaction, eq. (2) the formation of urethane, and eq. (3) the trimerization of the isocyanate, which forms isocyanurate.

Reaction constants were evaluated using Kissinger's method.[8,9] The result is presented in Figure 10. The method involves plotting—ln $(\pi/T^2_{\max})$ against $(1/T_{\max})$—then the preexponential constant and activation energy, E, are given by:
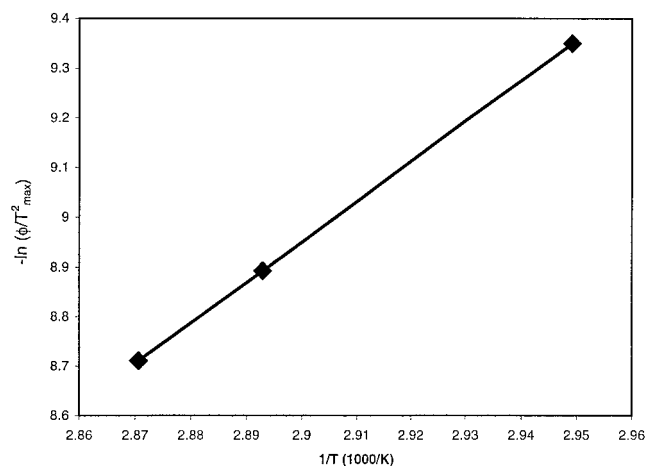
Figure 10 Activation energy calculation.

Table II Summary of Thermophysical Properties

Property	Value
Heat capacity (J kg^{-1} °C^{-1})	$967 + 6.24T$
Heat of reaction (kJ kg^{-1})	96
Activation energy (kJ mol^{-1})	67.6
Preexponential constant (min^{-1})	2.6×10^6
Thermal conductivity (J m^{-1} s^{-1} °C^{-1})	0.032

$$E = (\text{The slope of the line}) \times R$$

$$A = \frac{\phi E/(RT^2_{\max})}{\exp(-E/RT_{\max})n(1 - \alpha_{\max})^{n-1}}$$

where E is the activation energy, R is the universal gas constant, A is the preexponential constant, ϕ is the heat rate used in the DSC program, $T_{\max}$ is the exothermal peak temperature, n is the reaction order, and $\alpha_{\max}$ is the reactant conversion at $T_{\max}$.

The activation energy of the reaction is 67.6 kJ/mol. The preexponential constant A is 2.6×10^6 min^{-1}.

Thermal Conductivity. Thermal conductivity measurement was accomplished using a commercial test system manufactured by Anacon Inc. Measurements were done by setting constant temperatures of 10°C and 37°C on two plates through use of a heat pump located below the low temperature plate. The heat flow was measured using a thermoelectric sensor containing a material of known thermal conductivity, with the temperature drop across the sensor giving the heat flow. The values of thermal conductivity listed in the literature indicate this property is not very sensitive to temperature variation; for example, rubber thermal conductivities vary 0.15%/°C.

Our measurements indicated that the value of the thermal conductivity was 0.032 J/m °C, which we compared with values in the literature of 0.027 J/m °C. The value used in the simulation was $0.032 + 3.2 \times 10^{-4} *T$ (J/m °C).

A summary of the thermophysical properties is presented in Table II.

CONCLUSIONS

The numerical simulations developed based on the one-dimensional heat transfer model give an

accurate guide to determining operating variables and design of the parts. Demold times for thick parts were found to be insensitive to operating conditions. Thermophysical property measurements have been carried out and used with the one-dimensional numerical simulation.

Insensitivity of demold time to operating temperatures may be related to the increase in heat capacity with temperature and the resulting decrease in thermal diffusivity with temperature.

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