Transient Temperature Model for Reaction Injection Molding

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A model of the temperature response for reaction injection molding (RIM) operation is developed that assumes uniform mold temperature and a very fast reaction with slow heat transfer from the reacting mass to the mold and negligible heat losses to the surroundings. The model parameters are fit to data from a number of RIM experiments that agree well with published values of the physical constants for the reactants. The simple model can be fitted on-line to data from the RIM apparatus and the results used to detect and correct deviations of the part properties from its desired values which could otherwise result in the production of many defective parts.

Introduction

Reaction injection molding (RIM) has been in industrial use for almost two decades. Its popularity stems from its ability to produce large parts such as automobile bumpers that could not be produced by standard injection molding because of the extremely high pressures required. A common way of operating RIM machines is to set the machine parameters (reactants ratio, pressure, temperature, and so on) to pre-set values that have been experimentally found to produce parts having the required values of certain properties (yield offset and tensile strength, for instance). The quality of the parts is maintained by measuring the properties of selected parts according to a fixed schedule. When such measurements result in the destruction of the part, the fraction of parts that is tested must be set low to keep production efficiency up. This means that when something goes wrong between tests, a large number of parts may be produced that do not meet their specifications. This article proposes a method to detect variations in the operation of a RIM machine by characterizing the transient temperature response during the reaction period. A followup article will describe the strategy used to readjust the RIM operating variables based on the feedback provided by the transient temperature model.

Several researchers have developed simulations of the filling and curing stages that range from the simple (Macosko, 1989) to the very complex (Lo, 1991). What the simulations have in common is a desire to model RIM from first principles with some attempt at comparing the results to experimental data. A first principles three-dimensional (3-D) unsteady-state model of the flow, pressure and reaction equations that describe the filling and curing in a complex mold takes several hours of supercomputer time to solve (Lo, 1991). Such a model is therefore unsuitable for on-line characterization of the conditions of a run. The simple model of the transient temperature response presented here has adjustable parameters which, when fitted to temperature response data for each RIM shot, can characterize the shot in the short time between shots. The model parameters thus fitted are then used for estimating deviations in the part properties and the adjustments required to bring these properties back within their specifications.

Some part properties can be tested quickly and without damage to the part; such are storage and loss modulus which can be measured by mechanical impedance analysis (Jang and Zhu, 1986), or by ultrasound testing (Papadakis, 1974). Other property tests such as tensile strength tests and yield offset tests result in the destruction of the part tested. It is for the estimation of these properties that the simple reaction temperature model is developed here. The model gives timely feedback on problems that have occurred in the RIM unit. By using the model, the number of off-specification parts that might be produced is reduced.

Development of Transient Temperature Model

The temperature model is developed subject to the following assumptions:

(1) The mold is a perfectly mixed batch reactor.

(2) The reaction is fast compared to the rate of heat dissipation.

(3) The time lag in the temperature measurement is sig-

nificant relative to the reaction time, but insignificant relative to the part cooling time.

(4) Heat transfer from the mold to the surroundings may be neglected. The first assumption of perfect mixing is necessary because the temperature sensors must be installed in the mixing section of the mold so that they do not affect the shape of the part; this means that we must assume that the transient response of the temperature in the mixing section is representative of the response in the part section of the mold. Once longitudinal temperature uniformity is assumed, assuming a temperature profile in the direction perpendicular to the mold walls would create inconsistency in the degree of detail of the model.

Using the perfectly mixed reactor assumption, the following three differential equations are derived from an energy balance on the reacting part, a reactant balance, and the energy balance on the mold:

$$\frac{dT}{dt} = \frac{A_o C_0^2(-\Delta H_r)}{\rho C_p} e^{-\frac{E}{RT}}(1-\Phi)^2 - \frac{h_i A_i}{\rho C_p V}(T - T_{\text{mold}}) \tag{1}$$

$$\frac{d\Phi}{dt} = A_o C_0 e^{-\frac{E}{RT}}(1-\Phi)^2 \tag{2}$$

$$\frac{dT_{\text{mold}}}{dt} = \frac{h_i A_i}{MC_{pm}}(T - T_{\text{mold}}) - \frac{h_a A_{\text{mold}}}{MC_{pm}}(T_{\text{mold}} - T_{\text{air}}) \tag{3}$$

This set of equations has terms on three different time scales. The first terms on the righthand side of Eqs. 1 and 2 are the terms of the chemical reaction which are very fast, occurring in a few seconds. The second term in Eq. 1 and the first term in Eq. 3 are the heat-transfer terms between the reacting mass and the mold. Experiments have shown this heat-transfer characteristic time to be of the order of 30 s, which being slower than the reaction terms, constitutes the basis for assumption 2. The time constant of the temperature sensor was estimated to be of the order of one second; its rate of response is therefore comparable to the rate of reaction, but fast relative to the cooling of the part, which is the basis for assumption 3. We must point out, however, that the parts in this study are about four times thicker than most industrial RIM parts; because of the larger area to mass ratio in the industrial parts, the discrepancy between the rate of reaction and the rate of cooling will not be as high for industrial parts as it was in our experiments.

The second term in Eq. 3 is the heat transfer from the mold to the surroundings. This term is neglected by assumption 4, to be justified next.

Using a lumped-parameter model of the mold, a first-order time constant can be estimated using the thermal capacity of the mold and the film coefficient of heat transfer to the surroundings:

$$\tau_a = \frac{MC_{pm}}{h_a A_{\text{mold}}} \tag{4}$$

If the mold were at a uniform temperature, it would take five times this time constant for it to cool down to a ambient temperature after the reaction is complete. Using experimental data for a representative shot (#150), the heat-transfer coefficient from the mold to the air was estimated at $h_a = 9$ J/s·m^2·K which agrees with literature values for heat transfer by natural convection of 10 to 85 J/s·m^2·K (Bennett and Myers, 1982, p. 317). This gives a cooling time constant to the air of 166 min, resulting in a cooling time of 830 min (14 h) which is much longer than the duration of a run. Thus, heat transfer to the surroundings may be neglected as stated in assumption 4.

Adiabatic temperature rise

The adiabatic temperature rise of the reaction can be determined from Eqs. 1 and 2 by neglecting the heat transfer to the mold during the reaction period on the assumption that the reaction takes place in a very short period of time compared to the rate of heat transfer to the mold, as discussed above. Under this assumption, combining Eqs. 1 and 2 results in:

$$\frac{dT}{d\Phi} = \frac{(-\Delta H_r)C_0}{\rho C_p} \tag{5}$$

Now integrating from the initial to the final conditions, assuming the reaction goes to completion gives:

$$\int_{T_o}^{T_f} dT = \frac{(-\Delta H_r)C_0}{\rho C_p}\int_0^1 d\Phi$$

$$\Delta T_{ad} = T_f - T_o = \frac{(-\Delta H_r)C_0}{\rho C_p} \tag{6}$$

The reaction is exothermic with a heat of reaction of 83,000 kJ/kmol of isocyanate (Macosko, 1989). The heat produced by the reaction causes the temperature to rise rapidly for a short period of time, less than 8 s, until all the reactants are consumed. To show that the temperature transient response is an exponential rise, expand Eqs. 1 and 2 by Taylor series to obtain:

$$\frac{dT}{dt} - r_1 T = f_1(\Phi, T_{\text{mold}})$$

$$\frac{d\Phi}{dt} - r_2\Phi = f_2(T, T_{\text{mold}}) \tag{7}$$

where r_1 and r_2 are the local roots of each individual linearized equation and are given by:

$$r_1 = \frac{EA_o C_0^2(-\Delta H_r)}{\rho C_p R T^2} e^{-\frac{E}{RT}}(1-\Phi)^2 - \frac{h_i A_i}{\rho C_p V} \tag{8}$$

$$r_2 = -2A_o C_0 e^{-\frac{E}{RT}}(1-\Phi) \tag{9}$$

If one of these roots is positive, the transient response of the corresponding variable will grow exponentially with time. As the roots are functions of the state variables of the system,

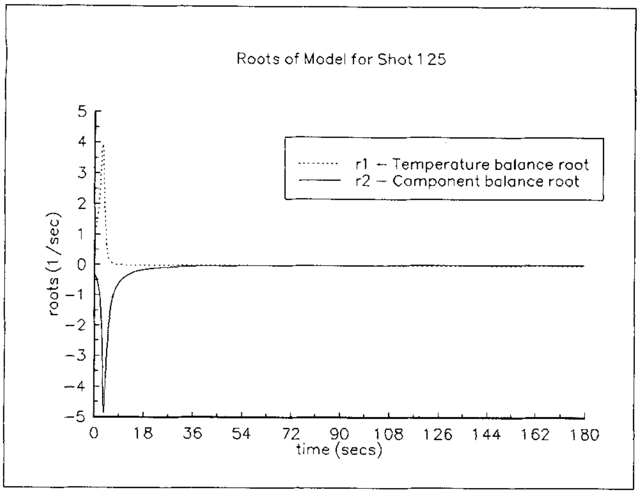

Figure 1. Roots for Eqs. 1 and 2 for shot 125.

temperature and extent of reaction, Eqs. 1–3 were solved after their parameters were fit to data from several RIM shots, to calculate the roots from the fitted parameters and the state variables. The value of the activation energy E was assumed known at 53,200 kJ/kmol (Macosko, 1989). The roots thus calculated are shown in Figure 1; the root of the energy balance equation r_1 is positive until the reactants are consumed indicating an exponentially increasing temperature response. When the reaction is complete ($\Phi = 1$), r_1 settles at a value determined by the heat transfer to the mold (second term in Eq. 8). This final value of r_1 is:

$$\lim_{\Phi \to 1} r_1 = -\frac{h_i A_i}{\rho C_p V} \tag{10}$$

The final value of r_1 for shot #125 (Figure 1) is -0.0177 rad/s which corresponds to a cooling time constant of the part of 56.5 s. From Figure 1, the roots reach their final values in about 5 s, which means the reaction is essentially complete in that period of time. The isothermal gel time at the maximum temperature in an adiabatic shot is 15 s (Sahay, 1992). While the time to gel is longer than the thermocouple response time, the largest amount of heat is released in the first few seconds of the reaction and then the reaction rate declines rapidly releasing heat at a lower rate.

Simplified reaction model

Because the reaction takes place in such a short time relative to the cooling time, the model equations can be simplified without compromising their ability to model the transient temperature by assuming that the heat of reaction is released instantaneously at the time of injection. However, as the thermocouple measurement cannot track the rapid increase in temperature, it is assumed that the thermocouple lag will spread out the temperature rise over several seconds. This response can be modeled by replacing the heat of reaction term in Eq. 1 with a lagged impulse function. Such a function has the following Laplace transform (Smith and Corripio, 1985):

$$F(s) = \frac{\Delta T_{ad}}{\tau_1 s + 1} \tag{11}$$

The time constant of this equation is the time constant of the thermocouple. Inverting this Laplace transform to the time domain gives:

$$f(t) = \mathcal{L}^{-1}[F(s)] = \frac{\Delta T_{ad}}{\tau_1}\mathcal{L}^{-1}\left[\frac{1}{s + \frac{1}{\tau_1}}\right] = \frac{\Delta T_{ad}}{\tau_1} e^{-\frac{t}{\tau_1}} \tag{12}$$

Like the impulse or Dirac delta function, this lagged impulse function has dimensions of temperature per unit time, as required for inclusion in the energy balance equation, and its time integral is equal to ΔT_{ad} which is related by Eq. 6 to the other reaction parameters.

Using the lagged impulse function to approximate the energy effects for the short period of the reaction, the rest of the temperature transient response model requires only the term for heat transfer from the reacting mass to the mold. Neglecting the heat losses to the surroundings, the following equation set results:

$$\frac{dT}{dt} = \frac{\Delta T_{ad}}{\tau_1} e^{-\frac{t}{\tau_1}} - \frac{h_i A_i}{\rho C_p V}(T - T_{\text{mold}}) \tag{13}$$

$$\frac{dT_{\text{mold}}}{dt} = \frac{h_i A_i}{M_{eff} C_{pm}}(T - T_{\text{mold}}) \tag{14}$$

By including the lag of the thermocouple measurement in the reaction term, the model temperature can be fitted directly to the measured temperature, but the question arises whether the lag should also be included in the heat-transfer term of the model. Although the thermocouple measurement is slow compared to the speed of the reaction term of the energy balance equation, (Eq. 13), its response time is an order of magnitude faster than the heat-transfer characteristic time between the part of the mold; therefore, the thermocouple lag can be neglected in the heat-transfer terms of Eqs. 13 and 14, that is, the measured temperature is not different from the actual temperature during the slow portion of the response in which the part is transferring heat to the mold.

Although the lagged impulse model for the temperature rise during the reaction was developed neglecting heat transfer to the mold, the simplified model given by Eqs. 13 and 14 includes the heat transfer to the mold during the reaction, but it assumes that the film coefficient of heat transfer from the part to the mold h_i is the same for the reaction and cooling periods. The value of this coefficient that matches the experimental temperature responses is dominated by the rate of cooling of the part, and the error introduced by the assumption that the coefficient is the same during the reaction period should be negligible since the reaction period is relatively short and only a small fraction of the total heat is transferred to the mold during this time.

There are four independent model parameters to be fit to the experimental temperature responses, ΔH_r, τ_1, h_i, and M_{eff}. The heat of reaction ΔH_r which is related to ΔT_{ad}

through Eq. 6 is selected so that the experimenter can detect changes in reaction conditions by comparing it to literature values (such as Macosko, 1989) and past fitted values. Although the heat of reaction is not expected to change from shot to shot, it becomes an indirect indication of the extent of the reaction because the model assumes complete conversion of the limiting reactant. If the estimated heat of reaction is lower than expected, it is probably due to incomplete conversion caused by poor mixing.

The time constant τ_1 is a measure of the speed of the thermocouple. The heat-transfer coefficient h_i describes the heat flux between the part and the mold. The last parameter M_{eff} is the effective mass of the mold. This is not the same as the mass of the mold which can be obtained by weighing it, because the mold is not at uniform temperature. It takes a finite time for heat to penetrate the mold from the surface in contact with the part to the surface in contact with the air. The period over which the temperature response is recorded during a shot is not long enough for the heat to completely penetrate the mold, so the entire mass of the mold is not used as a heat sink. The effective mass is a measure of the fraction of the total mass of the mold that actually absorbs heat. The effective mass of the mold can be estimated from known properties of the mold by the following equation (Bennett and Myers, 1982):

$$M_{eff} = A_i \rho_m \sqrt{\frac{k_m}{\rho_m C_{pm}} t_{\exp}} \qquad (15)$$

From this equation, the effective mass of the mold for a 200 s temperature measurement is 2.44 kg, or about one-third of the actual mass of the mold.

Equations 13 and 14 are linear and can be solved by Laplace transforms to give:

$$T(t) = T(0) + K_1\left(1 - \frac{\tau_3 - \tau_1}{\tau_{23} - \tau_1} e^{-\frac{t}{\tau_1}} + \frac{\tau_3 - \tau_{23}}{\tau_{23} - \tau_1} e^{-\frac{t}{\tau_{23}}}\right) \qquad (16)$$

where:

$$\tau_2 = \frac{\rho C_p V}{h_i A_i} \qquad K_1 = \frac{\Delta T_{ad} \tau_2}{\tau_2 + \tau_3} \qquad (17)$$

$$\tau_3 = \frac{M_{eff} C_{pm}}{h_i A_i} \qquad \tau_{23} = \frac{\tau_2 \tau_3}{\tau_2 + \tau_3} \qquad (18)$$

Parameter K_1 represents the temperature rise for the period of time during which the temperature response is recorded, of the order of 3 min. The model predicts this temperature rise because, as heat losses to the surroundings are neglected, the mold and the part behave as a closed system. The actual temperature of the mold and part would return to the ambient temperature if the response were measured for the several hours that it takes. In practice, however, the duration of a run is a fraction of that time. Parameter τ_{23} is the combined time constant of the part and mold and it is smaller than both τ_2 and τ_3.

The effect of the fitted variables on the shape of the temperature response is shown in Figure 2. The heat of reaction has the most dramatic effect on the transient temperature. As the heat of reaction increases, the adiabatic temperature rise increases and the final temperature of the part increases as well. The time constant τ_1 only effects the response during the initial temperature rise and has no effect during the cooling phase. As the time constant increases, the maximum temperature rise becomes smaller and the time it takes to reach the maximum temperature also increases. The heat-transfer coefficient affects the cooling portion of the response and has a much smaller effect on the initial temperature rise. Finally, the effective mass of the mold has no effect on the initial temperature rise but does have a large effect on the final temperature. This is because, as the effective mass of the mold increases, more of the total heat released in the reaction goes to heat up the mold.

Apparatus

The experiments in this work were performed using HI-Tech Engineering (Grand Rapids, MI) Reaction Injection Molding machine (serial number 114) at the LSU Dept. of Chemical Engineering. The RIM unit is shown in Figure 3. This is an experimental unit with a maximum shot size of 0.30 kg, and two feed tanks of 1L each. The pistons shown in Figure 3 can hold approximately 250 cm^3 each. Hydraulic fluid is used to actuate the pistons, block valves, and the mixhead.

When a part is made, the pistons move down at a controlled rate forcing the reactants to flow through the mixhead to their respective feed tanks. The reactants circulate for a period of time set by the operator to achieve a stable pressure in the reactant feed lines. The reactants must pass through needle valves located in the mixhead which are adjusted to set the pressures in each reactant feed line. When the reactants have circulated for the required length of time, the mixhead opens and the reactants mix together and enter the mold which attaches to the mixhead. This is not shown in Figure 3. The mixhead stays open for a period of time specified by the operator to achieve complete filling of the mold. When this time period has elapsed, the mixhead closes. The reactants continue to circulate for a set period of time. Block valves in the lines between the feed tanks and the pistons, as shown in Figure 3, open and the pistons are moved up drawing reactants into the piston. When the pistons are at the maximum height, the block valve closes and the unit is ready to produce another part.

The RIM unit is controlled by a programmable logic controller (PLC) which actuates the block valves, mixhead, and pistons by controlling the flow of hydraulic fluid to them. It also controls the temperature in the reactant tanks through solenoid valves that regulate hot and cold water flows into the reactant tank jackets. The PLC controls all timing functions mentioned previously and can abort a shot if the hydraulic pressure is too high, or if the reactant pressure is too high or too low. The PLC is also used to collect data from the sensors on the RIM unit and transmit them for storage in an IBM PS2 model 70 computer through an RS-232 cable.

Mold

The mold used in these experiments was made at the LSU Dept. of Chemical Engineering from mild steel and is

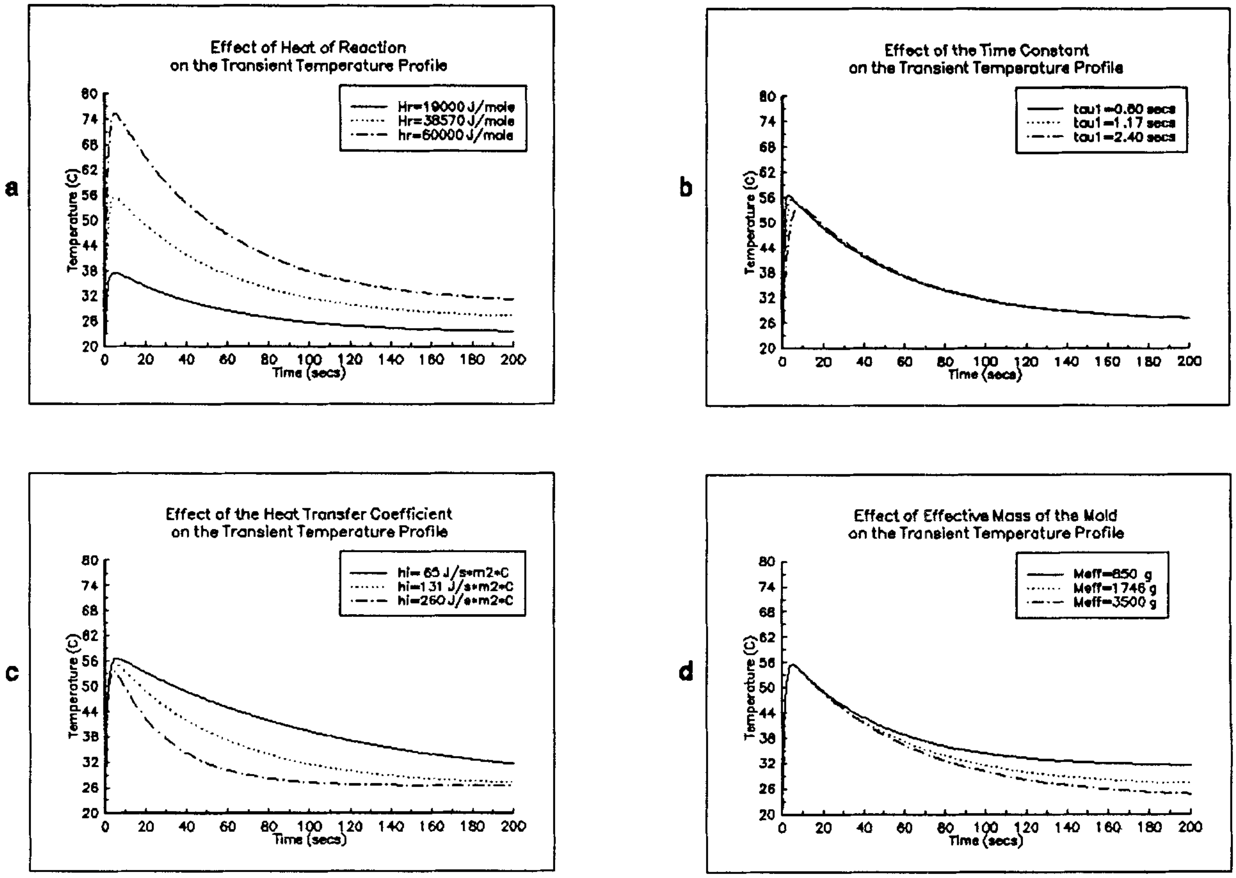

Figure 2. Effect of fitted variables on the shape of the transient temperature response.

(a) ΔH_r; (b) τ_1; (c) h_i; (d) M_{eff}.

sketched in Figure 4. An aftermixer in the mold was not used in these experiments. The mold is symmetric about the center line so duplicate tensile tests can be performed on the part produced by each shot. The part produced in the mold is 0.10 kg in mass. Two Omega type T thermocouples are inserted from the top of the mold (see Figure 4). The thermocouple locations are symmetric about the center line so the two temperature responses should be the same. The thermocouple diameter is 0.813 mm (0.032 in.) with a stainless steel sheathing and a 1.9 s time constant.

Chemicals

The chemical reactant system used was the Dow Spectrim 35BS, a polyurethane system that consists of two reacting

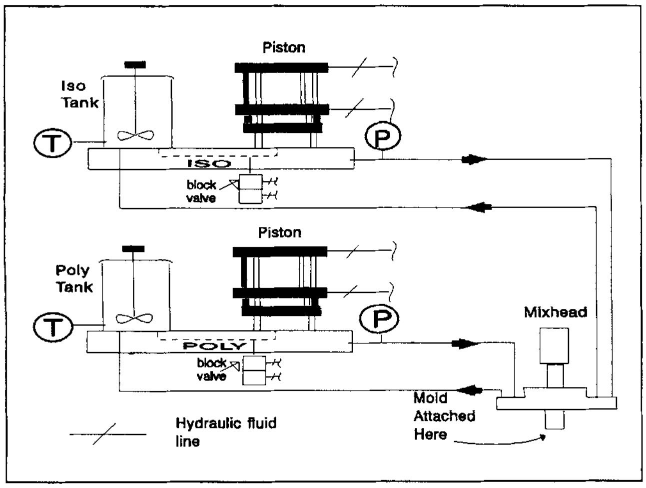

Figure 3. RIM unit

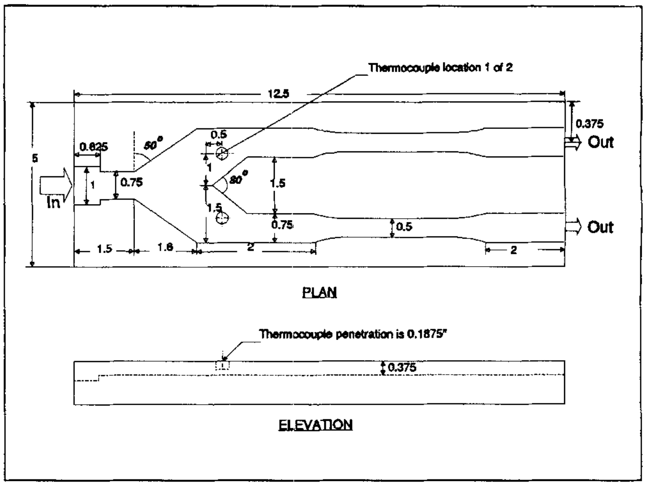

Figure 4. RIM mold (dimensions are in in.).

mixtures: a polyol and a diisocyanate. The polyol reactant mixture consists of: polyether polyol, diethyltoulene-diamine (DETDA) that is used as a chain extender, and dibutyltin dilaurate that is used as a catalyst. The diisocyanate reactant is 4,4-diphenylmethane diisocyanate (MDI) and a prepolymer of MDI and the polyol. The reactant temperatures were varied during the experiments from 300 K (80°F) to 322 K (120°F).

Experimental Results

An IBM PS2 model 70 computer collects the following data from the PLC and stores it in an ASCII file:

- Temperature in each tank
- Percent DETDA (chain extender) in the polyol
- Weight ratio of polyol to isocyanate
- Pressure of isocyanate and polyol in the feed lines to the mixhead
- Flow of isocyanate and polyol in grams per second.

These five variables are the independent variables associated with the RIM unit. They are considered important to the final part properties for several reasons. The flow rate and pressure of the reactants will influence the degree of mixing in the mixhead (Sebastian and Boukobbal, 1986); poorly mixed reactants will not completely react producing a defective part. The ratio of the reactants and the percent DETDA in the polyol determine the structure of the block copolymer formed during the reaction (Huang, Hsu, and Lee, 1985), which in turn affects the glass transition temperature of the polymer.

The number of independent variables can be reduced by fixing the sum of the polyol and isocyanate feed rates to 200 g/s, a rate at which the mold fills in 0.5 s. With the total flow fixed, each reactants ratio determines the flow rate of each reactant.

The temperature responses from the two thermocouples in the mold were recorded and stored in an ASCII file. To determine the parameters of the temperature model, the transient response predicted by the model was fit to the arithmetic mean of the two thermocouple measurements. Approximately 800 points were collected from each thermocouple during a shot. The two responses were averaged and then fit using the MATLAB software package (MathWorks, 1985). The Neadler-Mead Simplex algorithm was alternated with the sequential quadratic programming (SQP) algorithm to estimate the values of the model parameters that minimize the sum of the squares of the difference between the measured temperature and the temperature calculated from the model. Alternating these procedures improved the fit of the data, because the simplex algorithm did not get trapped by saddle points or local minima as the SQP method would, while the SQP method could quickly find the next local minimum using gradients. Thus, the simplex algorithm allowed a good approximation for the minimum to be found and then the SQP method quickly found the local minimum. The process was repeated until the minimum from the SQP method was within 5% of the previous value.

Figure 5 shows typical temperature responses for four different shots. The model response tracks the major characteristics of the experimental response: the initial sharp rise, the slow cooling, and the new steady state above the initial temperature.

A partial factorial set of experiments for the four independent variables with three levels each was carried out with the RIM unit for correlating the properties of the parts produced to the independent variables. Table 1 gives the estimated values of the temperature model parameters for the partial factorial experiments; the values of the independent variables for each shot are given in Table 2. Table 1 shows that the fitted heat of reaction has a mean value of 38.53 kJ/mol with a standard deviation of 7.78 kJ/mol compared to literature values of 48 kJ/mol (Sahay, 1992) and 83 kJ/mol of isocyanate (Macosko, 1989), where the value reported by Sahay used the LSU RIM unit and the same chemical system. The system used by Macosko is only similar to the one used here; his value of the heat of reaction is reported as a comparison.

The adiabatic temperature rise along with the other parameters of Eq. 16 are shown in Table 3, where the mean of the adabiatic temperature rise is 37.94 K with a standard deviation of 6.58 K. To determine the agreement between the thermocouple lag and the fitted time constant τ_2, the thermocouples were alternatively immersed in an ice bath and into hot water. A recording of the time responses of the thermocouples for these tests resulted in a mean time constant of 1.8 s, which agrees well with the fitted values of τ_1 in Table 3 which had a mean and standard deviation of 1.17 s and 0.175 s. This shows that, as postulated, the temperature measurement lag is the dominant cause of the lag in the initial temperature rise. The reaction occurs much faster than the thermcouple can respond, so the thermcouple spreads out the introduction of the heat evolved by the reaction over several seconds.

Table 3 shows that the fitted heat-transfer coefficient h_i with mean and standard deviation of 131 and 25.3 $J/s \cdot m^2 \cdot K$ is consistent with literature values that range from 100 to 1,000 $J/s \cdot m^2 \cdot K$ (Bennett and Myers, 1982, p. 317). The value of the part cooling time constant τ_2, defined in Eq. 16, had a mean and standard deviation of 66.3 and 10.1 s. The actual mass of the mold is 7.2 kg. The effective mass that was fitted using the temperature responses had a mean and standard deviation of 1.746 and 0.415 kg, or from one-sixth to one-half the actual mass of the mold. This agrees well with the previous estimate of the effective mass of 2.44 kg from known mold properties, and shows that the heat from the part does not penetrate the entire mold in the time of the tests, reducing the mass of the mold that absorbs heat.

Earlier the different magnitudes of the rates of heat transfer were discussed. The experimental results confirm the original assumptions made in the development of the model. Time constant τ_1, as shown in Table 3, has a mean value of 1.17 s and standard deviation of 0.175 s and the combined time constant of the part and mold τ_{23} has an average value of 54.87 s with a standard deviation of 10.1 s. This shows that the reaction time is at least an order of magnitude faster than the speed at which heat is transferred from the part to the mold.

Conclusions

This article has shown that a model of RIM does not have to be complicated to be useful. A simple model with four

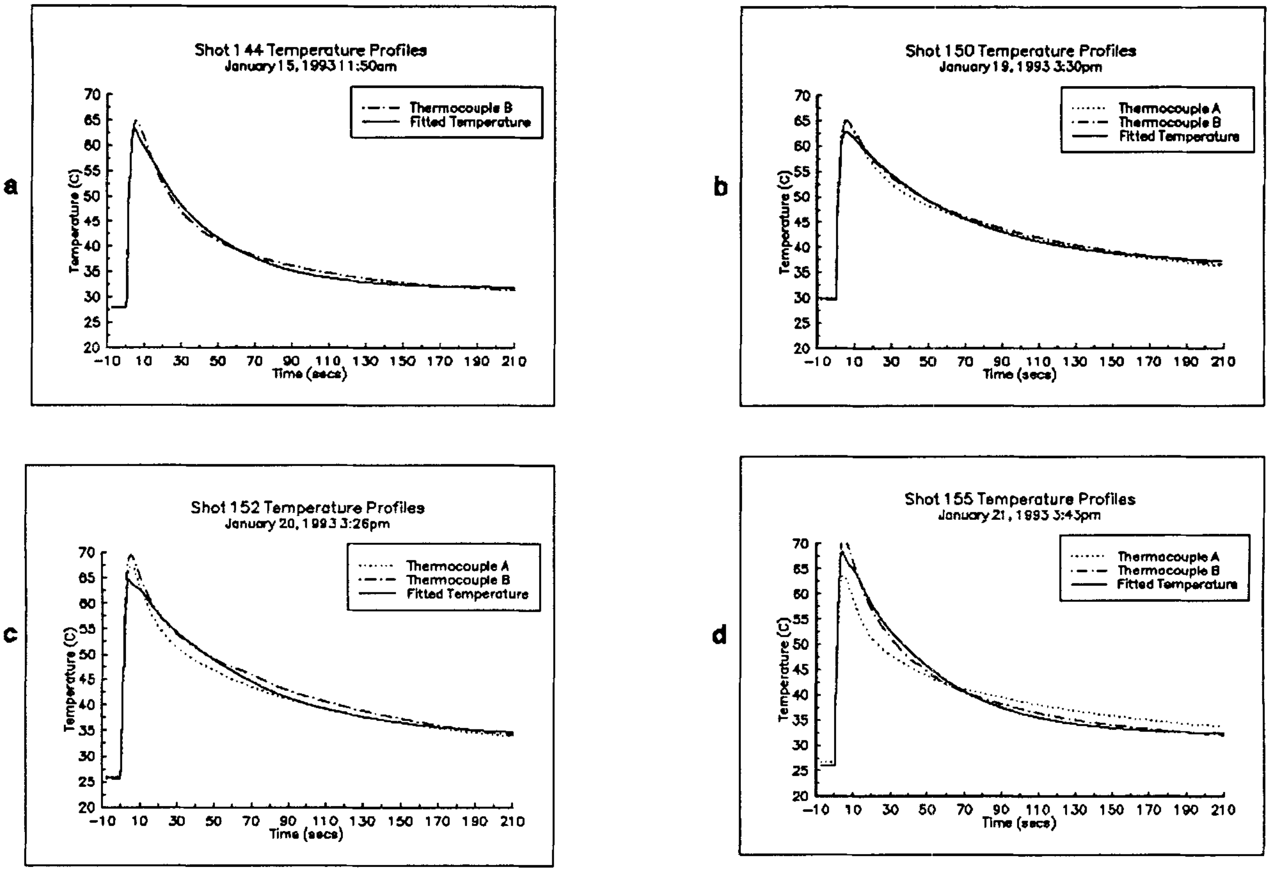

Figure 5. Transient temperature responses for four different shots with fitted temperature curves.

(a) Shot 144; (b) 150; (c) Shot 152; (d) Shot 155. See Table 3 for the values of the operating variables.

adjustable parameters can fit experimental responses from different RIM shots. The model gives estimates for the heat of reaction that agree well with values published by Macosko (1989) and Sahay (1992) on polyurethane systems. The simple model developed here can be used for on-line control of part properties in cases where direct measurement would be destructive to the part produced. Changes that would require feedback from the temperature response model include: ag-

Table 1. Fitted Coefficients for the Experimental Shots

Shot	ΔH_r, kJ/kmol	τ_1, s	h_i, J/s·m^2·K	M_{eff}, kg	Σ (error)^2, K^2
134	29,549	1.1752	125	1.670	1,505
135	24,627	1.2004	124	1.572	1,128
136	24,338	1.1783	135	1.344	762
138	38,196	1.0219	161	1.492	2,093
156	39,246	1.2530	121	1.679	1,355
143	42,621	0.9030	120	2.160	2,873
146	56,506	1.4245	114	1.997	1,299
163B	32,597	0.8714	128	1.484	1,608
153	38,105	1.3004	120	1.557	1,323
152	36,618	1.1860	115	1.433	924
164	39,446	1.3512	127	1.563	1,348
163A	39,703	1.2232	121	1.338	1,127
155	45,634	1.1208	160	1.670	874
144	42,912	1.5458	199	3.156	776
142	50,287	1.1160	117	1.777	1,505
166	37,141	1.1315	104	1.950	1,017
147	45,665	1.2359	192	2.316	1,909
165	37,485	0.8129	126	1.387	1,109
150	33,510	1.3144	115	1.530	416
158	36,366	1.1379	111	1.846	1,336

Table 2. Experimental Design

Part No.	Ratio	% DETDA, wt. %	Reactant Pres. kPa (psig)	Reactant Temperature, K (°F)
134	1.2	28	17,200 (2,500)	311 (100)
135	1.2	28	17,200 (2,500)	311 (100)
136	1.2	28	17,200 (2,500)	311 (100)
138	1.2	28	17,200 (2,500)	311 (100)
156	0.8	32	17,200 (2,500)	311 (100)
143	1.8	28	20,700 (3,000)	311 (100)
146	1.8	28	13,800 (2,000)	311 (100)
163B	1.8	24	17,200 (2,500)	311 (100)
153	1.2	32	20,700 (3,000)	311 (100)
152	1.2	32	13,800 (2,000)	311 (100)
164	1.2	24	20,700 (3,000)	311 (100)
163A	1.2	24	13,800 (2,000)	311 (100)
155	1.6	32	17,200 (2,500)	311 (100)
144	1.6	28	13,800 (2,000)	311 (100)
142	1.6	28	17,200 (2,500)	311 (100)
166	1.6	24	17,200 (2,500)	311 (100)
147	1.6	28	13,800 (2,000)	322 (120)
165	1.6	24	20,700 (3,000)	300 (80)
150	0.8	28	17,200 (2,500)	300 (80)
158	0.8	32	13,800 (2,000)	322 (120)

Table 3. Simplified Model Parameters Calculated from Fitted Coefficients

Shot	ΔT_{ad}, K	τ_1, s	τ_2, s	τ_3, s	τ_{23}, s	K_1, K
134	32.96	1.1752	67.90	325.5	56.18	5.69
135	27.50	1.2004	68.45	308.9	56.03	4.99
136	27.51	1.1783	62.87	242.6	49.93	5.66
138	41.32	1.0219	52.72	225.8	42.74	7.82
156	32.03	1.2530	70.14	338.0	58.09	5.50
143	38.16	0.9030	70.73	438.6	60.91	5.30
146	55.62	1.4245	74.45	426.9	63.39	8.26
163B	34.53	0.8714	66.31	282.5	53.70	6.56
153	42.64	1.3004	70.73	316.1	57.80	7.80
152	41.31	1.1860	73.80	303.6	59.37	8.08
164	42.16	1.3512	66.83	300.0	54.65	7.68
163A	42.77	1.2232	70.14	269.5	55.66	8.83
155	40.84	1.1208	53.05	254.3	43.89	7.05
144	38.14	1.5458	42.65	386.5	38.41	3.79
142	45.87	1.1160	72.54	370.2	60.65	7.52
166	34.11	1.1315	81.61	456.9	69.24	5.17
147	41.45	1.2359	44.21	293.9	38.43	5.42
165	34.27	0.8129	67.36	268.3	53.84	6.88
150	35.38	1.3144	73.80	324.3	60.12	6.56
158	30.28	1.1379	76.46	405.2	64.32	4.18

ing equipment and molds, use of different reactant feed stocks or different batches of reactant feed stocks, and errors in the measurements of the reactant temperatures, flows, and pressures.

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Notation

A_i = surface area of the part = 0.0206 m^2
A_{mold} = mold surface area in contact with air = 0.0403 m^2
A_o = frequency factor in Arrhenius rate equation, m^3/s·kmol
C_0 = initial composition of limiting reactant, kmol/m^3
C_p = specific heat of the solution = 1.88 kJ/kg·K
C_{pm} = specific heat of the mold = 0.502 kJ/kg·K
E = activation energy of reaction = 53.2 kJ/mol (Macosko, 1989)
h_a = convective heat-transfer coefficient to the air, J/s·m^2·K
h_i = heat-transfer coefficient between part and mold, J/s·m^2·K
ΔH_r = heat of reaction, kJ/mol
k_m = thermal conductivity of the mold = 16.3 J/m·s·K (9.4 Btu/ft·h·°F) (McCabe et al., 1985)
K_1 = final steady-state temperature rise, K
M = mass of the mold = 7.2 kg
M_{eff} = effective mass of the mold, kg
R = ideal gas constant
r_1 = root of the energy balance equation: Eq. 1, rad/s
r_2 = root of the component balance equation: Eq. 2, rad/s
t = time s
t_{exp} = experimental time or time that the part temperature is measured, s
T = temperature of the part K
ΔT_{ad} = adiabatic temperature rise, K
T_{air} = temperature of the part, K
T_{mold} = temperature of the mold, K
V = volume of the part = 93 cm^3

Greek letters

ρ = density of the solution = 1,000 kg/m^3
ρ_m = density of the mold = 7,030 kg/m^3
τ_1 = time constant of the reaction and thermocouple, s
τ_2 = cooling time constant of the part, s
τ_{23} = time constant of the mold and part system, s
τ_3 = heating time constant of the mold, s
τ_a = time constant of the mold cooling to the air, s
Φ = extent of reaction

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