lm = lower critical value based on $\overline{Nu}$
s = surface
u = upper critical value based on Nu_x [at intersection of Equations (6) and (10)]
um = upper critical value based on $\overline{Nu}$
∞ = bulk fluid

LITERATURE CITED

Churchill, Stuart W., and H. H.-S. Chu, "Correlating Equations for Laminar and Turbulent Free Convection from a Vertical Plate," *Intern. J. Heat Mass Transfer*, **18**, 1323 (1975).

Churchill, Stuart W., and H. Ozoe, "Correlations for Laminar Forced Convection with Uniform Heating in Flow over a Plate and in Developing and Fully Developed Flow in a Tube," *J. Heat Transfer, Trans. ASME*, **95C**, 78 (1973*a*).

————, "Correlations for Laminar Forced Convection in Flow over an Isothermal Flat Plate and in Developing and Fully Developed Flow in an Isothermal Tube," *ibid.*, **95C**, 416 (1973*b*).

Churchill, S. W., and R. Usagi, "A General Expression for the Correlation of Rates of Transfer and Other Phenomena," *AIChE J.*, **18**, 1121 (1972).

Dennis, S. R. C., and N. Smith, "Forced Convection from a Heated Flat Plate," *J. Fluid Mech.*, **24**, 509 (1966).

Hanna, O. T., and J. E. Myers, "An Analogy between Heat and Momentum Transfer on a Flat Plate," *Purdue Univ. Eng. Bull.*, **46**, No. 4, Research Series 148 (July, 1962).

Jakob, M., and W. M. Dow, "Heat Transfer from a Cylindrical Surface to Air in Parallel Flow with and without Unheated Starting Sections," *Trans. ASME*, **68**, 123 (1946).

Kestin, J., P. D. Maeder, and H. E. Wang, "Influence of Turbulence on the Transfer of Heat from Plates with and without a Pressure Gradient," *Intern. J. Heat Mass Transfer*, **3**, 133 (1961).

Parmalee, G. V., and R. G. Huebscher, "Heat Transfer by Forced Convection along a Smooth Flat Surface-Laminar and Transitional Boundary Layer Flow," *Heating Piping and Air Conditioning*, **19**, No. 8, 115 (1947).

Reynolds, W. C., W. M. Kays, and S. J. Kline, "Heat Transfer in the Turbulent Incompressible Boundary Layer," *NASA Memos 12-1-58W, 12-2-58W, 12-3-58W, and 12-4-58W*, Washington, D. C. (1958).

Slegel, L., and G. A. Hawkins, *Purdue Univ. Eng. Bull.*, **30**, No. 3, Research Series 97 (May, 1946).

Sugawara, S., and T. Sato, "Heat Transfer on the Surface of a Flat Plate in the Forced Flow," *Memoirs Faculty Eng., Kyoto Univ.*, **14**, 21 (1952).

Whitaker, Stephen, "Forced Convection Heat Transfer Correlations for Flow in Pipes, Past Flat Plates, Single Cylinders, Single Spheres, and for Flow in Packed Beds and Tube Bundles," *AIChE J.*, **18**, 361 (1972).

Žukauskus, A., and A. Šlančiauskus, *Heat Transfer in Turbulent Flow of Fluid*, Mintes, Vilnius, Lithuania (1973), in Russian.

Manuscript received October 7, 1975; revision received December 1, and accepted December 4, 1975.

Heat Transfer and Curing in Polymer Reaction Molding

A theoretical model is proposed for curing in polymer reaction molding operations like casting, potting, lamination, thermoset molding, or reaction injection molding. In many cases, convection and mass diffusion can be neglected. The resulting unsteady heat equation with temperature dependent generation is solved numerically. Temperature and property profiles, gel point, sol fraction, and modulus are presented for a typical urethane system under several conditions. Two dimensionless groups, the adiabatic temperature rise and the ratio of polymerization rate to heat conduction rate, are most significant. Process design criteria are discussed.

EPHRIAM BROYER
and
CHRISTOPHER W. MACOSKO
Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

SCOPE

A large number of polymer products are formed into their final shape by polymerization in situ. Examples include processes like monomer casting, potting or encapsulation, bonding with structural adhesives, in situ foaming, reinforced plastic lamination, and thermoset and rubber molding operations. The recent development of a number of very fast urethane systems with a wide choice of final properties has resulted in a new processing method, reaction injection molding (Wood, 1974; DelGatto, 1973), which has high growth potential.

There is a body of descriptive literature on these processes. Problems of nonuniform reaction due to heat transfer and the reaction exotherm are well recognized (for example: acrylics, Horn, 1960; epoxies, Lee and Neville, 1967; polyesters, Doyle, 1969; rubber, Hills, 1971). Some qualitative guidelines for processing are given, but there are few analytical studies. As Kamal (1974) states in a recent review of thermoset injection molding, "So far there has been no systematic study in the literature to relate basic kinetic, thermal and rheological parameters for thermosets to their injection molding behavior." In rubber molding, Hills (1971) reports some transient heat transfer calculations to predict cure development in thick sections. Engel-

---

Correspondence concerning this paper should be addressed to C. W. Macosko.

maier and Roller (1975) use transient heat transfer and a time and temperature dependent viscosity to model thickness change in epoxy electrical laminates. Stonecypher et al. (1966) also include heat of reaction in their model for curing thick sections of solid propellants. Each of these studies are sound, but they have dealt with very specific types of processes. It appears that a general approach can be taken to all molding operations which include polymerization.

CONCLUSIONS AND SIGNIFICANCE

Most polymer reaction molding processes appear to be controlled by a balance of internal heat generation and heat transfer through the mold walls. Convection and part geometry effects are generally secondary. Molecular diffusion can be neglected. This leads to a straightforward transient heat transfer problem which can be readily solved numerically.

Calculated temperature profiles for a typical system show that adiabatic conditions are often encountered near the center of real moldings. A critical thickness h_c is suggested for determining when a process is essentially adiabatic. This defines the maximum temperature, since high temperatures can cause side reactions, degradation, volatilization, and damage to components near the polymer, such as in electrical encapsulation.

From these temperature and concentration profiles, and with the network structure property relations of Macosko and Miller (1976 *a,b*), we can calculate gel point, molecular weight, sol fraction, and modulus changes with position and time in the mold. For cyclic processes like thermoset injection molding and reaction injection molding which involve significant capital equipment, it is advantageous to cure the part surface rapidly and follow with a postcure. It may be more desirable to control heat flux through the mold walls rather than T_w as is usually done. Mold cure cycles are usually controlled on surface hardness or flex modulus which can be predicted from our modulus relations.

Polymer reaction forming processes can be broken down into several operations as shown schematically in Figure 1. Each process must include component metering, either batch or continuous; intensive mixing to bring the reactants into intimate molecular contact within a time scale short compared to the process cycle time; flow into the final shape, such as filling a mold; reaction or curing in shape until part is stiff enough to remove; post-curing step sometimes used to improve modulus, and dimensional stability.

The important molecular changes that occur during these operations are illustrated for a trifunctional polymerizing with a bifunctional monomer in Figure 2. The most important molecular information is the gel point. This is the point at which the weight average molecular weight $\overline{M}_w$ becomes infinite, where one molecule becomes the size of the reactor. Beyond the gel point, more and more of the molecules attach to this infinite network; thus the weight fraction soluble w_s drops to zero. The fraction of A_3 acting as effective cross-links $P(X_3)$ increases to one at full reaction. Macosko and Miller (1976 *a, b*) have derived relations for these property changes as functions of extent of reaction p. For the case of $A_3 + B_2$ with equal stochiometry and reactivity of functional groups, these relations reduce to

$$\overline{M}_w = \frac{2/3(1+p^2)M_{A3}{}^2 + (1+2p^2)M_{B2}{}^2 + 4pM_{A3}M_{B2}}{(2/3M_{A3} + M_{B2})(1-2p^2)} \tag{1}$$

The extent of reaction at gel ($\overline{M}_w \to \infty$)

$$p_{\text{gel}} = \sqrt{1/2} \quad \text{For} \quad p > p_{\text{gel}} \tag{2}$$

$$w_s = w_{A3}\left(\frac{1-p^2}{p^2}\right)^3 + w_{B2}\left(\frac{1-2p^2+p^3}{p^3}\right)^2 \tag{3}$$

where

$$w_{A3} = \frac{M_{A3}C_{A_0}}{M_{A3}C_{A_0}/3 + M_{B2}C_{B_0}/2} \quad \text{and} \quad w_{B2} = 1 - w_{A3}$$

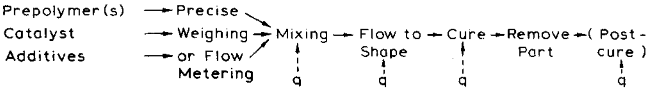

Fig. 1. Schematic representation of the unit operations of reactive polymer molding; *q* represents heat flow into or out of the process.

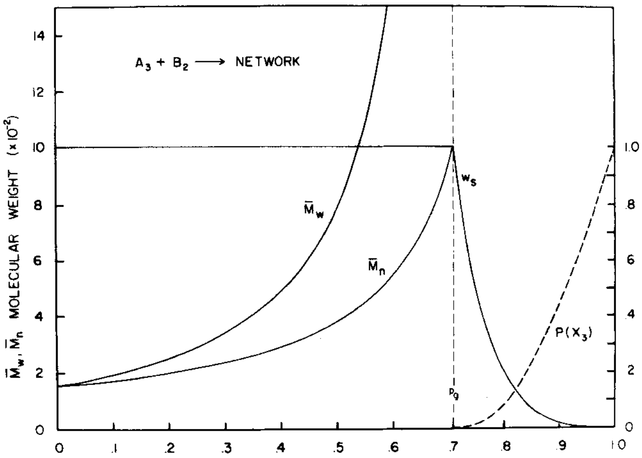

Fig. 2. Molecular property changes with extent of reaction in trifunctional network polymerization. From equations (1) to (4); $M_{A3} = 165$, $M_{B2} = 168$, equimolar in functional groups, bulk concentrations.

$$P(X_3) = \left(\frac{2p^2-1}{p^2}\right)^3 \tag{4}$$

These molecular changes, of course, govern the processing behavior through property changes such as viscosity and modulus vs. time and temperature. The data of Gordon, Ward, and Whitney (1971), Lipshitz et al (1975), and Valles and Macosko (1975) indicate that for a number of network polymers, the viscosity is directly

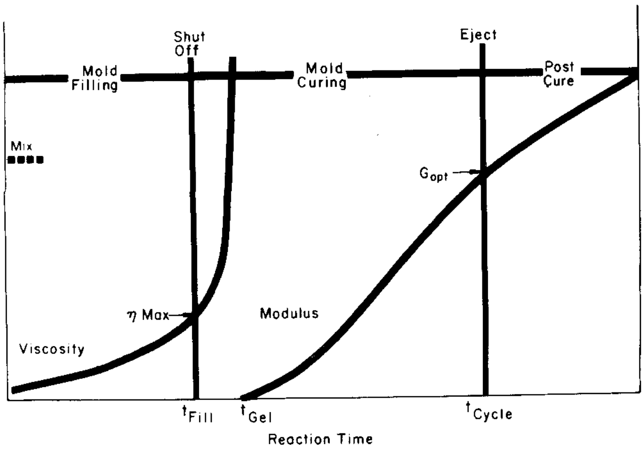

Fig. 3. Rheological changes during a polymer reaction molding cycle.

TABLE 1. COMPARISON OF TYPICAL FLOW AND CURE TIMES IN POLYMER REACTION MOLDING

Process	Flow time	Cure time
Monomer casting (epoxy) (Brydson, 1969)	60 s	24 hr.
Fiberglass lamination (Engelmaier and Roller, 1975; Roller, 1975; Lubin, 1969)	20 s	30 min.
Rubber compression molding (Blow, 1971; Hills, 1971)	15 s	60 min.
Thermoset injection molding (Beck and Golovay, 1972; Norfleet and Boone, 1974)	3 s	2 min.
Reaction injection molding (Prepelka and Wharton, 1975)	2 s	1 min. + 2 hr. post cure

related to $\overline{M}_w$:

$$\eta = K\overline{M}_w^a \tag{5}$$

If the shear modulus at small strains obeys the ideal equation of rubber elasticity (ignoring, for example, effects of entanglements, filler, crystallinity), then G is proportional to cross-link concentration:

$$G = \tfrac{1}{2} C_{A_0} P(X_3) RT \tag{6}$$

Given a kinetic expression, we can convert p to reaction time and generate a property vs. time plot such as Figure 3. This information is important to define the optimum stages in the cycle operation.

For $t < t_{gel}$ we have a liquid with increasing viscosity. In this liquid region, mixing should be accomplished at low viscosities. It may be necessary to add heat to melt or lower the viscosity of the reactants. Flow into the mold must also take place below some viscosity level to get complete filling. Ideally, we would like low viscosity throughout the filling process.

For $t > t_{gel}$, the material becomes a rubbery solid with increasing modulus. If there are temperature gradients in the part, modulus will vary with position. At some modulus and strength level, the part will be reacted enough to be removed. Further reaction can be accomplished in a post cure oven. These processing operations are shown superposed on the viscosity and modulus changes in Figure 3.

Below we propose a mathematical model for polymer reaction molding. The model is particularly aimed at predicted curing and molded part properties.

THE MODEL

No Flow Assumption

In most polymer reaction molding processes, the fill or flow time is significantly less than the total cure time. Table 1 summarizes some of the reported values for these times.

If the filling time is small, or if the composition and temperature of the part are fairly uniform at the end of filling, then we can neglect convection and greatly simplify the problem. The mold filling process can be modeled by using a finite element analysis (for example, Broyer, Tadmor, and Gutfinger, 1975) taking into account changes in viscosity due to polymerization. Some aspects of flow with network polymerization have been treated numerically and experimentally by Lipshitz and Macosko (1975).

No Diffusion Assumption

By neglecting flow, the one-dimensional mass transfer equation in terms of the concentration of functional groups of type A becomes

$$-\frac{\partial C_A}{\partial t} = \mathcal{D}\frac{\partial^2 C_A}{\partial y^2} + R_A \tag{7}$$

If we assume perfect initial mixing, the only driving force for diffusion of A groups arises from changes in reaction with y. Typically, the reactants involved have molecular weights greater than 10^2. At reaction conditions, the viscosities exceed 1 poise and increase continuously. Using the Stokes Einstein equation (Bird et al., 1960)

$$\mathcal{D} = \frac{k_b T}{6\pi r \eta} \tag{8}$$

and the values above with $T = 320°\text{K}$, we find $\mathcal{D} < 10^{-9}\text{cm}^2/\text{s}$. Crank and Park (1968) give 10^{-9} for diffusion of hydrocarbons into rubber. These low diffusion coefficients will decrease further with reaction.

Using 10^{-9} for $\mathcal{D}$, we can compare the order of magnitude of diffusion and generation terms on the right-hand side of Equation (7). Consider a fairly thick part with a rather slow reaction: $C_{A_0} = 0.2$ mole/l, $R_A = 10^{-4}$ mole/l/s, and $\Delta y = 1$ cm. We find

$$\mathcal{D}\left(\frac{\partial^2 C_A}{\partial y^2}\right)_{\max} \sim 10^{-9}\,\text{mole/l/s} << R_A \tag{9}$$

Thus, it appears quite reasonable for nearly all polymer reaction molding processes to neglect diffusion of reactants in the mold curing stage. This reduces mass transfer to just the kinetic expression for the rate of disappearance of A functional groups.

Chemical Kinetics

Determination of kinetics, particularly beyond the gel point, is difficult. Since the polymers formed are usually three dimensional and insoluble, indirect methods must be used. Calorimetry, infrared and other spectrographic methods, electrical conductivity, and dynamic mechanical and dielectric methods have all been tried (Kamal, 1974). For example, three studies with infrared measurements on different urethane systems report an increase in R_A (Mussatti, 1975), no change (Vilesova et al., 1972), and a decrease (French et al., 1970) after the gel point. With a hydrosilation system, Valles and Macosko (1975) find no change in order but a decrease of about 30% in k at the gel point. Several calorimetric studies on epoxies and polyesters indicate that one kinetic expression can fit the entire conversion (Prime, 1973; Kamal et al., 1973).

For lack of more precise data, it seems best to assume an n^{th} order reaction throughout the entire cure. Thus

$$R_A = kC_A^n \tag{10}$$

and we assume an Arrhenius temperature dependence

$$k = Ae^{-E_a/RT} \tag{11}$$

In our numerical solution, we allow for more complex schemes, particularly for change in k beyond the gel point.

Heat Transfer

All polymer reaction molding processes are exothermic, and both the reactants and products have low thermal conductivity. Thus, the generation term in the energy equation can be significant. Most molded parts are thin in one dimension, and the heat transfer can be reduced to a slab calculation. For this initial work we will consider only temperature gradients perpendicular to the mold walls, the y direction, to be significant. Thus, the energy equation reduces to

$$\rho c_v \frac{\partial T}{\partial t} = \frac{\partial}{\partial y}\left(k_T \frac{\partial T}{\partial y}\right) + H_R R_A \tag{12}$$

Nearly all thermosetting materials are amorphous; thus, thermal diffusivity, density, and heat capacity change little with reaction from liquid to solid or within the temperature range of a typical cure (Van Krevelan, 1972; Brandrup and Immergut, 1975). If one type of reaction predominates, then it is also reasonable to assume that H_R is constant throughout the reaction. However, changes in these thermal properties with extent of reaction and temperature can be readily included in our numerical solution.

Dimensionless Equations

Following is a summary of the assumptions which seem appropriate for the curing stage of polymer reaction molding:

1. Homogenous, well-mixed system at $t = 0$.
2. No flow.
3. One-dimensional heat conduction.
4. Negligible molecular diffusion.
5. n^{th} order kinetics.
6. Thermal properties, α, ρ, c_v, and H_R constant.

Thus, Equations (7) and (12) become

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial y^2} + \mathrm{H_R} Ae^{-E_a/RT} C_A^n/\rho c_v \tag{13}$$

$$-\frac{\partial C_A}{\partial t} = Ae^{-E_a/RT} C_A^n \tag{14}$$

Defining dimensionless variables, we get

$$t' = \frac{\alpha}{h^2} t,\ y' = y/h,\ C' = C_A/C_{A_o}$$

Temperature may be made dimensionless by initial temperature $T' = T/T_o$, which is most convenient for the heated wall case or by the adiabatic temperature rise $T^* = (T - T_o)/(T_{ad} - T_o)$. The governing equations become

$$\frac{\partial T'}{\partial t'} = \frac{\partial^2 T'}{\partial y'^2} + \Delta T'_{ad} k' C'^n \exp B(1 - 1/T') \tag{15a}$$

or

$$\frac{\partial T^*}{\partial t'} = \frac{\partial^2 T^*}{\partial y'^2} + k' C'^n \exp B\left(\frac{\Delta T'_{ad} T^*}{\Delta T'_{ad} T^* + 1}\right) \tag{15b}$$

TABLE 2. TYPICAL DATA RANGE FOR UNFILLED THERMOSETS

ρ = 0.9 – 1.4 g/cm³
c_v = 0.3 – 0.5 cal/g°C
α = 0.7 – 1.5 × 10^{-3} cm²/s
H_R = 15-30 kcal/mole
C_{A_o} = 0.01-0.5 mole/l
n = 0.5-2
E_a = 10-25 kcal/mole
$t_{1/2}$ = 10^1-10^4 s

Dimensionless groups

B = 15-40
$\Delta T'_{ad}$ = 0.01-0.75
k' = 10^{-3}-10^{+3} for $n = 1$

$$-\frac{\partial C'}{\partial t'} = k' C'^n \exp B(1 - 1/T') \tag{16a}$$

or

$$-\frac{\partial C'}{\partial t'} = k' C'^n \exp B\left(\frac{\Delta T'_{ad} T^*}{\Delta T'_{ad} T^* + 1}\right) \tag{16b}$$

It is instructive to examine each of the three dimensionless groups. $\Delta T'_{ad}$ is the adiabatic temperature rise

$$\Delta T'_{ad} = \frac{T_{ad} - T_o}{T_o} = \frac{H_R C_{A_o}}{\rho c_v T_o}$$

Since H_R, ρ, and c_v are expected to be approximately constant with T and p, $\Delta T'_{ad}$ is assumed constant. The choice of a chemical system then fixes all quantities but T_o. Note that inert fillers or diluents are often added to thermoset systems. These can be effective in reducing $\Delta T'_{ad}$, since fillers and diluents always reduce C_{A_o} and can increase ρ and c_v.

$B = E_a/RT_o$ is the dimensionless activation energy and is determined by chemical system and initial temperature. k' is a dimensionless reaction rate; $k' = C_{A_o}{}^{n-1} h^2 A e^{-B}/\alpha$. Through A, E_a, and perhaps n, the kinetics can change during the polymerization particularly after the gel point. k' is a ratio of polymerization rate $C_{A_o}{}^{n-1} A e^{-B}$ over heat conduction rate α/h^2. It is the quantity most sensitive to processing conditions, through h^2, through T_o in B, and catalyst concentration in A. Large k', as in thick parts or fast reactions, causes the solution to approach the adiabatic case.

Table 2 gives the range of thermal and kinetic data for some typical thermosetting systems: epoxies, polyesters, polyurethanes, phenolics, and melamines.

The boundary conditions become, in dimensionless form

$$\text{(homogenous initial conditions)} \quad T^*(0, y') = 0 \quad \text{or} \quad T'(0, y') = 1$$

$$C'(0, y') = 1 \tag{17}$$

$$\text{(symmetry about } y' = 0) \quad \frac{\partial T^*}{\partial y'}(t', 0) = \frac{\partial T'}{\partial y'}(t', 0) = 0$$

$$\frac{\partial C'}{\partial y'}(t', 0) = 0$$

For the adiabatic case

$$\frac{\partial T^*}{\partial y'}(t', 1) = 0 \tag{18}$$

For the isothermal wall case

$$T'(t', 1) = T_w' = T_w/T_o \tag{19}$$

For constant wall heat flux

$$\frac{\partial T'}{\partial y'}(t', 1) = q' = \frac{qh}{k_T T_o} \tag{20}$$

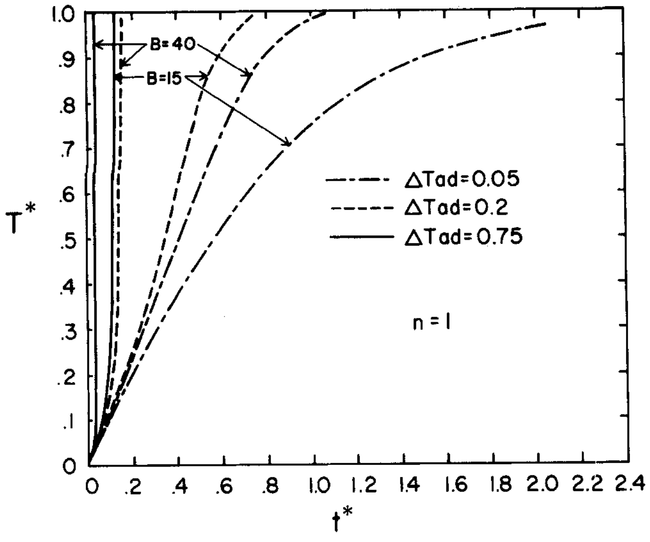

Fig. 4. Adiabatic temperature rise for first order polymerization with a range of generation rates.

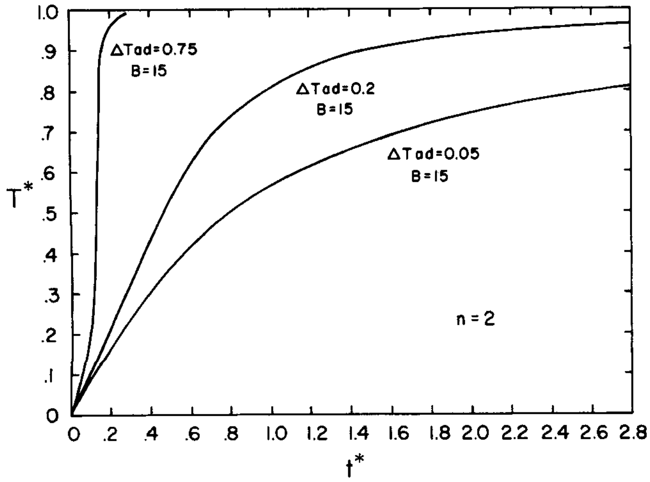

Fig. 5. Adiabatic temperature rise for second order polymerization with a range of generation rates. For $B = 40$ temperature rise is complete at $t' < 0.2$ for all $\Delta T'_{ad} > 0.05$

Stonecypher et al. (1966) have solved the dimensional Equations (13) and (14) numerically for the isothermal wall and the specific considerations of curing propellant motors. We have solved the dimensionless Equations (15) and (16) with the various boundary conditions using a Crank Nicolson implicit method (Carnahan et al., 1969). Best accuracy was obtained by varying the time increments to keep the average concentration change approximately constant; $0.01 < \Delta C'(t', 0) + \Delta C'(t', 1) < 0.03$. Twenty equal increments were used in $0 \leqq y' \leqq 1$. Increasing this gave greater accuracy for T' and C' gradients near the wall (see Figures 8 and 9). This numerical scheme presented no stability problems and gave excellent agreement with the analytical solutions for the adiabatic and isothermal cases. Further details of the solution are available from the authors.

CALCULATED TEMPERATURE PROFILES

Adiabatic

For the adiabatic boundary condition, the conduction term drop from Equation (15). Then, by dividing (16) into (15) and integrating, we obtain

$$C' = -T^* \tag{21}$$

Thus, C' can be eliminated from (15), giving

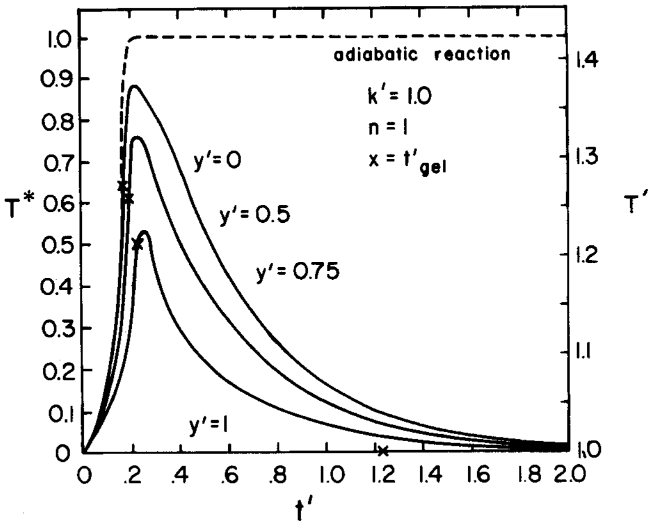

Fig. 6. Temperature rise in a reacting slab at different cross sections as a function of time for the isothermal case. $T_w' = 1$, $k' = 1$, $n = 1$, $\Delta T'_{ad} = 0.423$ and $B = 18.7$, $p_{gel} = 0.707$.

$$\frac{dT^*}{dt'} = k'(-T^*)^n \exp B\left(\frac{\Delta T'_{ad}T^*}{\Delta T'_{ad}T^* + 1}\right) \tag{22}$$

or

$$t^* = \int_0^{T^*} \frac{dT^*}{(-T^*)^n \exp B\left(\dfrac{\Delta T'_{ad}T^*}{\Delta T'_{ad}T^* + 1}\right)} \tag{23}$$

where

$$t^* = k't' = C_{A_0}^{n-1}Ae^{-B}t$$

Douglas and Eagleton (1962) have solved Equation (23) for $n = 0$, 1, and 2. However, the solution involves the exponential integral, a tabulated function; thus it is generally simpler to integrate (23) numerically and present the results graphically. This is done for $n = 1$ in Figure 4 and $n = 2$ in Figure 5 for several values of $\Delta T'_{ad}$ and B.

The adiabatic case is particularly useful, first because it represents the maximum temperature rise possible in a polymer reaction molding. The adiabatic limit is obeyed near the midplane of many actual moldings. Adiabatic data can also be used to generate useful kinetic information. From temperature vs. time curves on adiabatic experiments, $\Delta T'_{ad}$ can be determined directly and the kinetic parameters n, A, and B can be obtained by numerically fitting Equation (22) to the data. Stonecypher et al. (1966) have done this for a methylmethacrylate polymerization using the experimental method of Allen (1969). We are presently carrying out experiments to determine the usefulness of an adiabatic reactor for generating kinetic data on thermosets.

Isothermal Wall

Calculated temperature distributions with conduction through the mold wall are shown in Figures 6 and 7. Properties of a polyurethane network formation at 45°C by a polyester triol and a chain extended 1,6-hexamethylene diisocyanate, HDI, with dibutyltin dilaurate as a catalyst was used for the calculations (Lipshitz, Macosko, and Mussatti, 1975, and Table 2). The dimensionless groups for this system are given in Figure 6 and are typical of many urethane foams and cast elastomers.

We see in Figure 6, as expected, that when heat transfer is included, there is a temperature gradient across the slab. It is significant to note that the center of the slab has nearly an adiabatic temperature rise. Only very close to the mold wall is the exotherm reduced to less than half of the adiabatic rise. This is of course due to the large

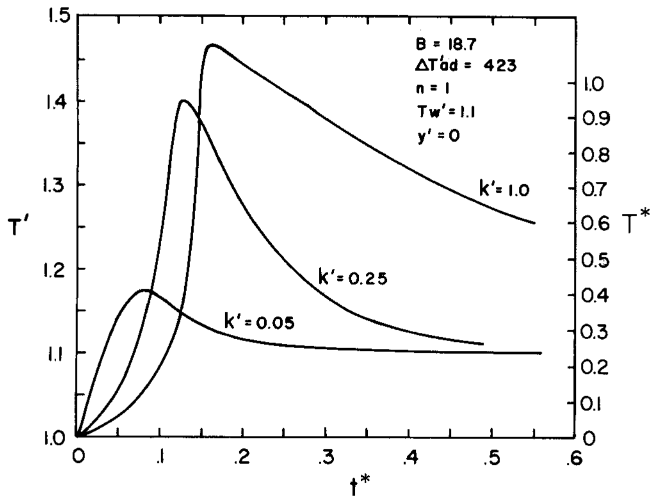

Fig. 7. Temperature rise at center of slab for several k' and isothermal (hotter) walls $T_w' = 1.1$ shows the effect of increasiing sample size on T'

heat of formation of the urethane bond $\Delta T'_{ad}$ and poor conductivity compared to reaction rate k' for nearly all unfilled thermosets.

Figure 7 shows the effect of changing k' on the center line exotherm for the same urethane system. For a given chemical system, k' can be increased essentially by increasing catalyst concentration (increase A) or by increasing part thickness h. We also let $T_w = 1.1\ T_o = 350°K$, which is typical in casting. Most other thermoset processes also use heated molds ($T_w > T_o$). As expected, increasing the rate of reaction or decreasing the heat transfer; that is, increasing k' raises the exotherm. Such temperature changes have been observed experimentally when the size of a casting increases (see Lee and Neville, 1967, Figure 9-5).

CALCULATED PROPERTY CHANGES

With mold temperature as a function of y' and t', we can calculate the extent of reaction at every point and time in the mold. Through relations like those of Equations (1) to (6), molecular and rheological property profiles can readily be calculated. The triol-HDI urethane system used in Figures 6 and 7 is an $A_3 + B_2$ type of network formation and should follow the property relations given in Equations (1) to (6).

Gel Point

As discussed earlier, the most important of these properties is the gel point which in this case is $p_{gel} = 0.707$, Equation (2). By plotting t'_{gel} vs. y', we can visualize how the solidification front moves across the slab. Figure 8 shows these gelation profiles for a range of k' values for the urethane system. The dimensionless group $k't'_{gel} = t^*_{gel} = Ae^{-B}\ t_{gel}$ ($n = 1$) is again used to reduce the scale of the data. For fast reactions or thick parts, thus large k', the center gels much sooner than the surfaces. The isothermal and adiabatic limits bound all the real intermediate solutions. The distance between these two limits is determined by the dimensionless adiabatic temperature rise $\Delta T'_{ad}$. Reduction in the heat generated, for example, by reducing C_{A_o}, brings the limits closer together.

Once the chemical system, catalyst level, and initial temperatures are picked, the only way k' can be changed is through h. This suggests that we can define a critical thickness above which the system is very close to adiabatic. Note from Figure 8 that for $k' = 1$, the center 75% of the slab reaches the gel point essentially as if it were adiabatic. By using $k' = 1$, the critical half thickness for adiabaticlike curing is

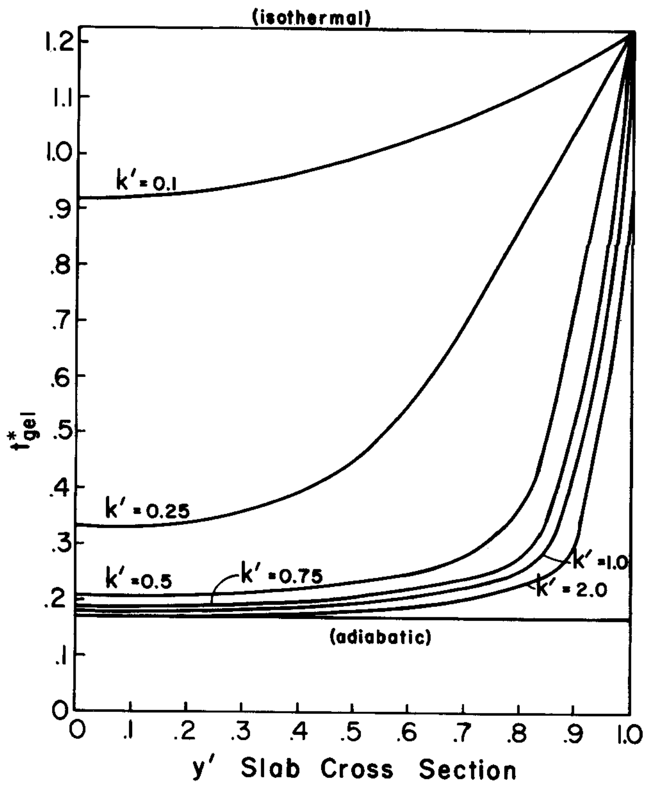

Fig. 8. Time to gel as function of the cross section at various rates of reaction. $T_w' = 1$, $n = 1$, $\Delta T'_{ad} = 0.423$ and $B = 18.7$.

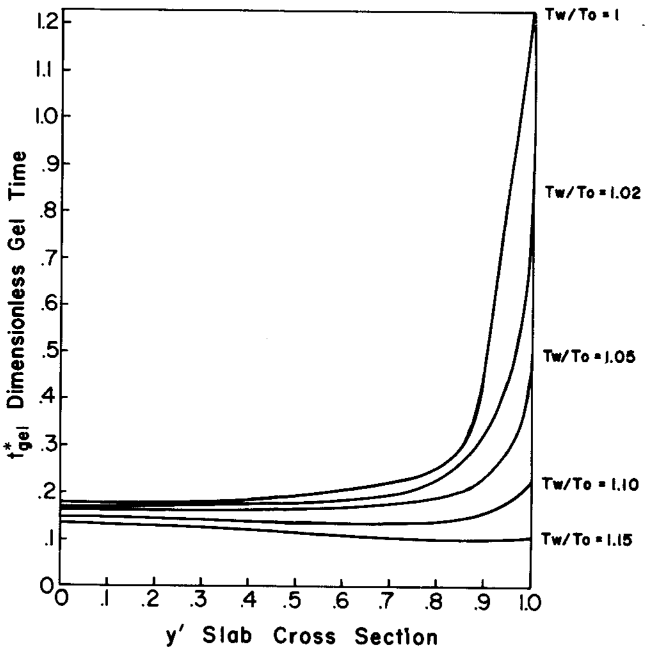

Fig. 9. The effect of heated walls on the time to gel as function of the cross section. $k' = 1$, $n = 1$, $\Delta T'_{ad} = 0.423$ and $B = 18.7$.

$$h_c = \sqrt{\frac{\alpha}{Ae^{-B}}} \tag{24}$$

Reducing $\Delta T'_{ad}$ will raise the lower limit in Figure 8. This will affect slightly the intermediate curves, but the concept of a critical slab thickness will still hold.

Figure 9 shows the effect of heating the mold wall on t^*_{gel}. We see that by heating the walls enough, $T_w/T_o > 1.15$ in our case, it is possible to have the skin material gel before the core. This is a desirable situation, if the total temperature rise does not cause other problems such

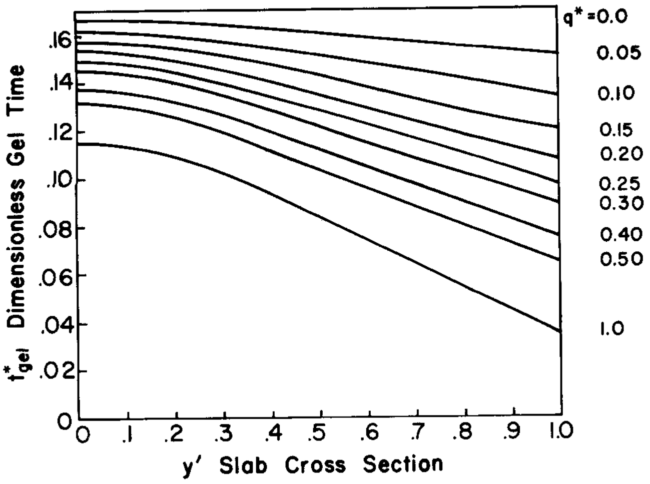

Fig. 10. The time to gel as function of cross section at various wall heat flux $k' = 1$, $\Delta T'_{ad} = 0.423$ and $B = 18.7$.

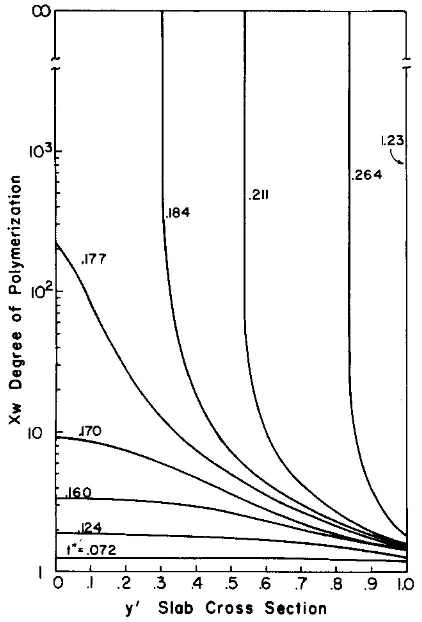

Fig. 11. The weight average degree of polymerization as function of the location and time. $k' = 1$, $T_w' = 1$, $\Delta T'_{ad} = 0.423$ and $B = 18.71$. $X_w = \overline{M}_w/\overline{M}_{w_0}$.

as degradation or volatilization or a reaction so rapid as to interfere with filling. Curing the skin first allows rapid demolding, thus shorter mold cycle times. Finally, properties of the core can often be reached more economically in post curing ovens. For gelling to occur first at the skin, the gel time at T_w must be less than the gel time at the slab center which is usually very close to the adiabatic gel time:

$$t_{\text{gel}}(T_w, \text{isothermal}) < t_{\text{gel}}(y = 0) \simeq t_{\text{gel(adiabatic)}}$$

Figure 10 shows the effect of supplying a constant heat flux at the mold wall q', with $k' = 1$, $T_w(t = 0) = T_o$, and the same urethane system. We see that the skin always gels first, and the wall temperature will rise greater than ΔT_{ad}. Maintaining $q' = 0$ is the only way to have truly an adiabatic reaction throughout the slab. Allen has used feedback control to maintain $q' = 0$ and operate adiabatically. For fast reactions like reaction injection molding, it may not be possible to maintain control of q'.

Other Property Changes: M_w, w_s, G, E_f

Using Equation (1) and p vs. position and time, we can calculate the molecular weight increase in the mold.

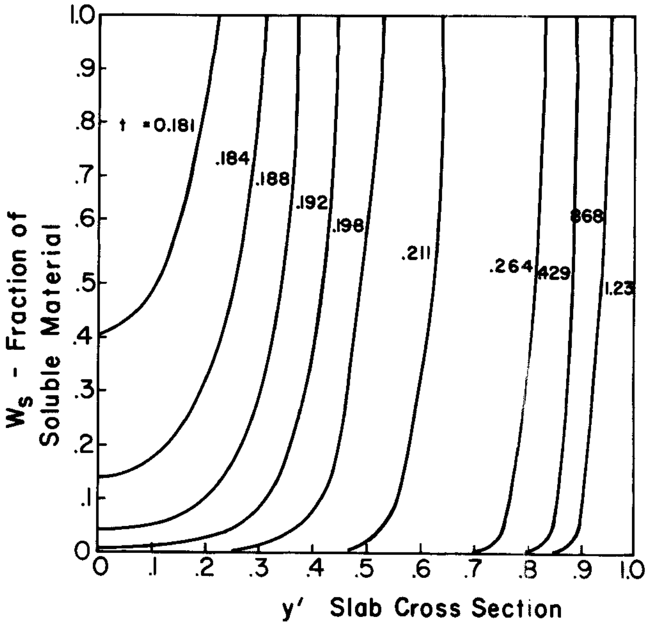

Fig. 12. The fraction of soluble material as function of the location at various times. $k' = 1$, $T_w' = 1$, $\Delta T'_{ad} = 0.423$, and $B = 18.7$.

We define the weight average degree of polymerization

$$X_w = \frac{M_w(p)}{M_w(p = 0)} \tag{25}$$

Figure 11 shows X_w profiles across the slab at various reaction times for $k' = 1.0$, $T_w' = 1$ and the same urethane system. These will be directly related to viscosity rise through Equation (5). The high temperature rise at the core of the slab will cause high rates of reaction which in turn result in a rapid rise of molecular weight followed by gelation.

From Equation (3) and the concentration profiles, we can calculate the fraction of soluble material at any point in the mold. Figure 12 shows some of these calculations. Note that $w_s = 1.0$ gives t'_{gel}. Because of the steep decrease in solubility beyond t'_{gel} (see Figure 2), the typical cure can be described as layered curing. This could have detrimental effects on properties owing to nonuniform shrinkage and locked in stresses.

A cure cycle is usually determined when the surface of the part has reached a certain cure level, for example, clean release from the mold, no marks from the knockout pins, or sufficient flex modulus (for example, no hang-up in the mold, minimum sag in the post cure). Shear modulus can be calculated by using Equation (6) and the T and C_A profiles. G profiles will be be similar to those of the fraction of soluble material.

The modulus of elasticity in flexure E_f is very important in thin wall products. For material with modulus as a function of position (but with a constant Poisson ratio), the flexural modulus is defined as

$$E_f = \frac{\int_0^h E(y)y^2dy}{\int_0^h y^2dy} \tag{26}$$

where E is the tensile modulus. In rubberlike materials, $E = 3G$. Figure 13 shows the buildup of the flexural modulus in three cross-linked elastomer systems. Curve A indicates a compact network resulting from the reaction of low molecular weight monomer. Curve B describes the system that has been used in the calculations throughout

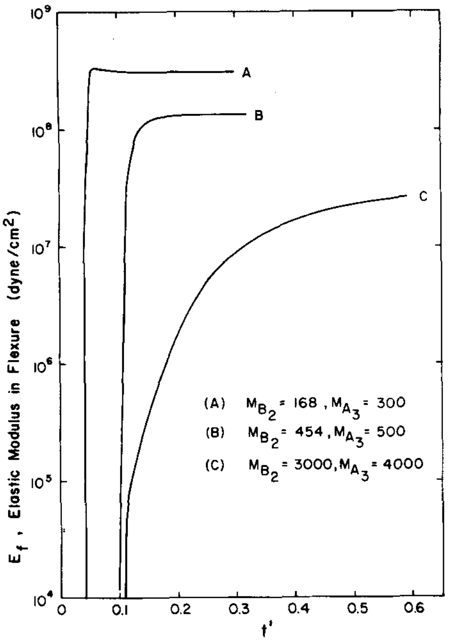

Fig. 13. The buildup of flexural modulus with reaction time for three urethane systems. $T_w/T_o = 1.15$, $B = 18.7$, $k' = 1.0$, $n = 1$, $\Delta T'_{ad} = 0.935$(A); 0.423 (B); 0.061 (C).

this paper, and curve C indicates a commercial system with higher molecular weight prepolymers. We have assumed the same kinetics and physical properties. Decreasing the molecular weight of the monomers leads to an increase in the concentration of the functional groups, thus increasing $\Delta T'_{ad}$. This increase causes a higher rate of reaction for the curve A mixture. In Figure 13 $T_w' = 1.15$; thus, we accelerate the reaction near the wall which increases the flexural modulus. With $T_w' = 1.0$, the E_f rise would be much slower than shown, since by Equation (26) the modulus of the skin material dominates flexure modulus. Barth and Robertson (1970) have reported similar shape flexure modulus vs. cure time curves for a thermosetting polybutadiene system.

By using the relations for hardness of an ideally elastic material derived by Timoshenko (1934), it is possible to predict the change in, for example, Shore hardness (ASTM D-1415), of the part surface with cure time. The resulting curves are qualitatively similar to Figure 13.

ACKNOWLEDGMENT

This work was partially supported by the Union Carbide Corporation and National Science Foundation Grant DMR75-04508.

NOTATION

A = frequency coefficient of reaction rate
A_3 = monomer with 3 A functional groups
a = exponent in viscosity relation, Equation (5)
$B = E_a/RT_o$ = dimensionless activation energy
B_2 = monomer with 2 B functional groups
$C' = C_A/C_{A_o}$ = dimensionless concentration
C_A, C_{A_o} = concentration of A functional groups
c_v = heat capacity
$\mathfrak{D}$ = average diffusion coefficient of molecules in polymerizing mixture
E_a = reaction rate activation energy
E = tensile modulus
E_f = modulus of elasticity in flexure
G = equilibrium shear modulus
H_R = heat of reaction
h = half slab thickness
$h_c = \sqrt{\dfrac{\alpha}{Ae^{-B}}}$ = critical thickness for adiabaticlike behavior
K = viscosity coefficient, Equation (5)
k = polymerization rate constant
$k' = C_{A_o}{}^{n-1}h^2Ae^{-B}/\alpha$
k_b = Boltzmann's constant
k_T = thermal conductivity
$\overline{M}_w$ = weight average molecular weight
M_{A_3}, M_{B_2} = molecular weight of monomers
n = order of reaction
$P(X_3)$ = fraction of A_3 molecules acting as cross-links
$p = \dfrac{C_{A_o} - C_A}{C_{A_o}}$ = extent of reaction
p_{gel} = extent of reaction at gel point
q' = dimensionless wall heat flux, Equation (20)
R = gas constant
R_A = rate of polymerization
r = average radius of monomers
T = temperature
T_o = initial polymer temperature
T_w = mold wall temperature
$T' = T/T_o$ = dimensionless temperature based on initial temperature
$T^* = \dfrac{T - T_o}{T_{ad} - T_o}$ = dimensionless temperature based on ΔT_{ad}
$\Delta T'_{ad} = \dfrac{T_{ad} - T_o}{T_o} = H_R C_{A_o}/\rho c_v T_o$ = dimensionless adiabatic temperature rise
t = reaction time
$t^{1/2}$ = time to $p = 0.5$
t_{gel} = gel time
$t' = \alpha_o t/h^2$ = dimensionless time based on conduction
$t^* = k't' = C_{A_o}{}^{n-1}Ae^{-B}t$ = dimensionless time based on polymerization rate
w_{A_3}, w_{B_2} = weight fraction monomer, Equation (4)
w_s = weight fraction solubles
X_w = weight average degree of polymerization
y = position coordinate perpendicular to mold walls
$y' = y/h$ = dimensionless position
α = thermal diffusivity = $k_T/\rho c_v$
η = viscosity
ρ = density

LITERATURE CITED

Allen, E. L., "Adiabatic Calorimeter for the Study of Exothermic Chemical Reactions," *Ind. Eng. Chem. Fundamentals*, 8, 828 (1969).

Barth, H. L., and J. J. Robertson, "Fast-Curing Polybutadiene Thermosetting Resins," *Modern Plast.*, 47, No. 11, 142 (1970).

Beck, R. H., Jr., and A. Golovoy, "Prescription for Injection Molding of Thermosets," *SPE J.*, 28, No. 9, 52 (1972).

Bird, R. B., W. E. Stewart, and E. L. Lightfoot, *Transport Phenomena*, pp. 248 and 514, Wiley, New York (1960).

Blow, C. W., ed., *Rubber Technology and Manufacture*, Butterworth, London, England (1971).

Brandrup, J., and E. H. Immergut, *Polymer Handbook*, pp. V7-12, Wiley, New York (1975).

Broyer, E., C. Gutfinger, and Z. Tadmor, "A Theoretical Model for the Cavity Filling Process in Injection Molding," *Trans. Soc. Rheol.*, 19, 423 (1975).

Brydson, J. A., *Plastic Materials*, Chapt. 22, Iliffe, London, England (1969).

Carnahan, B., H. A. Luther, and J. D. Wilkes, *Applied Numerical Methods*, pg. 451, Wiley, New York (1969).

Crank, J., and G. S. Park, ed., *Diffusion in Polymers*, pp. 85-100, Academic Press, London, England (1968).

DelGatto, J. V. "Boom in Castable Polyurethane," *Rubber World*, **169**, 43 (Dec., 1973).

Douglas, J. M., and L. C. Eagleton, "Analytical Solutions for Some Adiabatic Reactor Problems," *Ind. Eng. Chem. Fundamentals*, **1**, 116 (1962).

Doyle, E. N., *The Development and Use of Polyester Products*, pp. 297-299, McGraw-Hill, New York (1969).

Engelmaier, W., and M. B. Roller, "Temperature-Viscosity-Time Profiles Provide Some Understanding of MLB Lamination," *Insulation/Circuits*, **21**, No. 4, 43 (1975).

French, D. M., R. A. H. Strecker, and A. S. Tompa, "The Maximum Extent of Reaction in Gelled Systems," *J. Appl. Polymer Sci.*, **14**, 599 (1970).

Gordon, M., T. C. Ward, and R. S. Whitney, *Polymer Networks*, A. G. Chompf and S. Newman, ed., pg. 1, Plenum, New York (1971).

Hills, D. A., *Heat Transfer and Vulcanization of Rubber*, Chapt. 5, Elsevier, London, England (1971).

Horn, M. B., *Acrylic Resins*, pp. 38-40, Reinhold, New York (1960).

Kamal, M. R., S. Sorour, and M. Ryan, "Integrated Thermo-Rheological Analysis of the Cure of Thermosets," *SPE Tech. Papers*, **19**, 187 (1973).

Kamal, M. R., "Thermoset Characterization for Moldability Analysis," *Polymer Eng. Sci.*, **14**, 231 (1974).

Lee, H., and K. Neville, *Handbook of Epoxy Resins*, pp. 77-79, McGraw-Hill, New York (1967).

Lipshitz, S. D., and C. W. Macosko, "Tube Flow of Thermosets," paper 93f, AIChE Annual Meeting, Los Angeles, November 1975.

———, and F. G. Mussatti, "Kinetic and Viscosity Relations for Urethane Network Polymerization," *S.P.E. Tech. Papers*, **21**, 239 (1975).

Lubin, G., ed., *Handbook of Fiberglass and Advanced Plastics Composites*, Chapt. 14. Van Nostrand Reinhold, New York (1969).

Macosko, C. W., and D. R. Miller, "A New Derivation of Average Molecular Weights of Nonlinear Polymers," *Macromolecules*, **9**, 000 (1976*a*).

Miller, D. R., and C. W. Macosko, "A New Derivation of Post Gel Properties of Network Polymers," *ibid.*, 000 (1976*b*).

Mussatti, F. G., "Rheology of Network Forming Systems," Ph.D. thesis, Univ. Minn., Minneapolis (1975).

Norfleet, J. S., and C. C. Boone, "MAD Approach to Optimum Thermoset Injection Molding," *Mod. Plast.*, **51**, No. 7, 62 (1974).

Prepelka, D. J., and J. L. Wharton, "Reaction Injection Molding in the Automotive Industry," *J. Cell. Plast.*, **11**, 87 (1975).

Prime, R. B., "Differential Scanning Calorimetry of the Epoxy Cure Reaction," *Polymer Eng. Sci.*, **13**, 365 (1973).

Roller, M. B., "Characterization of the Time-Temperature-Viscosity Behavior of Curing B-Staged Epoxy Resin," *ibid.*, **15**, 406 (1975).

Stonecypher, T. E., E. L. Allen, D. E. Mastin, and D. A. Willoughby, "Special Problems in Curing Highly Exothermic Propellants," *Chem. Eng. Progr. Symposium Series*, **62**, 7 (1966).

Timeshenko, S., *Theory of Elasticity*, pg. 343, McGraw-Hill, New York (1934).

Valles, E. M., and C. W. Macosko, "Some Structure-Property Measurements on a Hydrosilation Network Polymerization," *Coatings and Plastics Preprints*, **35**, 44 (1975).

Van Krevelan, D. W., *Properties of Polymers*, Chapt. 5A and 14, Elsevier, Amsterdam (1972).

Vilesova, M. S., N. P. Spasskova, L. V. Lesnevskaya, G. N. Guseva, L. G. Izrailev, and V. M. Zolotarev, "Kinetic Study of the Formation of Polyurethane Elastomers in the Solid State by the Multiple Internal Reflection Method," *Polymer Sci. U.S.S.R.*, **14**, 1883 (1972).

Wood, A. S., "RIM New High-Speed Processing Option," *Mod. Plast.*, **51**, No. 6, 54 (1974).

Manuscript received August 12, 1975; revision received November 10 and accepted November 13, 1975.

Adsorption and Desorption of Particles and Their Chromatographic Separation

ELI RUCKENSTEIN

Faculty of Engineering and Applied Science
State University of New York at Buffalo
Buffalo, New York 14214

and

DENNIS C. PRIEVE

Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Rates of adsorption/desorption are calculated by considering Born, double-layer, and van der Waals forces. Conditions exist where rates are highly sensitive to particle size, shape, and chemical constitution because diffusion over a potential barrier controls. On this basis, a new separation technique, called potential-barrier chromatography, is suggested.

SCOPE

Removal of suspended solids from a liquid may be required, either to recover valuable products or to remove obnoxious particulates. Clarification of dilute aqueous suspensions is frequently performed in deep-bed granular filters, where the grains provide a surface on which the particles may adsorb. If two types of particles differ in their adsorption rate, separation of them may be accomplished by selectively adsorbing one species on the grains. Furthermore, reversibility of adsorption would allow chromatographic separation of particle mixtures, analogous to gas chromatography.

Physical adsorption arises from physical interactions between the suspended particles and the collector, such as van der Waals attraction, double-layer repulsion, and Born repulsion. The total interaction energy, as a function of the particle-collector gap width, displays either one minimum and no maximum or two minima and one maximum. Several mechanisms for chromatographic sep-