

Estimation of Viscosity Functions for Thermosets from Spiral Mold Filling

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ABSTRACT: It is typically difficult to measure viscosity of a fast polymerizing molding compound using a rheometer. So, spiral mold filling experimental data were used to obtain viscosity functions of a silica filled epoxy–novolac molding compound. The functions could describe the effect of temperature and conversion on viscosity change during cure. With the flow rate data obtained from the mold filling experiments, parameters of the viscosity functions were determined through regression of a simulation model developed in this study. The reaction kinetic equation considering an autocatalytic reaction mechanism was used for the molding compound in the simulation model. The viscosity function of the molding compound determined from the rheometer data and the reaction kinetic data measured at a relatively slow reacting condition was compared with simulation results. The viscosity function determined through nonlinear regression of the spiral mold filling simulation model showed a good correlation with the viscosity function obtained from the rheometric study. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 873–884, 2001

Key words: spiral mold filling; viscosity function; thermoset; simulation model; chemorheology

INTRODUCTION

The most common method of large-scale encapsulation of electronic devices is transfer molding of a thermoset polymer such as epoxy resin.^{1–4} The transfer molding is a sort of compression molding in which the resin is first melted in a heated cylinder or pot, and then transferred to a mold cavity and compressed into the desired shape. The encapsulation of microelectronic devices is very important step to obtain a good electronic device. The devices need to be filled well with the resin during encapsulation process to protect the sensitive electronic components from mechanical

damage and from the environment. In order to prevent wire sweep during filling, viscosity of the polymer has to be small enough at inlet. A nice review concerning the encapsulation process was published by Manzione.⁵ The transfer molding process for encapsulation of integrated circuits is described well by Blyer et al.⁶

It is important to understand precisely the flow behavior of a thermoset polymer inside a mold cavity during filling process not only to optimize process parameters such as flow rate, molding pressure, mold wall temperature, and inlet temperature of a reacting mixture, but also to predict the conditions which incomplete filling occur.

The spiral flow mold (ASTM D-3123) has been used as a long mold to test moldability. Moldability of a molding compound is measured by injecting the resin into the mold and observing how far it flows under constant molding pressure before

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gelling. The flow length can be measured by installing an apparatus to follow the displacement of the ram pushing the resin directly.

Despite the fact that the spiral flow test is a required test used in the electronic device encapsulation industry,⁷ practical moldability problems can not be easily related to the spiral flow test results.⁸ Typical molding problems encountered during the integrated circuit encapsulation molding process are as follows⁶: (1) incomplete mold filling caused by the premature gelation, (2) lead frame displacement during filling, and (3) movement of the fine wires electrically connecting the individual integrated circuit (IC) to the lead frame. All the three molding problems are directly related to the processing conditions and chemorheological characteristics of the molding compounds used for encapsulation. The flow behavior of a thermoset resin during mold filling is complicated because viscosity of the resin is affected continually by the chemical reaction and heat transfer. So, in order to obtain the practical moldability data for thermoset polymers, a chemorheological study has to be carried out.

Hale et al.⁹ simulated the spiral mold filling process of the epoxy–cresol–novolac molding compound using a two-dimensional model. They carried out filling experiments that included changing the composition of the molding compound (add or reduce accelerator, with or without filler).

Viscosity functions of thermosets have been obtained typically from the viscosity data measured by rheometers and the cure kinetics data obtained using infrared (IR) or differential scanning calorimetry (DSC).^{10–13} However, in case of a fast polymerizing system, viscosity cannot be measured by a rheometer.

A spiral mold filling model like that developed by Hale et al.⁹ can predict accurately the final flow length from the gate after filling is stopped by gelation. The flow rate with filling time or flow front position can be also estimated using the model. On the other hand, a set of good flow rate data with flow front positions measured from the displacement of ram under constant molding pressure can be used to estimate viscosity of a reacting thermoset polymer system. So, a viscosity equation as a function of temperature, conversion and shear rate (if the viscosity of the polymer depends on shear rate) can be obtained by nonlinear regression of the spiral mold filling model. Using this kind of idea and the relationship between pressure rise at the mold entrance and viscosity increase due to conversion increase dur-

Table I Properties of the Silica Filled Epoxy–Novolac Molding Compound

Property	Value
Gel time	45 s at 175°C
Density	1.82 g/cm ³ at 25°C
Thermal conductivity	0.0067 J/cm/s/K
Specific heat	1.197 J/g/K
Spiral flow length (ASTM D-3123)	86 cm
Thermal diffusivity	0.00308 cm ² /s

ing a rectangular mold filling under constant flow rate, Kim et al.¹⁴ estimated a viscosity function for a fast polymerizing thermoset polyurethane (PU) system.

The reaction kinetics and chemorheological data are essential to simulate a mold filling process since the flow inside a mold cavity is significantly affected by the viscosity change of a reacting thermoset polymer resulted from conversion increase and temperature change due to heat transfer from the wall and the reaction exotherm.

The objective of this study is to estimate a viscosity function of a thermoset epoxy–novolac molding compound through nonlinear regression of a spiral mold filling model using a set of flow rate vs flow length data obtained during mold filling under constant mold pressure. The effect of process parameters such as molding pressure, the initial mixture temperature, and mold wall temperature on fitting the experimental flow rate data is also analyzed.

EXPERIMENTAL

All of the experimental data reported here have been taken from the study by Garcia.¹⁵

Materials

Garcia¹⁵ used a silica filled epoxy–novolac molding compound, and some information about the molding compound are summarized in Table I.

Spiral Mold Filling Experiments

A spiral flow mold satisfying the ASTM D-3123 specifications was modified in order to carry out the mold filling experiments. The modification consisted in a circular cross section for a mold

cavity instead of the ASTM semicircular cross section. The diameter of the mold cavity was 0.3125 cm and its length was 254 cm. The mold was placed in a Fujiwa Seiki Co. TEP 12-16 12-ton transfer press, clamped in place, and allowed to equilibrate at a required temperature for about 10 min. The molding compound was pressed into cylindrical preforms, which were electrically preheated for 30 s to an average temperature of 92°C, and then placed inside the transfer pot. The compound was then forced into the mold cavity using a predetermined pressure in the ram. The position of the ram as a function of time was recorded during the resin transfer. Mold wall temperature ranged from 140 to 180°C. More details on the mold filling experiments are given by Garcia.¹⁵

RESULTS AND DISCUSSION

Mathematical Model

In order to model the spiral mold filling process, the momentum, energy, and species balance equations are needed. The three balance equations have to be solved simultaneously to simulate the thermal and physical changes within the mold. The spiral mold flow can be approximated as a long straight cylindrical tube. The model used here is the same as that used by Hale et al.⁹ and by Garcia.¹⁵

The momentum balance in a cylindrical tube can be simplified using lubrication and quasi-static approximation, which has been commonly used in mold filling modeling.^{16–18} The velocity field in the flow front region, where the fountain flow effect occurs, is described with the approximated solution of Bhattacharji and Savic¹⁹ as in Castro and Macosko.¹⁷ Explicit expressions for the velocity field and the pressure drop are obtained. The following assumptions have been used to simplify the mold filling process:

- constant thermal and physical properties,
- unidirectional laminar flow in the main flow,
- unidirectional heat flow,
- inertia terms neglected, and
- gravity force neglected.

An additional assumption for the spiral mold flow modeling is

- constant mold inlet pressure.

The flow field is divided into two subdomains, main flow and front flow region. With assumptions described above, the momentum balance in the main flow region can be expressed as follows:

$$\frac{\partial P}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \eta \frac{\partial v_z}{\partial r} \right) \quad (1)$$

$$\frac{\partial P}{\partial r} = 0 \quad (2)$$

where z corresponds to the flow direction and r the radial direction, and P is pressure, η is the viscosity of the compound, and v_z is the axial velocity in the z direction.

Integration of Eq. (1) in the radial direction with an assumption of symmetry at the axis gives the following equation on shear rate (γ).

$$\frac{\partial v_z}{\partial r} = \frac{r}{2\eta} \frac{\partial P}{\partial z} = -\gamma \quad (3)$$

Since the viscosity is a function of conversion (α), temperature (T), and shear rate as follows, viscosity can be expressed as $\eta = \eta_o(\alpha, T) \gamma^{n-1}$. So shear rate is

$$\gamma = \left(-\frac{r}{2\eta_o} \frac{\partial P}{\partial z} \right)^{1/n} \quad (4)$$

Integrating Eq. (3) in the radial direction with no slip condition at the wall gives

$$v_z = \frac{\partial P}{\partial z} \frac{1}{2} \int_r^R \frac{r'}{\eta} dr' \quad (5)$$

where R is the radius of the cylindrical mold cavity.

The overall mass balance on the volumetric flow rate (Q) can be expressed as follows:

$$Q = \pi R^2 \langle v_z \rangle = 2\pi \int_0^R r v_z dr = -\frac{\pi}{2} \frac{\partial P}{\partial z} \int_0^R \frac{r^3}{\eta} dr \quad (6)$$

where $\langle v_z \rangle$ is the gapwise average velocity. Integrating Eq.(6) in the axial direction from the gate ($z = 0$) to the flow front position (z_f)

$$\Delta P(z_f) = \frac{2Q}{\pi} \int_0^{z_f} dz / \left(\int_0^R \frac{r^3}{\eta} dr \right) \quad (7)$$

Since the mold inlet pressure (P_{inlet}) is assumed to be constant, the flow rate can be calculated from the above equation:

$$Q(z_f) = \frac{\pi P_{\text{inlet}}}{2} \frac{1}{\int_0^{z_f} dz \left/ \left(\int_0^R \frac{r^3}{\eta} dr \right)} \quad (8)$$

In the front flow region, the velocity field is described with the solution obtained by Bhattacharji and Savic.¹⁹ In a frame with the origin fixed at the inlet and forcing the velocity profile at the beginning of the front flow region to coincide with the profile at the end of the main flow region (v_{zm}), the solution is as follows:

$$v_z = (v_{zm} - \langle v_z \rangle) \frac{(1 - \exp(-\sqrt{6}((z_f - z)/R)))}{(1 - \exp(-\sqrt{6}(z_o/R)))} + \langle v_z \rangle \quad (9)$$

$$v_r = \sqrt{6(\langle v_z \rangle / 2R)} \left(\frac{2}{r \langle v_z \rangle} \int_0^r r v_{zm} dr' - r \right) \times \frac{(\exp(-\sqrt{6}((z_f - z)/R)))}{(1 - \exp(-\sqrt{6}(z_o/R)))} \quad (10)$$

where v_r is the axial velocity in r direction and z_o is the size of the front flow region (order of R).

The viscosity temperature and conversion dependence couple above equation with the energy and species balances. With assumptions described above, these balance equations are expressed as follows:

$$\rho C_p \left(\frac{dT}{dt} + v_z \frac{dT}{dz} + v_r \frac{dT}{dr} \right) = k \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \Delta H_{rxn} \frac{d\alpha}{dt} \quad (11)$$

$$\frac{d\alpha}{dt} + v_z \frac{d\alpha}{dz} + v_r \frac{d\alpha}{dr} = \frac{1}{C_o} \frac{d\alpha}{dt} \quad (12)$$

where ρ is density of the compound, C_p is heat capacity, k is thermal conductivity, ΔH_{rxn} is the heat of reaction of the compound, and C_o is the initial concentration of epoxides in the compound. Initial and boundary conditions for these balance equations are (1) symmetry at center of the mold in radial direction, (2) $T = T_o$, and $\alpha = \alpha_o$ at the

entrance, (3) a convective boundary condition at the wall.

Reaction Kinetics

In order to model the filling process of a mold with a reactive polymer, a reaction kinetic equation expressed in terms of temperature and conversion is necessary. Differential scanning calorimetry (DSC), which calculates the chemical conversion by measuring heat evolution caused by the exothermic polymerization, has been the most popular techniques in analyzing the reaction kinetics of thermoset polymer systems.

To analyze reaction kinetics of an amine cured difunctional epoxide reaction, Sourour and Kamal²⁰ introduced an autocatalytic reaction mechanism. The autocatalytic reaction mechanism was caused by the hydroxyl groups produced by the reaction between amine hydrogens and epoxides. They reported that the hydroxyl group only helped epoxide ring opening by forming hydrogen bonding as like a catalyst. However, the reaction is accelerated also in the case that the hydroxyl group reacts with epoxides. The reaction kinetics of bifunctional and multifunctional epoxy systems has been analyzed successfully by many workers²¹⁻²⁴ using the following reaction kinetic equation describing an autocatalytic reaction mechanism:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^p \quad (13)$$

where α is the conversion of epoxide groups, k_1 and k_2 are reaction rate constants that follow an Arrhenius temperature dependence, and $m + p$ represents the overall reaction order. The reaction rate constant k_1 is for the primary reaction, which is assumed to involve catalytic ring opening by the curing agents, and k_2 is for the secondary reaction, which is assumed to involve an autocatalytic ring opening. For typical epoxy systems, $m + p$ is known to be about 2.²⁵

Using a Perkin-Elmer DSC-7, the reaction kinetics of the epoxy–novolac molding compound was studied by Garcia.¹⁵ Isothermal and dynamic DSC techniques were used. Isothermal runs were carried out at 130–180°C. The kinetic parameter were determined by fitting the isothermal DSC run data, and the kinetic equation could describe well the dynamic DSC run data. The reaction kinetic parameters are summarized in Table II.

Table II Parameters of the Kinetic Equation [Eq. (13)]¹⁵

Parameter	k_1 (1/s)	k_2 (1/s)	m	n
Value	$\exp(12.582-8063/T[\text{K}])$	$\exp(17.760-8823/T[\text{K}])$	1.748	2.252

The exothermic heat of reaction (ΔH_{rxn}) of the molding compound was 53.33 J/g.

Chemorheology

The viscosity change of a thermoset during reactive processing affects the processability of the polymer in many processing applications such as RIM (reaction injection molding), RTM (resin transfer molding), SRIM (structural reaction injection molding), compression molding, pultrusion, etc. In the case of the molding processes, the viscosity of a reacting mixture needs to be low enough to avoid incomplete filling. So, it is important to understand exactly the chemorheology of a thermoset during polymer processing to optimize process parameters such as filling time, flow rate, initial and wall temperature, etc.

In order to model a reactive polymer process, a viscosity function can express the relationship between viscosity change and process condition (temperature and shear rate) as well as the degree of polymerization (conversion).

Garcia¹⁵ measured the viscosity of the epoxy-novolac molding compound system as a function of time and temperature. Using the reaction kinetic equation [Eq. (13)], the viscosity vs conversion data could be estimated from the measured viscosity vs. time data because the thermal history was also known.

The following empirical Castro-Macosko viscosity equation containing the Vogel relation for temperature dependence was employed by Garcia¹⁵ to analyze the viscosity change of the epoxy-novolac molding compound during polymerization.

$$\eta = \eta_o(T) \left(\frac{\alpha_{\text{gel}}}{\alpha_{\text{gel}} - \alpha} \right) a + b\alpha \quad (14)$$

$$\eta_o(T) = A_\eta \exp\left(\frac{1}{(c + d(T - T_g))} \right) \quad (15)$$

where A_η is a preexponential factor, α_{gel} is the gel point, T_g is the glass transition temperature, and a , b , c , and d are constants supposed to be deter-

mined experimentally. The Castro-Macosko equation containing the Arrhenius temperature dependence on viscosity also could be used to analyze the viscosity vs conversion data²⁶:

$$\eta_o(T) = A_\eta \exp(E_\eta/RT) \quad (16)$$

where E_η is the activation energy for the viscosity dependence on temperature and R is the ideal gas constant (8.314 J/mol/K). However, the Vogel relation, which accounts the glass transition effect on viscosity, was employed since it is known that it is more appropriate for $T - T_g < 100$.²⁷

The relation between T_g and conversion for the compound was experimentally determined to follow the following simple relation²⁸:

$$T_g = \frac{322.58}{(1 - 0.212\alpha)} \quad (17)$$

Best fitting parameters of the viscosity function [Eq. (14) with Eq. (15)] were determined from the rheometer data and the reaction kinetic data obtained at a relatively slow reacting condition through multivariable nonlinear regression. Table III summarizes the parameters of the viscosity function considering temperature and conversion effects. The viscosity function was compared with viscosity functions estimated from the spiral mold filling experiments. The gel point (0.285) was determined by the gel time data and the kinetic equation.

Estimation of Viscosity Functions from the Spiral Mold Filling Data

The pressure rise at the mold inlet at constant flow rate and the flow rate change at constant inlet pressure during mold filling are related to the viscosity change of a molding compound. Therefore, the viscosity change of a molding compound can be estimated by a mold filling model using pressure rise data and flow rate data measured at the mold entrance, respectively. In the previous study,¹⁴ the viscosity function parameters of two PU systems were determined through

Table III Parameters of the Viscosity Function Obtained from the Flow Rate Data and from the Rheometer Data Respectively

	A_η (poise)	E_η (J/mol)	α_{gel}	a	b	c	d (1/K)
1	0.4568	—	0.285	4.65	-13.1	7.94×10^{-2}	3.88×10^{-4}
2	0.4482	—	0.285	4.36	-9.71	7.97×10^{-2}	3.79×10^{-4}
3	645.23	6573	0.285	3.26	-7.85	—	—

^a 1: Castro–Macosko viscosity function with Vogel equation from the rheometer data.¹⁵ 2: Castro–Macosko viscosity function with Vogel equation from the flow rate data. 3: Castro–Macosko viscosity function with Arrhenius equation from the flow rate data.

regression of a rectangular mold filling model using the pressure rise data.

The grid size used in the computation scheme using the finite difference method (FDM) was one mold radius (R). The front flow length was equivalent to one mold radius and subdivided into three grid spacings for the numerical calculation. A first-order Taylor series expansion of Eq. (8) in terms of the viscosity function parameters was used for the regression procedure:

$$\frac{\partial Q(z_f)}{\partial C_k} = \frac{\pi P_{\text{inlet}}}{2} \frac{-1}{\left\{ \int_0^{z_f} dz / \left(\int_0^R \frac{r^3}{\eta} dr \right)^2 \right\}} \times \int_0^{z_f} \frac{\int_0^R (r^3 \partial \eta) / (\eta^2 \partial C_k) dr}{\left\{ \int_0^{z_f} dz / \left(\int_0^R \frac{r^3}{\eta} dr \right)^2 \right\}} dz \quad (18)$$

where C_k indicates the parameters (A_η , E_η , α_{gel} , a , and b for the Arrhenius temperature dependence; and A_η , c , d , α_{gel} , a , and b for the Vogel relation) of the Castro–Macosko viscosity function. In order to fit the experimental flow rate data, the Marquardt algorithm,²⁹ which combines the gradient search technique with the linearization of the flow rate equation, was used.

It is expected that the exponent in Eq. (14) will increase with conversion (molecular weight). For a linear polymer the exponent goes from 1 to 3.4. So ($a + b\alpha$) in Eq. (14) has to increase with conversion. The conditions to satisfy this criterion can be obtained from Eq. (14):

$$b \leq \frac{3.4 - a}{\alpha_{\text{gel}}}, a + 2b\alpha_{\text{gel}} - b\alpha \geq 0 \quad (19)$$

These conditions for a and b were used in regression.

In order to obtain reasonable fitting parameters, parameter values of the viscosity function obtained from the rheometric study were referred and minimum and maximum value criteria were given for each parameter: 1.0×10^{-7} – 1.0×10^3 (Pa s) for A_η , 1.0×10^3 – 5.0×10^4 (J/mol) for E_η , 1.0×10^{-1} – 1.0×10^{-4} for c , 1.0×10^{-3} – 1.0×10^{-6} for d , and a and b according to Eq. (19).

The process conditions and final flow length data for the spiral flow molding experiments are summarized in Table IV. The parameter values of viscosity functions that best fit the flow rate data were determined for each set. The parameter values of the viscosity function determined by this way were changed just a little according to the data measured at different process conditions. So a viscosity function that can best fit several sets of flow rate data at the same time was determined by regression of the mold filling model. The best fitting parameter values of the viscosity function is summarized in Table III together with those from the rheometric study. The parameter α_{gel} (0.285) was fixed in regression because it was determined from the reaction kinetics and gel time data.

Figure 1 shows three sets of flow length vs filling time data (Exp. 1–3) obtained at T_o .

Table IV Process Conditions of the Spiral Mold Filling Experiments

Experiment	T_o (°C)	T_w (°C)	P_{inlet}	L (cm)
1	103	150	276	52
2	103	150	552	93
3	103	150	829	120
4	101	140	552	85
5	101	140	829	115

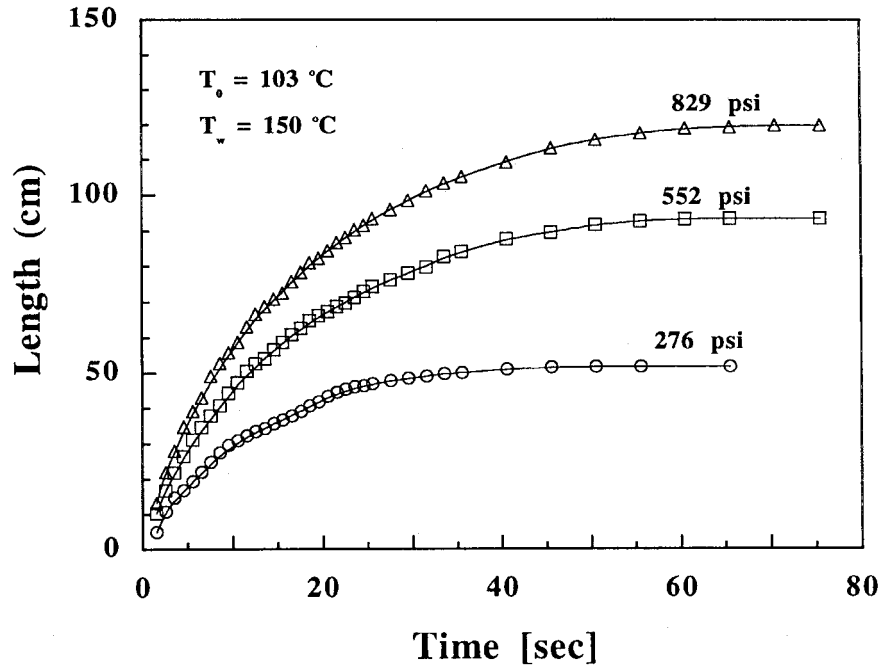


Figure 1 Flow front position as a function of filling time for Exp.1-3.

= 103°C and $T_w = 150^\circ\text{C}$ for three different inlet pressures of 276, 552, and 829 psi. Figure 2 also shows two sets of flow length vs filling time data (Exp. 4-5) obtained at $T_o = 101^\circ\text{C}$ and $T_w = 140^\circ\text{C}$ for two different inlet pressures of 552 and 829 psi.

The final flow length increased almost linearly as the inlet pressure was increased. The flow was stopped in a few minutes due to gelation.

The flow rate vs flow front position data can be obtained from the slope of the length vs time

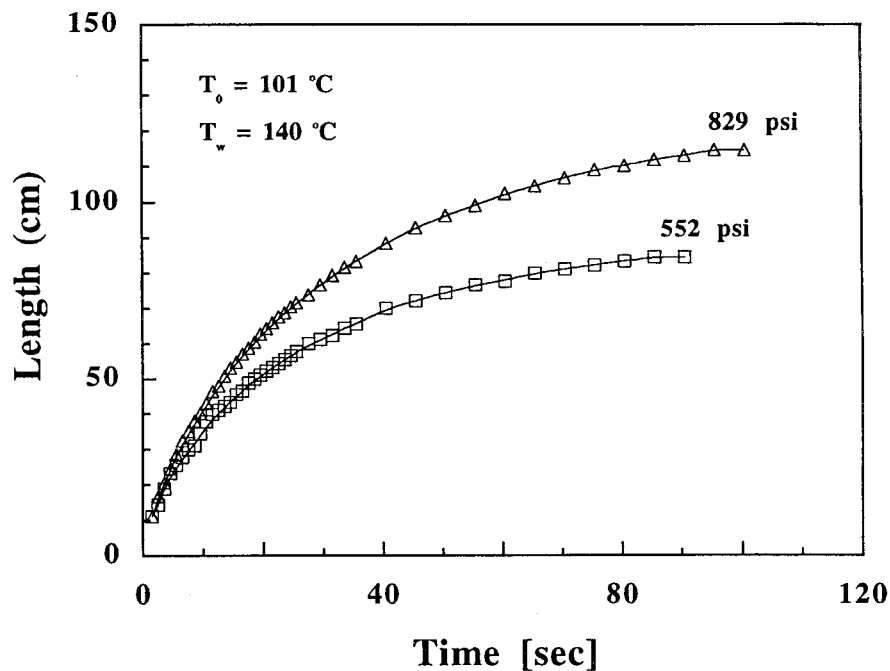


Figure 2 Flow front position as a function of filling time for Exp.4-5.

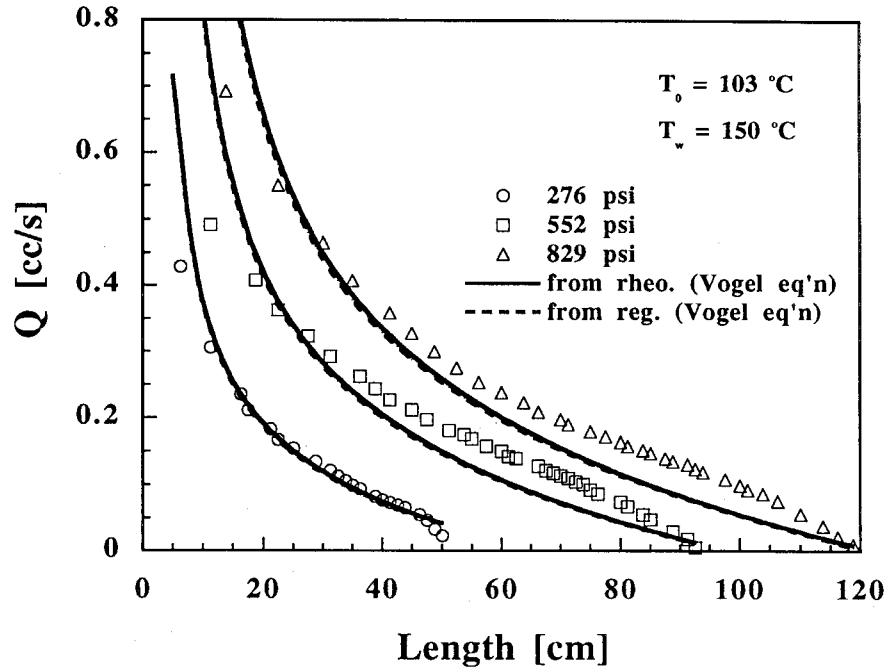


Figure 3 Comparison between the experimental data and the fit (dotted curves) obtained using the Castro–Macosko viscosity function with the Vogel equation. Solid curves show the flow rate calculated using the viscosity function obtained from the rheometric study.

curves. The points in Figures 3–6 show the flow rate data as a function of flow front position, which is reproduced from Figure 1 and Figure 2, respectively. In the case of a Newtonian fluid, the flow rate is inversely proportional to the flow front position and approaches gradually to the flow front position axis. However, since the epoxy–novolac molding compound was not only a non-Newtonian fluid but also a polymerizing system, the flow rate curves down and dropped to zero at the end stage of the filling process due to gelation.

In order to fit the flow rate vs flow front position data, two types (Arrhenius and Vogel equation) of Castro–Macosko viscosity function were tested. The power law index n with respect to the shear rate was assumed to be 0.70 because the reported values of the power law index for similar compounds are 0.70, 0.67,⁶ and 0.83.⁹

Figure 3 (Exp. 1–3) and Figure 4 (Exp. 4–5) shows a comparison between the experimental flow rate data and the fit (dotted curves) obtained using the function with Vogel equation together with the flow rate (solid curves) calculated using the function with Vogel equation obtained from the rheometric study. Figure 5 (Exp. 1–3) and Figure 6 (Exp. 4–5) also show a comparison be-

tween the experimental flow rate data and the fit (dotted curves) obtained using the function with Arrhenius equation together with the flow rate (solid curves) calculated using the function with Vogel equation obtained from the rheometric study. Only negligible differences between the fit and the rheometric results were observed. The function with Vogel equation could fit the experimental flow rate data better than the function with Arrhenius equation. However, this result might be due to the fact that the function with Vogel equation (six parameters) has one more parameter than the function with Arrhenius equation (five parameters). From the results of Figures 3–6, the viscosity functions estimated from regression of the spiral mold filling model look reasonable.

Comparison between the viscosity function obtained from the rheometric study (solid curve) and two viscosity functions obtained from regression of the flow rate data (dotted curves) is shown in Figure 7. The viscosity function parameter values were supposed to be determined to minimize the sum of error squares. According to the fitting results shown in Figures 3–6, most of the sum of error squares was resulted from the early stage of filling. Since the regression procedure proceeded

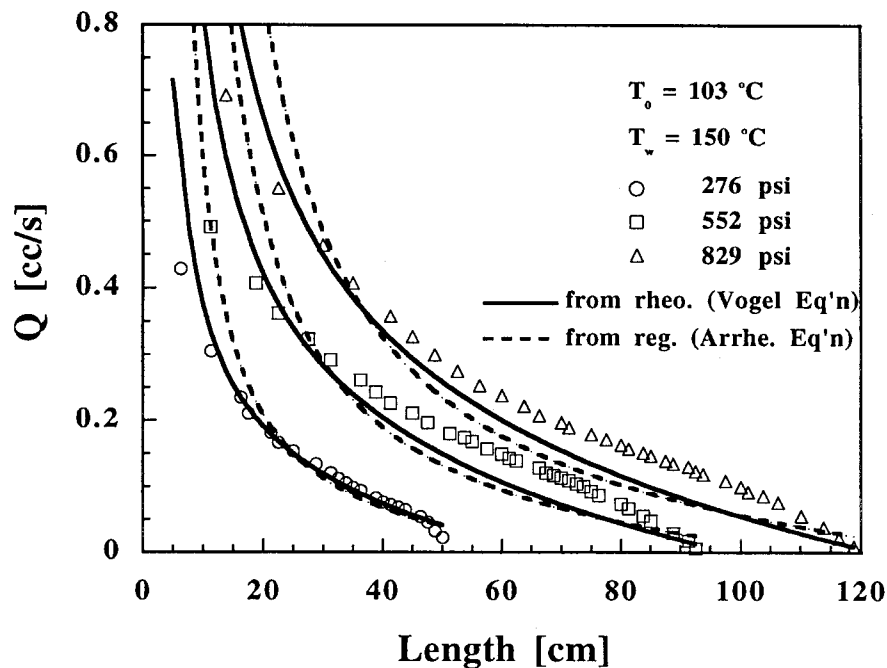


Figure 4 Comparison between the experimental data and the fit (dotted curves) obtained using the Castro–Macosko viscosity function with the Vogel equation. Solid curves show the flow rate calculated using the viscosity function obtained from the rheometric study.

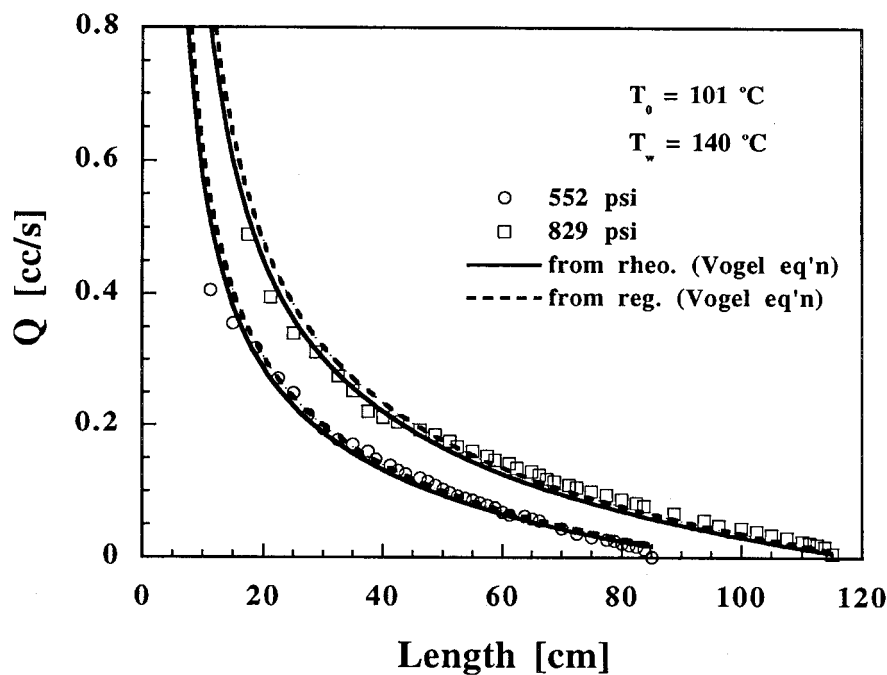


Figure 5 Comparison between the experimental data and the fit (dotted curves) obtained using the Castro–Macosko viscosity function with the Arrhenius equation. Solid curves show the flow rate calculated using the viscosity function obtained from the rheometric study.

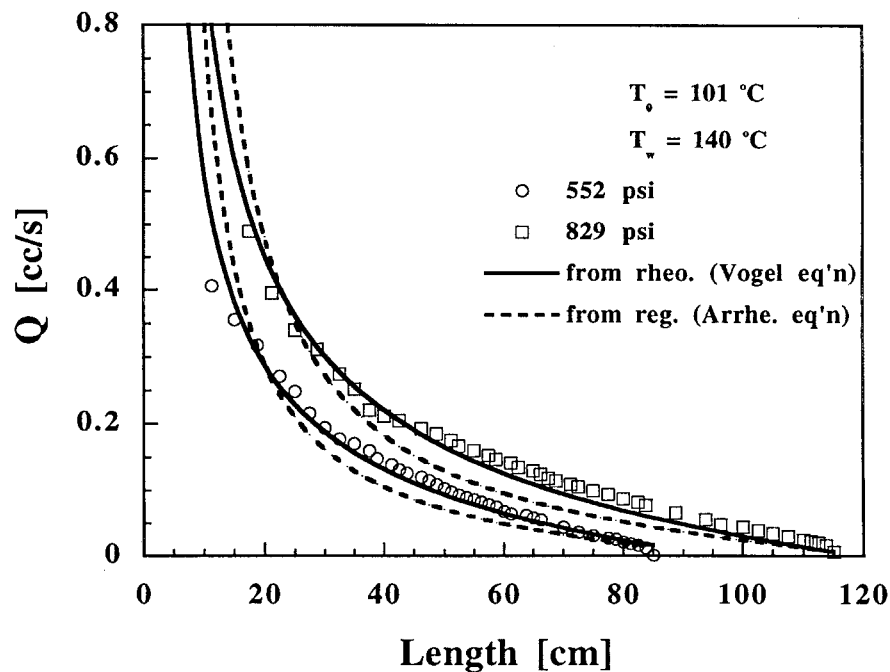


Figure 6 Comparison between the experimental data and the fit (dotted curves) obtained using the Castro–Macosko viscosity function with the Arrhenius equation. Solid curves show the flow rate calculated using the viscosity function obtained from the rheometric study.

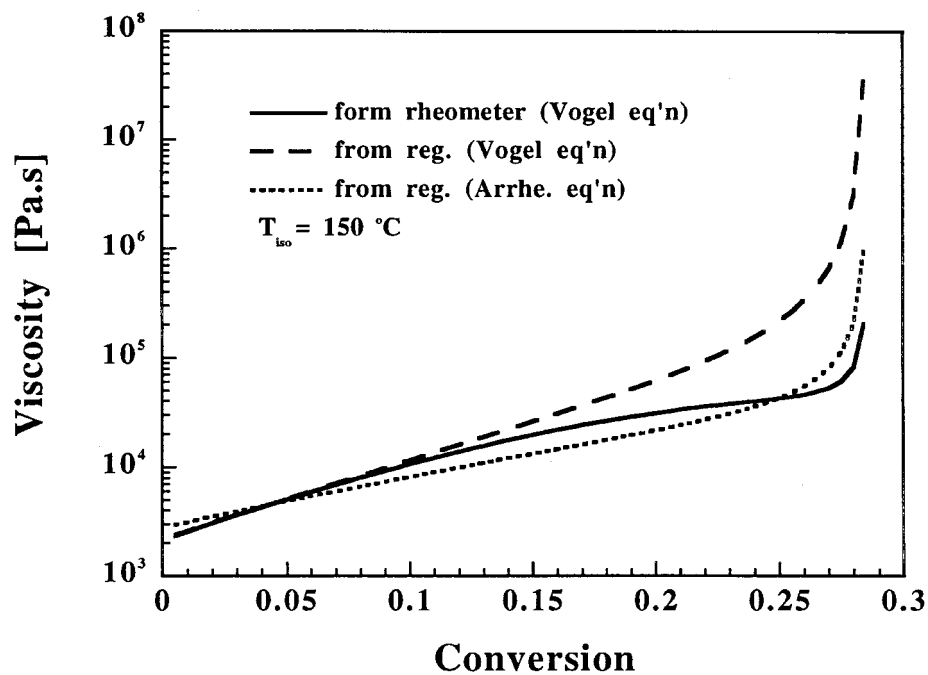


Figure 7 Comparison between the viscosity functions obtained from regression of the flow rate data and the viscosity function obtained from the rheometric study.

to the direction of minimizing the sum of error squares, the viscosity calculated using the viscosity functions estimated from the flow rate data was almost same in the lower conversion range ($\alpha \leq 0.1$).

The flow rate decrease at constant mold pressure during the spiral mold filling could be used to obtain the viscosity functions of the silica filled novolac molding compound. A good correlation between the experimental flow rate data and the fits depends on the type of given viscosity function. But the viscosity function still has to have reasonable physical meaning even though it is an empirical equation obtained through engineering analysis. Mathematically, a function, for example a polynomial, which does not have any theoretical or physical meaning may fit the experimental data more exactly. The viscosity function needs to describe the rheological changes associated with polymerization and temperature changes. In case of a phase separating polymer system, since viscosity change may be also affected by the phase separation dynamics,^{12,30} the viscosity function has to be chosen to explain the rheological change due to the phase separation process.

In estimating a viscosity function for a molding compound from the spiral mold filling experiment, accurate flow rate data and selection of proper physical property values (density, heat of reaction, heat capacity, and thermal conductivity, etc.) are important. Besides, there are some other important factors that can affect the fitting of the flow rate: (1) Reaction kinetics of the polymer system—the flow rate is affected by reaction rate. So, it is important to use an accurate reaction kinetic data in the simulation model. (2) Constant inlet pressure during filling—the flow rate depends strongly on the inlet pressure. (3) Thermal boundary condition at the resin–mold wall interface. The isothermal boundary condition was employed in this mold filling model. (4) Inlet conditions (temperature and conversion) at the gate. They affect also the fitting results. The effect of these factors on fitting of pressure rise at the gate during mold filling of a thermoset polyurethane system was analyzed in the previous study.¹⁴

A suggestion for obtaining reasonable viscosity function parameters from regression was given in the previous study.¹⁴ The suggestion can be summarized as follows: (1) Fix known parameters—the temperature dependent viscosity parameters ($A\eta$, c , d , $E\eta$) may be determined using a rheometer. (2) Gel point may be also fixed by a theoretical value or an experimentally determined value.

(3) For initial guess of the power a and b , use literature values for similar systems. The theoretical criterion [Eq. (19)] for a and b and reasonable limits for other parameters can be placed to avoid unreasonable results. Based on the suggestion, the viscosity functions of the silica filled epoxy novolac molding compound could be determined from nonlinear regression of the spiral mold filling model using the flow rate data.

CONCLUSIONS

The two types of Castro–Macosko viscosity function for the epoxy–novolac molding compound were determined as a function of temperature and conversion through nonlinear regression of the spiral mold filling model using the flow rate vs flow front position data. The viscosity functions determined through nonlinear regression of the spiral mold filling model were compared to the viscosity function obtained from the rheometric study. The viscosity functions obtained from regression of the flow rate data agreed well with the function from the rheometric study, especially in the lower conversion range under 0.1. This new technique can be used to estimate viscosity change of a reactive polymer system as a function of temperature and conversion, especially for a fast polymerizing system whose chemorheology can not be analyzed by a rheometer.

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