

Modeling reaction injection molding process of phenol-formaldehyde resin filled with wood dust

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Abstract

A theoretical model was developed to describe the flow behavior of a filled polymer in the packing stage of reaction injection molding and predict the residual stress distribution of thin injection-molded parts. The model predictions were compared with experiments performed for phenol-formaldehyde resin filled with wood dust and cured by urotropine. The packing stage of reaction injection molding process presents a typical example of complex non-isothermal flow combined with chemical reaction. It is shown that the time evolution of pressure distribution along the mold cavity that determines the residual stress in the final product can be described by a single 1D partial differential equation (PDE) if the rheological behavior of reacting liquid is simplistically described by the power-law approach with some approximations made for describing cure reaction and non-isothermality. In the formulation, the dimensionless time variable is defined in such a way that it includes all necessary information on the cure reaction history. Employing the routine separation of variables made possible to obtain the analytical solution for the nonlinear PDE under specific initial condition. It is shown that direct numerical solution of the PDE exactly coincides with the analytical solution. With the use of the power-law approximation that describes highly shear thinning behavior, the theoretical calculations significantly deviate from the experimental data. Bearing in mind that in the packing stage the flow is extremely slow, we employed in our theory the Newtonian law for flow of reacting liquid and described well enough the experimental data on evolution of pressure.

Keywords : reaction injection molding, packing stage, power-law liquid, analytical solution, residual stress

1. Introduction

Reaction injection molding is widely employed in processing of various thermoset polymers. It usually contains two or more liquids, accumulated in a high pressure mixing unit and then injected into a mold, where they are polymerized or cured to form a desired part. Hence, it presents a typical example of complex non-isothermal and compressible flows of liquid with reaction at high pressure and high temperature. Being mostly motivated by practical applications many researchers worked in the field and made quite a few attempts to describe experimentally or theoretically residual stresses remaining in the injection-molded parts (*e.g.* see the papers by Lee and Kwon, 2001; Kim *et al.*, 2002). It is because this research was considered as a very difficult task that needed a deep understanding of complicated dynamical behavior of polymeric fluids caused by chemical reactions

proceeding under high pressure and temperature. The residual stresses, remaining in the molded part due to incomplete relaxation, typically result in warping, shrinkage and even crack of the final products. It means that the mechanical properties of molded products are closely related to the residual stresses and therefore to the flow history experienced by the reacting fluids.

In this study, a mathematical model of reaction injection molding process was developed and compared with experimental data for phenol-formaldehyde resin cured by urotropin and filled with wood dust. The filled polymer fluid was described by the power-law flow model. The mathematical formulation of this non-isothermal flow problem with chemical reaction in the packing stage was reduced in the book by Leonov *et al.* (1977) to a nonlinear "piezo-conductivity" 1D PDE that describes the time evolution of pressure distribution along the mold channel. In this paper we obtained the analytical solution of this equation under specific initial conditions. This theoretical description is then compared with experimental results.

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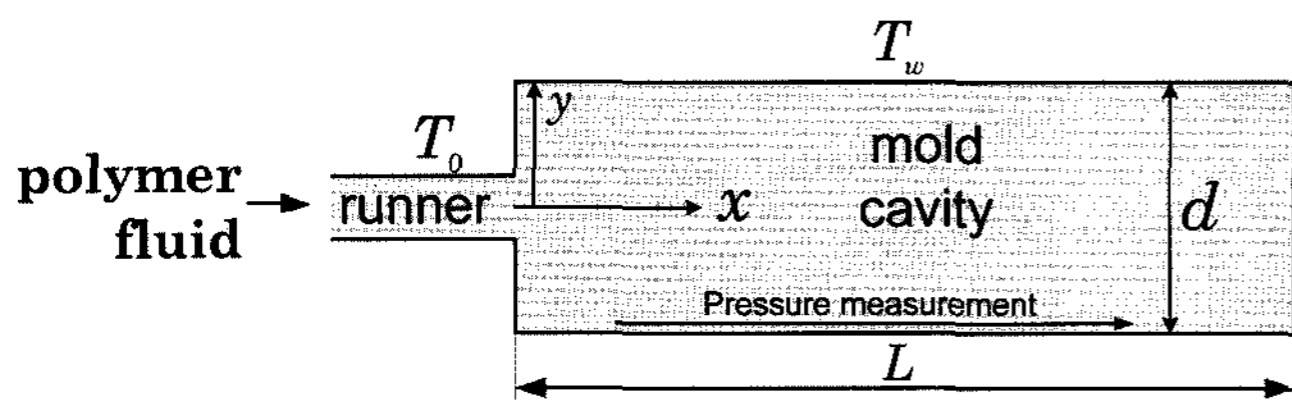


Fig. 1. Schematic of the reaction injection molding process employed in this study.

2. Formulation (Leonov *et al.*, 1977)

We consider the problem of residual stress distribution in the packing stage of the reaction injection molding process for phenol-formaldehyde resin filled with wood dust. The simplest geometry of the mold cavity sketched in Fig. 1 was used for the studies in the book mentioned above. This geometry also allows almost analytical analysis.

The packing stage is characterized by a slow non-isothermal reactive flow of thermosets under the action of very high pressure. The heat and reaction kinetic equations with appropriate initial and boundary conditions, describe the temporal and spatial variation of temperature T and degree of reaction c as:

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c_p} \frac{\partial^2 T}{\partial y^2} + \frac{h_0}{\rho c_p} \frac{\partial c}{\partial t}, \quad T|_{t=0} = T_0, \quad T|_{y=\pm d/2} = T_w, \quad (1)$$

$$\frac{\partial c}{\partial t} = k_p(T)(1-c)^{n_p}, \quad k_p(T) = k_{p0} e^{-U/(RT)}, \quad c|_{t=0} = c_0. \quad (2)$$

Here T is the absolute temperature, ρ is the fluid density, c_p is the heat capacity, c is the degree of reaction, h_0 is the heat of reaction, κ is the thermal conductivity, $k_p(T)$ is the reaction kinetic constant strongly dependent on the temperature, U is the *activation energy of chemical reaction* that describes Arrhenius-type temperature dependence of the kinetic constant, R is the gas constant, and n_p designates the order of chemical reaction. We assume the following simple pressure-dependence of the density:

$$\frac{\rho - \rho_0}{\rho_0} = \frac{p - p_0}{K_v(T)}, \quad (3)$$

where $K_v(T)$ is the bulk modulus. When we employ the power-law liquid approximation for the reacting polymeric fluid, the shear stress τ is expressed as

$$\tau = k(T)\varphi(c)|\dot{\gamma}|^n \operatorname{sgn}(\dot{\gamma}), \quad k(T) = k_0 e^{E/RT}. \quad (4)$$

Here $\dot{\gamma}$ is the shear rate, n is the power-law index and $k(T)\varphi(c)$ is the consistency coefficient in the power-law assumption decomposed into temperature-dependent and reaction-dependent parts, where E is the *activation energy of flow*. The reaction-dependent part has the following functional form, depending on the critical degree of reaction c_* :

$$\varphi(c) = \begin{cases} 1; & c \leq c_* \\ \varphi_0(c) = 1 + \frac{(c-c_*)^{m_1}}{(1-c)^{m_2}}; & c > c_* \end{cases} \quad (5)$$

When the slow reaction flow along the mold cavity is approximated as simple Poiseuille flow, the equation of motion yields the mathematical form of shear stress as:

$$\tau = y \frac{\partial p}{\partial x}, \quad (6)$$

where p is the pressure. Eqs. (4) and (6) yield the explicit solutions for shear rate and velocity:

$$\dot{\gamma} = \frac{\partial v}{\partial y} = \left[\frac{y |\partial p / \partial x|}{\varphi(c) k(T)} \right]^{1/n} \operatorname{sgn} \left(\frac{\partial p}{\partial x} \right),$$

$$v = - \left| \frac{\partial p}{\partial x} \right|^{1/n} \operatorname{sgn} \left(\frac{\partial p}{\partial x} \right) \int_y^{d/2} \left[\frac{y_1}{\varphi(c) k(T)} \right]^{1/n} dy_1 \quad (7)$$

In the above equations it is commonly assumed that the height of mold cavity d is much less than its length L and width W . Thus one can employ only the variables averaged over the thickness direction y . According to this approximation, the average velocity is defined as:

$$\bar{v}(t,x) = \frac{2}{d} \int_0^{d/2} v dy = - \frac{2}{d} \int_0^{d/2} y \dot{\gamma} dy$$

$$= - \left| \frac{\partial p}{\partial x} \right|^{1/n} \frac{2}{d} \int_0^{d/2} \frac{y^{1+1/n} e^{-E/(nRT)}}{[k_0 \varphi(c)]^{1/n}} dy \cdot \operatorname{sgn} \left(\frac{\partial p}{\partial x} \right). \quad (8)$$

With the similar definition for the averaged density $\bar{\rho}$, the averaged continuity equation becomes

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial (\bar{\rho} \bar{v})}{\partial x} = 0. \quad (9)$$

Boundary and initial conditions specified for the pressure are

$$p|_{x=0} = p_0; \quad \left. \frac{\partial p}{\partial x} \right|_{x=L} = 0; \quad p|_{t=0} = p_i(x). \quad (10)$$

Here p_0 is the packing pressure, usually kept constant during the packing stage, and $p_i(x)$ is unknown initial pressure distribution along the channel, which in principle has to be specified as final pressure distribution in the previous filling stage.

Substituting Eqs. (3) and (8) into (9) yields

$$\frac{\partial}{\partial t} \left(\frac{p}{K_v} \right) - \frac{\partial}{\partial x} \left[f(t) \operatorname{sgn} \left(\frac{\partial p}{\partial x} \right) \cdot \left| \frac{\partial p}{\partial x} \right|^{1/n} \left(1 + \frac{p}{K_v} \right) \right] = 0$$

$$\Rightarrow \frac{\partial p}{\partial t} = K_v f(t) \frac{\partial}{\partial x} \left[\left| \frac{\partial p}{\partial x} \right|^{1/n} \operatorname{sgn} \left(\frac{\partial p}{\partial x} \right) \right]. \quad (11)$$

Here $f(t) = \frac{2}{d} \int_0^{d/2} \frac{y^{1+1/n} e^{-E/(nRT)}}{[k_0 \varphi(c)]^{1/n}} dy$ and the bulk modulus is

considered as a constant. We now introduce dimensionless variables z , ξ , q and parameter \tilde{L} defined as

$$z = \frac{2x}{d}, \quad \xi = K_v \left(\frac{2}{d}\right)^{\frac{n+1}{n}} p_0^{\frac{1-n}{n}} \int_0^t f(t') dt', \quad q = \frac{p}{p_0}, \quad \tilde{L} = \frac{2L}{d}. \quad (12)$$

Here the new variable ξ which substitutes the independent variable t , contains all necessary information related to the chemical reaction and temperature history. Then Eqs. (10) and (11) are re-written in the dimensionless form as:

$$\frac{\partial q}{\partial \xi} = \frac{\partial}{\partial z} \left[\left| \frac{\partial q}{\partial z} \right|^{1/n} \operatorname{sgn} \left(\frac{\partial q}{\partial z} \right) \right] \quad (13)$$

$$\left(0 < z < \tilde{L}; \quad 0 \leq \xi \leq \xi_*, \quad \xi_* = K_v \left(\frac{2}{d}\right)^{\frac{n+1}{n}} p_0^{\frac{1-n}{n}} \int_0^\infty f(t) dt < \infty \right),$$

$$q|_{\xi=0} = q_0(z) = \frac{p_i(x(z))}{p_0}, \quad q|_{z=0} = 1, \quad \left. \frac{\partial q}{\partial z} \right|_{z=L} = 0. \quad (14)$$

Hence the problem of describing the time-evolution of stress distribution in the packing stage of reaction injection molding is reduced to solving a single nonlinear PDE (13) for the dimensionless pressure q under the initial and boundary conditions (14). However it should be kept in mind that the initial condition $q_0(z)$ still remains unknown, since the initial pressure distribution $p_i(x)$ in Eq. (10) has to be determined by the process of earlier cavity filling stage, which is not the object of the present study. The PDE (13) actually yields an analytical solution under some specific initial condition, which is illustrated afterwards.

3. Experimental

All the experimental data presented in this Section are given in the book by Leonov *et al.* (1977). Phenol-formaldehyde resin filled with wood dust and using urotropine as a curing agent has been chosen for the base polymeric fluid. The pressure p_0 applied for packing is equal to 24 MPa, the length L and the width of the mold cavity are 200 mm and 50 mm, respectively, and its thickness d is 2 mm.

Fig. 2 presents the temperature dependence of the bulk modulus K_v . In this study we assume that its variation with respect to temperature is negligible and thus utilize its approximate constant value. The average value of K_v , evaluated from Fig. 2 is equal to 4.25×10^3 MPa. Dependence of the function $f(t)$ that contains information of chemical reaction is presented in Fig. 3. The proper time integration determines the behavior of the dimensionless time variable ξ which in turn depends on actual time t . Fig. 4 shows the relationship between shear rate and stress that has been estimated with a rotational type rheometer of coaxial cylinders. These curves exhibit typical power-law type behavior of the reacting polymeric mixture. From their slope, the power-law index n is evaluated as 0.175.

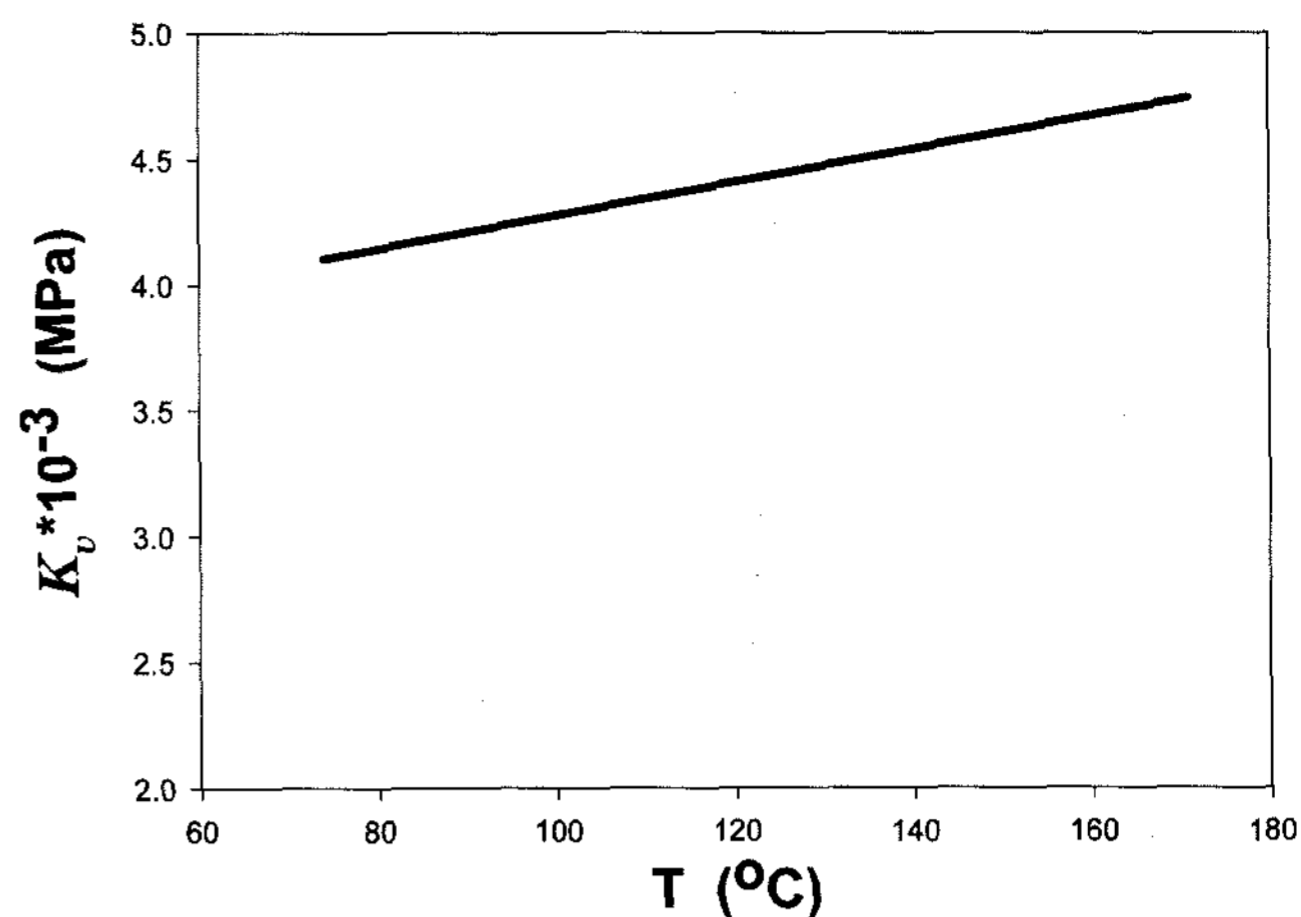


Fig. 2. Dependence of the bulk modulus K_v on temperature.

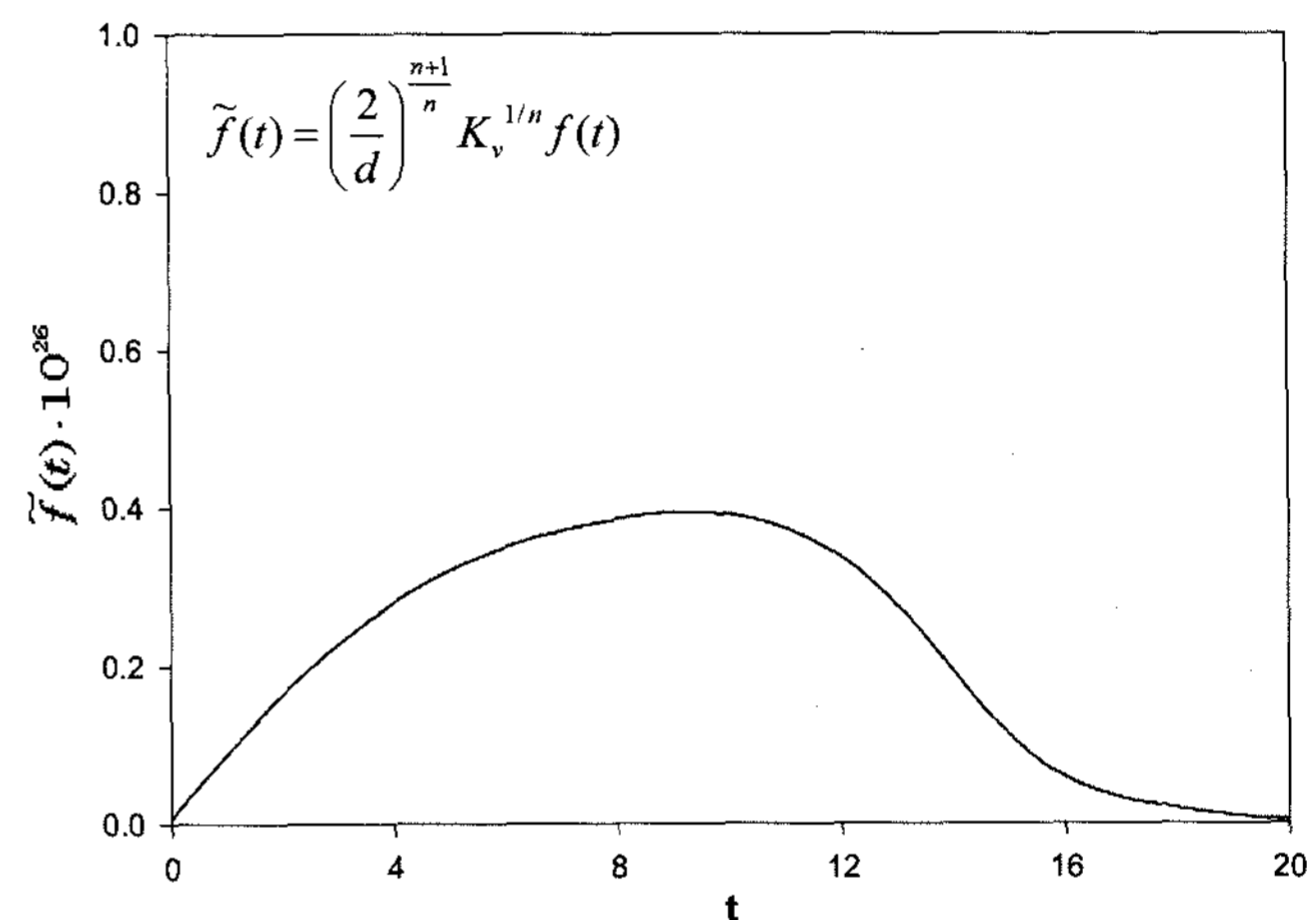


Fig. 3. The time-evolution of the function $f(t)$.

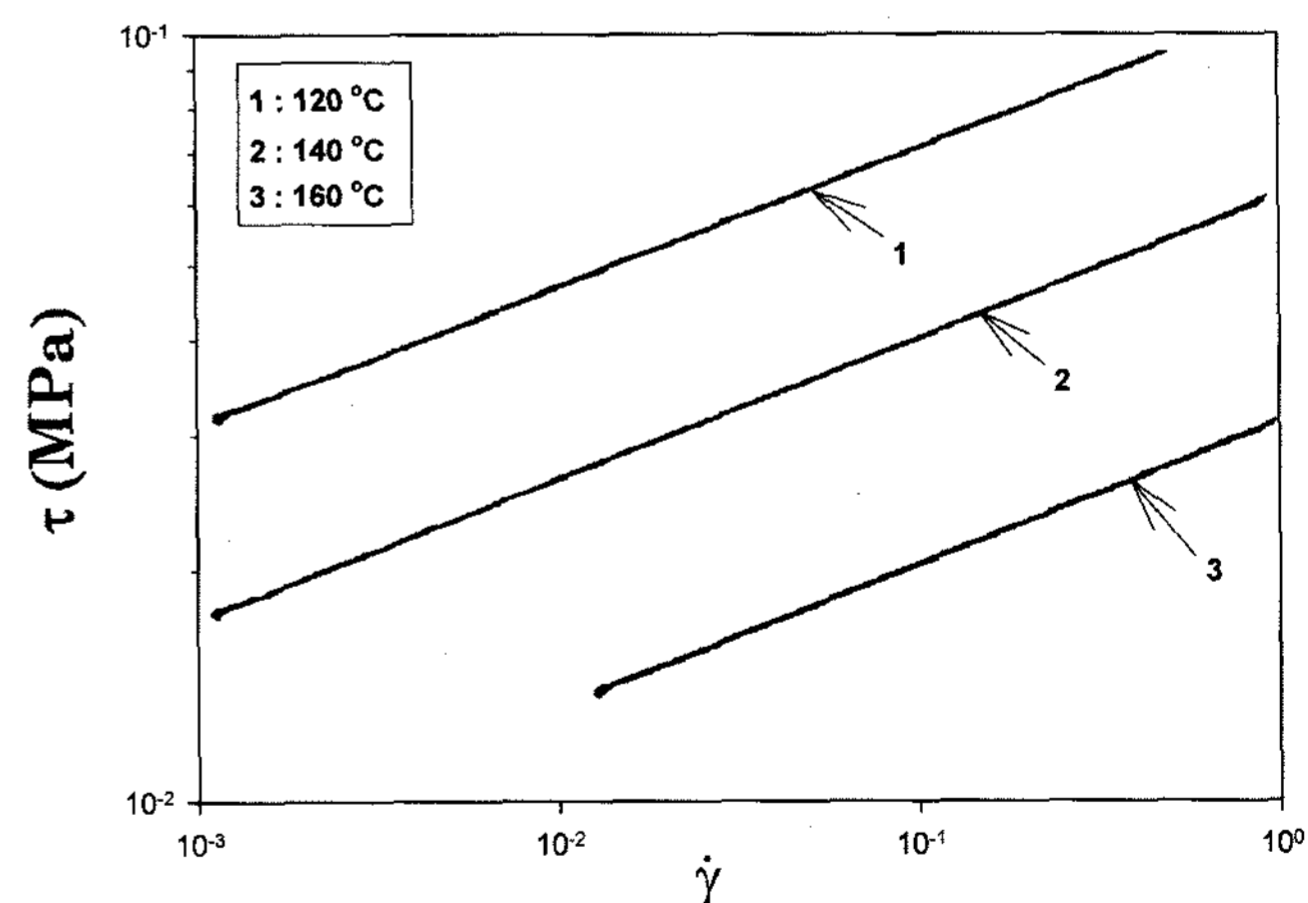


Fig. 4. Shear stress vs. shear rate for phenol-formaldehyde liquid filled with wood dust.

4. Results and Discussion

4.1. Analytical solution

The analytical solution of Eq. (13) can be simply obtained by using the method of separation of variables.

We first represent the function $q(\xi, z)$ as

$$q(\xi, z) = 1 - \psi(\xi, z); \quad \psi(\xi, z) = a(\xi) \cdot u(z). \quad (15)$$

Then substituting (15) into Eqs. (13) and (14) yields two ordinary differential equations subject to their respective initial and boundary conditions as follows:

$$a'/a^{1/n} = \frac{1}{n}(u')^{1/n-1} u''/u = -\lambda$$

$$\Rightarrow \begin{cases} a' = -\lambda a^{1/n}, & a(0) = 1 \\ \frac{1}{n}(u')^{1/n-1} u'' = ((u')^{1/n})' = -\lambda u, & u(0) = 0, \quad u'(\tilde{L}) = 0 \end{cases} \quad (16)$$

$$(17)$$

Here λ is the eigenvalue that has to be positive for stable solutions. The solution of Eq. (16) becomes

$$a(\xi) = \left[1 + \lambda \frac{1-n}{n} \xi \right]^{-\frac{n}{1-n}}. \quad (18)$$

The first integral of the nonlinear ordinary differential equation (17) always satisfies the boundary condition at $z=1$. Then one can obtain an implicit representation of the solution in the following integral form:

$$\chi \frac{z}{L} = \int_0^u \frac{dv}{(u_1^2 - v^2)^{\frac{n}{n+1}}} \quad (0 \leq u \leq u_1), \quad (19)$$

where $\chi \equiv \left[\frac{(n+1)\lambda}{2} \right]^{\frac{n}{n+1}} = \int_0^{u_1} \frac{du}{(u_1^2 - u^2)^{\frac{n}{n+1}}}$ and $u_1 = u(z=\tilde{L})$ is a

fitting parameter determined from the initial distribution of q . The integral in the right-hand side of Eq. (19) can be represented via a special function as:

$$\chi \frac{z}{L} = u_1^{\frac{1-n}{1+n}} \int_0^{\frac{u}{u_1}} \frac{dx}{(1-x^2)^{\frac{n}{1+n}}} = u_1^{\frac{1-n}{1+n}} \cdot \frac{u}{u_1} \cdot F\left(\frac{1}{2}, \frac{n}{2}, \frac{3}{2}; \left(\frac{u}{u_1}\right)^2\right), \quad (20)$$

Here F is the hypergeometric function defined as

$$F(\alpha, \beta; \gamma; z) = {}_2F_1(\alpha, \beta; \gamma; z) = \frac{\Gamma(\gamma)}{\Gamma(\beta)\Gamma(\gamma-\beta)} \int_0^1 t^{\beta-1} (1-t)^{\gamma-\beta-1} (1-tz)^{-\alpha} dt. \quad (21)$$

The evolution of pressure distribution described by Eqs. (13) and (14) may also be obtained numerically. In this work, the numerical solutions are obtained by employing the modified Euler method combined with the finite difference spatial discretization. The numerical solutions were further compared with both the experimental data and analytical solutions defined by the chain equations (15), (18), (19) and (20).

4.2. Experimental comparison of theoretical calculations with experimental data

We first compared the numerical solution with the

analytical one. Note that the initial condition $q_0(z)$ in (14) for the differential equation (13) is still unknown. However for the solution analytically represented, specification of a single value u_1 in Eq. (20) completely determines the initial distribution of the pressure $q_0(z)$. When we specify the same initial values for $q(z)$, the numerical solution exactly coincides with the analytical one except for minute numerical errors. From the numerical experiments, it seems that the numerical solution first reaches the distribution represented by Eq. (20) with a proper value of u_1 and then evolves according to the analytical solution if we designate a linear functional form for $q_0(z)$.

The comparison of the analytical solutions under the power-law assumption with experimental data is shown in Fig. 5. The experimental data are represented by solid lines while the calculations by dashed lines. Here the value of u_1 is set as 0.75 that most closely describes the data for $t=0.4$ sec. Even though the relaxation of the pressure gradient is

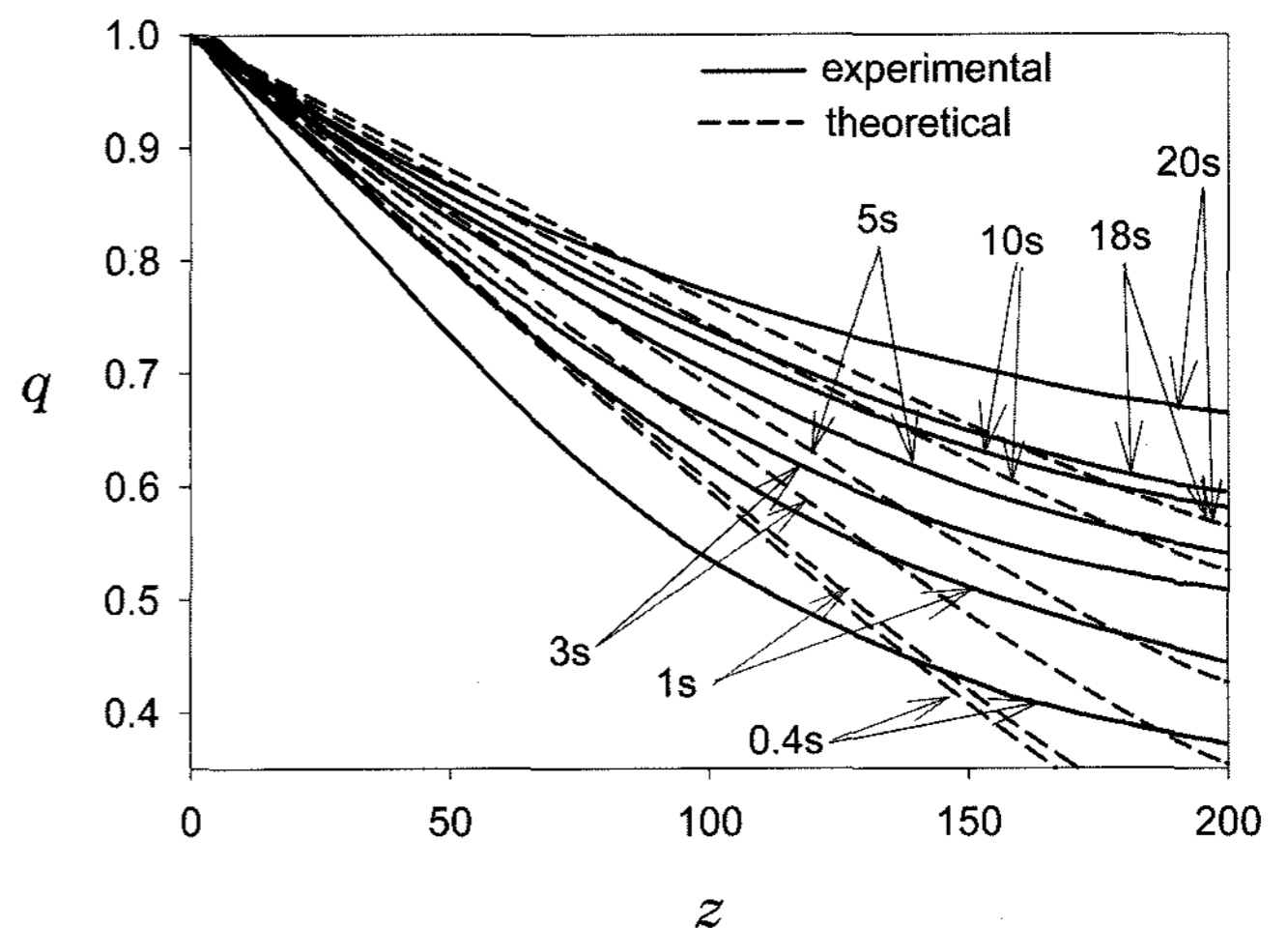


Fig. 5. Evolution of the pressure distribution along mold cavity under the power-law fluid assumption ($n=0.175$).

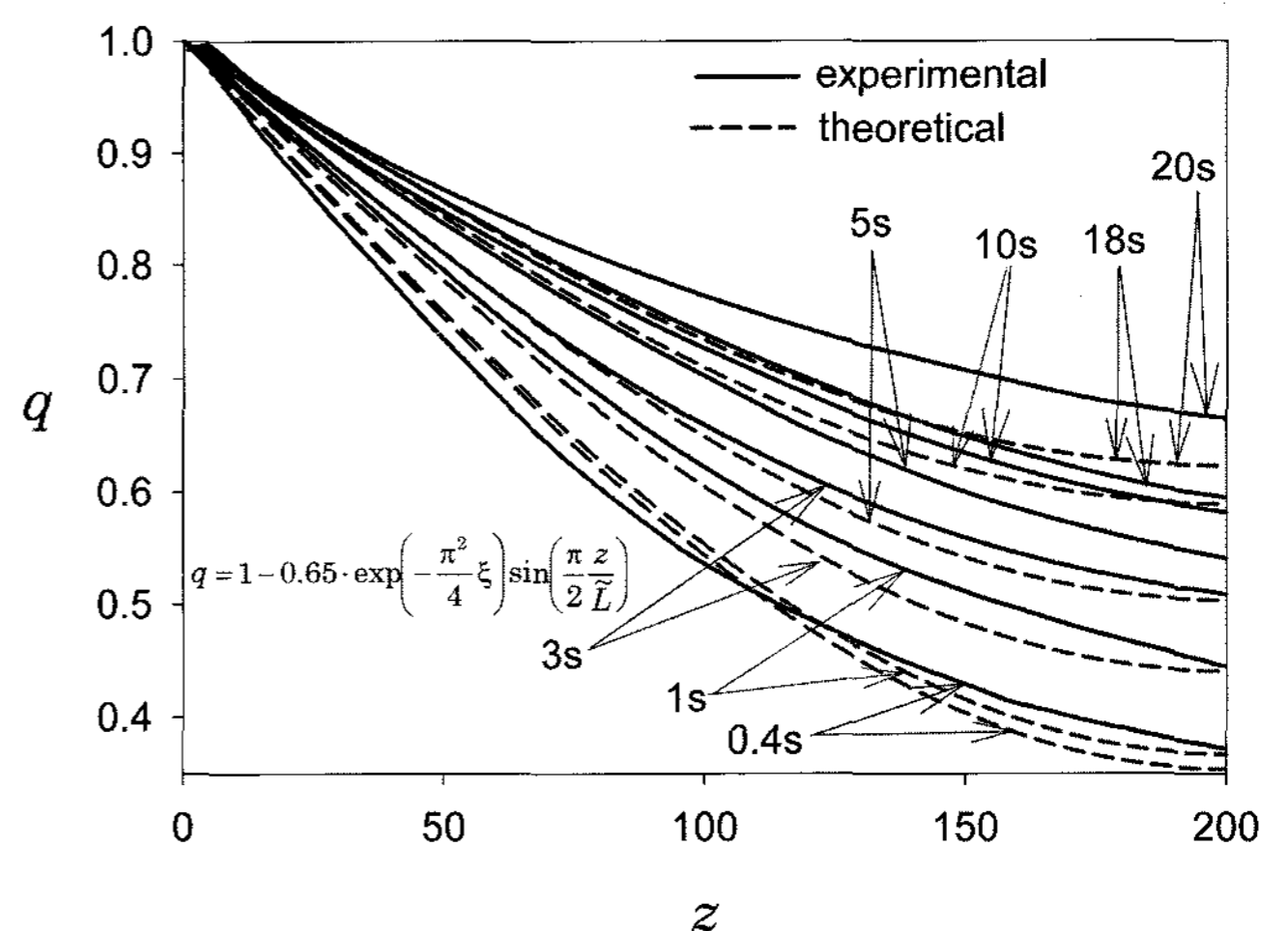


Fig. 6. Evolution of the pressure distribution along mold cavity under the Newtonian fluid assumption ($n=1$).

qualitatively described by our theoretical calculations, their deviations from the experimental data are quite severe. In particular, convexity (the variation of slope along z) of lines for the experimental data is not suitably expressed by the theory.

In attempt to improve this comparison, we remind that the flow of polymer is extremely slow in the packing stage of injection molding. Therefore it may be more appropriate to regard the flow of the liquid in this stage as Newtonian. Computational results obtained under the Newtonian fluid assumption ($n=1$) are compared with experimental data in Fig. 6. In this case with $n=1$, the implicit representation (20) involving the hypergeometric function F can be written as a simple sinusoidal function, and thus the analytical solution with the initial values optimally chosen

becomes $q = 1 - 0.65 \cdot \exp\left(-\frac{\pi^2}{4}\xi\right) \sin\left(\frac{\pi z}{2L}\right)$. Here the value of

u_1 is set as 0.65 in order to appropriately match the data for $t=0.4$ sec. Although one can still observe certain deviation of the theoretical description from the data, almost quantitative agreement may be seen with proper expression of the convexity of lines. In fact, if one takes into account possible experimental errors due to difficulty in correctly measuring time-evolution of pressure distribution, the coincidence between theory and experiment is quite good.

In obtaining the computational result depicted in Fig. 6, we have simply employed the functional values of $a(\xi)$ already used for Fig. 5. Due to the lack of experimental data (equivalent to Fig. 3) necessary for the calculation of $a(\xi)$ in the Newtonian case, we apply such crude approximation that $a(\xi)$ varies little with the change of n . The function $a(\xi)$ explains the time evolution of the pressure q . Thus it carries all the information on the temperature variation and chemical reaction represented by Eqs. (1) and (2) via the variable ξ . As shown by Eqs. (1) and (2), the flow characteristic, *i.e.*, the power-law index n affects the temperature or reaction only through the density ρ which is linearly proportional to the pressure p (and pressure is a function of shear rate). Since K_0 is estimated to be two order of magnitude higher than the applied pressure p_0 (and thus the pressure difference inside the mold), the variation of ρ during packing becomes little. Therefore the value of n seems to have weak effect on the temperature evolution and chemical reaction. Considering the low flow rate with the above consequences during the

packing stage, we may crudely assume that the flow characteristic n has main influence not on the time evolution $a(\xi)$ of the pressure but on its distribution $u(z)$ along the mold cavity.

5. Conclusions

In this work, we have developed a theoretical model of the packing stage in reaction injection molding. The phenol-formaldehyde resin filled with wood dust was chosen as representing a typical example demonstrating complex non-isothermal non-Newtonian flow with chemical reaction. According to the previous study (Leonov *et al.*, 1977), the time evolution of pressure distribution along the mold cavity during the packing stage has been expressed by a single nonlinear PDE in 1D under the power-law fluid assumption. In the formulation, the dimensionless time variable contains necessary information on the chemical reaction and temperature evolution. Employing the routine method of variable separation, we have been able to obtain the analytical solution under the restricted initial condition. From the numerical comparison of results, the direct numerical solution of the governing partial differential equation exactly coincides with the analytical solution. Under the power-law approximation with highly shear thinning behavior, the theoretical description of experimental data is poor. However if the Newtonian flow assumption is applied for the reacting liquid, the theory describes the pressure evolution quite satisfactorily. This may suggest that the liquid behavior is nearly Newtonian since the flow is extremely slow in the packing stage.

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