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## RHEODYNAMICS AND EXCHANGE OF HEAT IN THE FLOW OF POLYMERIZING FLUIDS IN A CYLINDRICAL CHANNEL

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*We examine a method by which to study the rheokinetic factor in an investigation of the hydrodynamics and heat exchange of reactive oligomers.*

The development of scientific foundations for chemical formation, i.e., of methods to produce composition materials through the utilization of reactive oligomers, requires analysis of the role played by the rheokinetic factor in the problems of hydrodynamics and convective heat exchange in rheologically complex reacting media. The flow of reactive oligomers is accompanied by polymerization which leads to an increase in molecular mass and correspondingly to an increase in viscosity, by several tens of orders. To calculate the thermohydraulic characteristics of the flow, it is essential that we know the kinetics involved in the change in composition viscosity, i.e., rheokinetics.

In order to study the role of the rheokinetic factor, we employ the method of space-time separation (STS) between the thermochemical and thermohydrodynamic states [1]. A nonmoving composition is hardened in a reservoir (the thermochemical stage). Neither the flow channel nor the liquid heat exchange are, for all intents and purposes, encumbered by the kinetics of polymerization (the thermohydrodynamic stage). The constant-pressure unit consists of an individually thermostatted reservoir and of a channel with identical or different temperatures. An ÉD-20 epoxy resin was used in the experiments in addition to a metaphenylene diamine hardener. The STS is achieved through special selection of regime parameters:  $d_r/d_c \ll 1$  ( $d_r$  and  $d_c$  represent the diameters of the reservoir and the channel);  $t_{\text{stay}} \sim t_{\text{kin}}$ ,  $(t_{\text{cha}}/t_{\text{res}}) \approx 0.2$ ;  $t_{\text{res}}/t_{\text{kin}} \ll 1$  ( $t_{\text{stay}}$ ,  $t_{\text{cha}}$ ,  $t_{\text{res}}$ , and  $t_{\text{kin}}$  represent the stay times within the reservoir, the time of motion through the channel, and the time of reservoir evacuations, in addition to the characteristic hardening time). The optimum regimes for the carrying out of these experiments in terms of the initial polymerization temperature, the ratio of reagents, and the length of time that the hardening composition remains within the reservoir, these were all determined from the condition of proximity of this process to the isothermal state. Thus, the initial process temperatures were 60, 65, and 67.5°C, the reagent ratios were assumed to be stoichiometric, while the stay time of the reacting mixture in the reservoir varied from 30 to 60 min. The effect of rheokinetics on convective heat exchange in a partially polymerized composition was investigated for the case of a nonisothermal flow through a round channel with a constant wall temperature of  $T_w = 40^\circ\text{C}$ . The thermophysical characteristics of the composition were as follows: density  $\rho$ , thermal conductivity  $\lambda$ , thermal diffusivity  $a$ , in the range of 40-70°C, where they change only slightly as heating takes place [2]. They were therefore assumed to be constant and, on the average, equal to:  $\lambda = 0.153 \text{ W/(m}\cdot\text{K)}$ ;  $\rho = 1.14 \cdot 10^3 \text{ kg/m}^3$ ; and  $a = 0.86 \cdot 10^{-7} \text{ m}^2/\text{sec}$ .

With consideration of the chemical and rheological kinetics, we selected two stay times of the reacting mixture in the reservoir for the hardening composition, namely  $t = 30$  and  $35$  min. These corresponded to the following depths of conversion:  $\beta = 0.072$  and  $0.088$ . Three fixed loads were used for each of these, and two of these, i.e.,  $\Delta P = 3.65 \cdot 10^4$  and  $6.547 \cdot 10^4 \text{ Pa}$ , were reproduced for all stay times. The range of velocities 0.003-0.18 m/sec was chosen from the following conditions: a) the extent of the initial thermal segment is greater than the channel length (approximation of the thermally short channel); b) the flow time is sufficiently large to permit the mean-mass temperature metering probe to attain a steady regime at the inlet to the channel. Since the coefficient of thermal diffusivity for the epoxy compositions is small, the Peclet criterion (Pe), even at such low flow rates, amounts to  $(0.6-5) \cdot 10^3$ ,

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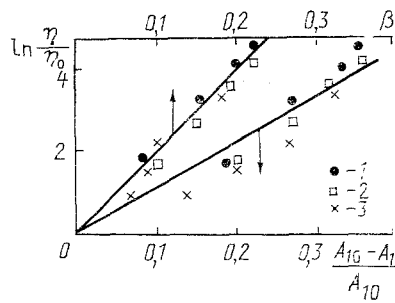


Fig. 1. Reduced viscosity of the hardened composition as a function of the fraction of reacted primary amines and as a function of the conversion ratio at various initial temperatures for the polymerization process: 1)  $T_0 = 60^\circ\text{C}$ ; 2)  $65^\circ\text{C}$ ; 3)  $67.5^\circ\text{C}$ .

while the relative length of the thermal segment is 55-110 calibers. Thus, the heat exchange occurs in the region of the thermal initial segment. During these experiments we measured: a) the temperature  $T_{\text{in}}$  of the medium at the inlet to the channel; b) the mean mass temperature  $T_{\text{out}}$  at the outlet from the channel, based on the readings of a special probe which averages the temperatures through the cross section; c) the wall temperature  $T_w$  at three points; d) the mean volumetric flow rate for the polymerizing liquid in the channel, based on the rate of reservoir evacuation and the open cross section of the channel. Reliability of experiments on convective heat exchange for the polymerizing liquid was confirmed by data for a nonhardening resin. These demonstrated good agreement between the Nusselt number as a function of the inlet and channel-wall temperatures, in conjunction with the familiar Zider-Tate correction factor. Thus, the exponent in the temperature-viscosity correction factor ranged from 0.11 to 0.18, which is rather close to the normally accepted average value of 0.14. Measurement of the temperature relationship between the viscosity of the nonhardened "pure resin" demonstrated that it is described by the equation

$$\eta_0 = a \exp[-b(T - T_0')], \quad (1)$$

where  $a = 10.78 \text{ Pa}\cdot\text{sec}$ ,  $b = 0.114 \text{ 1}^\circ\text{C}$ ,  $T_0' = 298 \text{ K}$ . The activation energy of the viscous flow in a nonhardened resin amounts to  $E_\eta = bRT_0'^2 = 84 \text{ kJ/mole}$  [1]. The effect of the shearing velocity on the viscosity of the polymerizing liquid is determined by the change in the load on the piston at a given conversion ratio. For the range of shearing velocities studied here ( $100\text{--}500 \text{ sec}^{-1}$ ) we have ascertained a Newtonian nature for the flow curve (thrust versus the flow characteristics, as straight lines) and the independence of viscosity relative to the rate of strain [1].

The numerical calculations of thermal and kinetic polymerization parameters for the epoxide composition were carried out on the basis of a macrokinetic model [3]. Analysis of the model's phase portrait demonstrated that it correctly reflects the features encountered in hardening kinetics: the final makeup of the composition corresponds to a stable point of rest [4]. Based on the found fields of reagent and temperature concentration in the reservoir, we have calculated the local and volume-averaged temperature  $\bar{T}$  and the conversion ratio  $\beta$ . The integral characteristics for various stay-time regimes for the composition in the reservoir are subsequently utilized as the initial parameters in experiments involving flow and convective heat exchange in the channel.

Numerical calculation of polymerization in the reservoir and measurement of viscosity for various stay times allows us to relate the viscosity with the makeup of the hardening composition. We then measure the viscosity values  $\eta(t)$  for each selected instant of time  $t$  and for a specific value for the hardening temperature  $T_w$ . The mean-integral temperature  $\bar{T}(t)$  in the reservoir and the makeup of the composition at this same instant of time are determined from the numerical calculation. Based on an advanced measured function  $\eta(T)$  for the resin, we calculate the value of  $\eta_0(T)$ , corresponding to the found temperature. We then analyze the relationship between the reduced viscosity  $\eta(t)/\eta_0(t)$  and the makeup of the composition at the instant of time  $t$  (Fig. 1). The linkage of viscosity with the fraction of joined epoxide groups (or reacted primary amines) was found to be independent of  $T_w$ . Using the method of least squares to process the data, we were able to demonstrate the adequacy of both of these concepts. However, in the dependence on  $\beta$  (the fraction of bound epoxide groups) dispersion is lower. As  $\beta$  increases, viscosity rises exponentially:

$$\eta = a \exp \left[ \frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) + c\beta \right], \quad \beta \leq 0.22, \quad (2)$$

where  $a = 10.78 \text{ Pa}\cdot\text{sec}$ ,  $c = 19.7$ , and  $T_0 = 298 \text{ K}$ .

The activation energy  $E = 84.1$  kJ/mole for the viscous flow is determined exclusively by the properties of the resin. The convective heat exchange at the inlet thermal segment is determined for Peclet numbers  $(0.7-5) \cdot 10^3$ . The Nusselt number as a function of the Peclet number in the case of nonisothermal flow for a partially hardened composition is found to be the same as in the case of a Newtonian fluid with the Zider–Tate nonisothermal correction factor:

$$\overline{Nu} = C \left( \frac{1}{Pe} - \frac{L}{d} \right)^{-\frac{1}{3}} (\eta_w / \eta_l)^{-0.14}. \quad (3)$$

Here  $\eta_w / \eta_l = \exp [(E/R)(1/T_w - 1/T_l)]$ ,  $T_l = T_w - 1/2(T_{out} - T_{in}) : \ln [(T_w - T_{in}) / (T_w - T_{out})]$  is the effective temperature;  $T_{in}$  and  $T_{out}$  are the temperatures at the inlet to the channel and at the outlet from the channel. The values of  $C$  are found to range between 1.55-1.86, as is the case for the Newtonian fluids [5]. The viscosity ratio in (3) is independent of the conversion ratio at the inlet to the channel and is determined by the temperature relationship for the viscosity of the nonhardened resin. Processing of hydraulic resistance data for a channel in the nonisothermal regime demonstrated the possibility of using the Poiseuille formula with effective viscosity in the form  $\eta_{eff} = \eta_{in} \exp [(E/R)(1/T_l - 1/T_{in})]$ , where  $\eta_{in}$  represents the viscosity of the composition at the inlet to the channel. Combined solution of the equations for hydraulic resistance and heat exchange allows us to calculate the characteristics of the nonisothermal flow for a partially hardened liquid at a given pressure difference  $\Delta P$ . We used the following parameters:  $Pe = RePr$  is the Peclet number, calculated on the basis of the viscosity for a partially hardened liquid at the channel inlet;  $\overline{Gz} = Pe d/L$ ,  $\overline{St} = 4\overline{Nu}/\overline{Gz}$ ,  $B = (E/RT_w)\kappa$  are the Graetz and Stanton numbers, as well as the Pearson criterion, characterizing the relative change in viscosity due to the relative temperature difference  $\kappa = (T_{in} - T_w)/T_w$  across the channel:

$$\overline{Gz} = \overline{Gz}_0 \exp \left[ B\kappa \left( -\frac{1}{\kappa + 1} \right) + \frac{1 - \exp(-\overline{St})}{2\overline{St} + \kappa[1 - \exp(-\overline{St})]} \right], \quad (4)$$

$$\overline{St} = \frac{4C}{\overline{Gz}^{2/3}} \exp \left[ -0,07B\kappa \frac{1 - \exp(-\overline{St})}{\overline{St} + 0,5\kappa[1 - \exp(-\overline{St})]} \right].$$

The  $\overline{Gz}$  and  $\overline{St}$  numbers are distinguished from traditional numbers by the factors  $4/\pi$  and  $d/4L$ , respectively. The first equation defines the hydraulic resistance in the nonisothermal regime, while the second equation determines the convective heat exchange. Analysis of system (4) showed that when  $\kappa \leq 0$  (the flow out of the cold reservoir into a hot channel) its solution is singular. When  $\kappa > 0$ , it is possible to have two solutions which correspond to the low-temperature and high-temperature flow regimes. Their appearance from system (4) is associated with the use of the approximate method beyond the limits of its applicability.

The derived system of equations describes the exchange of heat and resistance in the one-dimensional approximation. To evaluate the area of applicability for such an approximation, let us examine the problem of nonisothermal liquid flow through a circular tube in the boundary-layer variant, under the action of the constant force  $F$  of piston downstroke. We will take into consideration the relationship between viscosity and temperature, the remaining physical properties assumed to be constant. We will adopt the following assumptions, serving as the base for the method of calculating heat exchange and resistance at a constant rate of flow: a) in the inlet section of the tube the velocity profile is developed and parabolic; b) the temperature of the liquid at the inlet is distributed uniformly through the cross section, while the temperature of the wall is constant over the surface; c) the thickness  $\Delta$  of the thermal boundary layer is significantly smaller than the tube radius  $R_0$ ; d) the transfer of heat along the axis as a consequence of heat conduction is small in comparison to the transfer of heat ascribed to the flow; e) we can neglect the evolution of heat due to viscous dissipation. Instead of the exact equation of momentum and energy conservation, according to the method from [5], we use approximate equations which, in the variables  $\Theta = (T - T_w)/(T_0 - T_w)$ ,  $W_X = V_x/V_0$ ,  $W_Y = V_y/V_0$ ,  $X = x/R_0$ ,  $Y = y/R_0$ , and  $K = \Delta/R_0$ , have the form

$$\frac{1}{1-Y} \frac{\partial}{\partial Y} \left[ (1-Y) \frac{\partial \Theta}{\partial Y} \right] = B(X), \quad (5)$$

$$\frac{1}{1-Y} \frac{\partial}{\partial Y} \left[ (1-Y) \frac{\eta}{\eta_0} \frac{\partial W_X}{\partial Y} \right] = A(X), \quad (6)$$

$$\frac{\partial W_X}{\partial X} + \frac{1}{1-Y} \frac{\partial}{\partial Y} [(1-Y) W_Y] = 0. \quad (7)$$

Here

$$A(X) = \int_0^1 \left\{ \frac{\partial}{\partial X} \left( \frac{R_0}{V_0} \frac{P}{\eta_w} \right) + \frac{\text{Re}_w}{2} \left( W_X \frac{\partial W_X}{\partial X} + W_Y \frac{\partial W_X}{\partial Y} \right) - \right. \\ \left. - 2 \frac{\partial}{\partial X} \left( \frac{\eta}{\eta_w} \frac{\partial W_X}{\partial X} \right) - \frac{1}{(1-Y)} \left[ (1-Y) \frac{\eta}{\eta_w} \frac{\partial W_Y}{\partial X} \right] \right\} dY, \\ B(X) = \frac{\text{Pe}}{2K} \int_0^K \left[ W_X \frac{\partial \Theta}{\partial X} + W_Y \frac{\partial \Theta}{\partial Y} \right] dY, \\ \text{Pe} = \text{Pe}_0 \bar{V}, \text{Pe}_0 = \frac{2R_0 V_0}{a}, \bar{V} = \frac{V_m}{V_0}.$$

For the characteristic velocity we assume  $V_0 = F/(8\pi\eta_0 L)$ , i.e., the mean velocity of the liquid which it would exhibit if its rheological properties had been determined at the inlet temperature [ $\eta_0 = \eta(T_0)$ ,  $L$  is the length of the tube]. The boundary conditions are as follows:

$$\text{when } X \geq 0; Y = 0 \quad \Theta = 0; W_X = W_Y = 0, \quad (9)$$

$$\text{when } X \geq 0; K \leq Y \leq 1 \quad \Theta = 1; \partial\Theta/\partial Y = 0, \quad (10)$$

$$\text{when } X \geq 0; Y = 1 \quad \partial W_X/\partial Y = 0. \quad (11)$$

Having solved Eq. (5) under condition (10) and limiting ourselves to the third-order terms of  $Y/K$ , we obtain

$$B = -6/[K^2(3-K)], \quad (12)$$

$$\Theta = C_1(K) \frac{Y}{K} + C_2(K) \left( \frac{Y}{K} \right)^2 + C_3(K) \left( \frac{Y}{K} \right)^3, \quad (13)$$

where  $C_1(K) = 3(2-K)/(3-K)$ ,  $C_2(K) = -3(1-K)/(3-K)$ , and  $C_3(K) = -(K/(3-K))$ .

For the relationship between yield and temperature we take the Arrhenius approximation

$$\frac{\eta_w}{\eta} = \Psi(\Theta, \bar{F}, \bar{B}) = \exp \left( \frac{\tilde{\gamma}\Theta}{1 - \tilde{\kappa} + \tilde{\kappa}\Theta} \right), \quad (14)$$

where

$$\Theta = \frac{T - T_w}{T_{in} - T_w}, \quad \tilde{\gamma} = \frac{\bar{F}}{1 - \tilde{\kappa}}, \quad \tilde{\kappa} = \frac{T_{in} - T_w}{T_{in}} = \frac{\kappa}{\kappa + 1}$$

( $\tilde{\kappa} \ll 1$ ,  $\bar{B} = E/RT_{in}$  is the Franck–Kamenetskii parameter, characterizing the thermal sensitivity of the liquid and where  $\bar{F} = \bar{B}\tilde{\kappa}$  is the Pearson parameter which determines the change in the effective viscosity, due to the radial difference in the temperatures  $T_{in}$  and  $T_w$ ). In using the method from [5] we will expand  $\Psi(\Theta, \bar{F}, \bar{B})$  in powers of  $\Theta$ . In many cases of practical importance the quadratic approximation is sufficient:

$$\tilde{\Psi}(\Theta) = 1 + a_1\Theta + a_2\Theta^2, \quad (15)$$

where

$$a_1 = (1 - \lambda)(\exp \bar{F} - 1); \quad a_2 = \lambda(\exp \bar{F} - 1) \text{ when } |\bar{F}| \geq 0.5, \\ a_1 = \tilde{\gamma}(1 + \tilde{\kappa}); \quad a_2 = \tilde{\gamma} \left( \frac{1}{2} \tilde{\gamma} - \tilde{\kappa} \right) \text{ when } |\bar{F}| < 0.5.$$

The parameter  $\lambda$  is taken from the condition of monotonicity for the approximation curve and equality of the functions  $\Psi(\Theta, \bar{F}, \bar{B})$  and its approximation  $\tilde{\Psi}(\Theta)$  at the ends of the interval, as well as the derivatives at one of the ends of the region. The natural condition of a minimum in the mean-square error does not ensure the monotonicity of the derived curve (15).

From (13) and (14), in explicit form, we obtain the relationship between viscosity and the transverse coordinate

$$\frac{\eta_w}{\eta} \sum_{i=0}^n b_i \left( \frac{Y}{K} \right)^i, \quad (16)$$

where  $b_0 = 1$ ,  $b_1 = a_1c_1$ ,  $b_2 = a_1c_2 + c_1^2a_2$ ,  $b_3 = a_1c_3 + 2a_2c_1c_2$ ,  $b_4 = a_2(c_2^2 + 2c_1c_3)$ ,  $b_5 = 2a_2c_2c_3$ ,  $b_6 = a_2c_3^2$ ;  $n = 3m$ .

From relationships (6), (11), and (16), with consideration given to the conditions of equality between the total flow rates in the boundary layer and in the core, common to the previously unknown rate of liquid flow, we find the profile of longitudinal velocity and then, now that we know this quantity, from the equation of continuity (7) we determine the transverse velocity. From relationship (12) we then find

$$\bar{V}g_1(K) = 2Gz_0^{-1}, \quad (17)$$

where

$$g_1(K) = \int_0^K \bar{f}_1(K) dK; \quad Gz_0 = \text{Pe}_0 \frac{d}{L} = \frac{F}{8a\eta_0\pi} \left(\frac{d}{L}\right)^2,$$

$$\bar{f}_1(K) = \frac{1}{12} \frac{K^2(3-K)}{\left(1 - \frac{K}{2}\right)} \left\langle \frac{K}{R} \sum_{i=0}^K b_i \left\{ K \left[ \frac{d_1}{(i+2)(i+4)} + \right. \right. \right.$$

$$+ \left. \frac{d_2}{(i+2)(i+5)} + \frac{d_3}{(i+2)(i+6)} \right] \frac{2i+3}{i+1} - \left[ \frac{d_1}{(i+1)(i+3)} + \right.$$

$$+ \left. \frac{d_2}{(i+1)(i+4)} + \frac{d_3}{(i+1)(i+5)} \right] - K^2 \left[ \frac{d_1}{(i+2)(i+5)} + \right.$$

$$+ \left. \frac{d_2}{(i+2)(i+6)} + \frac{d_3}{(i+2)(i+7)} \right] \left. \right\} + \frac{6}{3-K} \times$$

$$\times \sum_{i=0}^n \frac{b_i(iR+T) - KRb_i}{R^2} \left\{ \frac{1}{(i+1)(i+2)(i+3)(i+4)} - \right.$$

$$- \frac{2(i+2)K}{(i+1)(i+2)\dots(i+5)} + \frac{(i^2+6i+3)K^2}{(i+1)(i+2)\dots(i+6)} -$$

$$\left. \frac{i(i+4)K^3}{(i+1)(i+2)\dots(i+7)} \right\} \rangle,$$

$$d_1 = \frac{3(-K^2+4K-6)}{K(3-K)^2}; \quad d_2 = \frac{6(K^2-3K+3)}{K(3K)^2};$$

$$d_3 = -\frac{3(K-2)}{(3-K)^2}; \quad \text{Pe}_0 = \frac{\bar{V}_0 d}{a},$$

here

$$R = P_0 + P_1K + P_2K^2 + P_3K^3 + P_4K^4;$$

$$P_0 = \frac{1}{4} \frac{\eta_w}{\eta_0}; \quad P_1 = -\frac{\eta_w}{\eta_0} + \sum_{i=0}^n \frac{b_i}{i+1}; \quad P_2 = \frac{3}{2} \frac{\eta_w}{\eta_0} -$$

$$- 3 \sum_{i=0}^n \frac{b_i}{i+2}; \quad P_3 = -\frac{\eta_w}{\eta_0} + 3 \sum_{i=0}^n \frac{b_i}{i+3};$$

$$P_4 = \frac{1}{4} \frac{\eta_w}{\eta_0} - \sum_{i=0}^n \frac{b_i}{i+4}.$$

The second relationship, linking  $\bar{K} \equiv K(\bar{L})$  with the dimensionless mean-flow velocity  $\bar{V}$ , is found from the law of the conservation of momentum by integration over the entire volume of the channel:

$$\int_0^1 [W_X^2(\bar{L}, Y) - W_X^2(0, Y)](1-Y) dY = \mathcal{F} \frac{2}{\text{Re}_w} \int_0^{\bar{L}} \frac{\partial W_X}{\partial Y}(X, 0) dX, \quad (18)$$

where

$$\text{Re}_w = 2\rho V_0 \frac{R_0}{\eta_w}, \quad \bar{F} = \frac{\mathcal{F}}{2\pi\rho V_0^2 R_0^2}, \quad \bar{L} = \frac{L}{R_0}.$$

After substitution of the longitudinal velocity profile, we find

$$\bar{V}^2 g_2(\bar{K}) = 16 \text{Gz}_0^{-1}, \quad (19)$$

here

$$\begin{aligned} g_2(\bar{K}) &= \left( I_1 + I_2 - \frac{2}{3} \right) \text{Pr}_0^{-1} + 2 \exp\left( \frac{\bar{F}\bar{B}}{\bar{B} - \bar{F}} \right) I_3; \quad \text{Pr}_0 = \left( \frac{\rho a}{\eta_0} \right)^{-1}; \\ I_1(\bar{K}) &\equiv \bar{V}^{-2} \int_0^{\bar{K}} \mathcal{W}_x^2(\bar{L}, Y)(1-Y) dY = \frac{1}{R^2(\bar{K})} \sum_{i,j=0}^n \frac{b_i(\bar{K}) b_j(\bar{K})}{(i+1)(j+1)} \times \\ &\times \left[ \frac{\bar{K}^3}{i+j+3} - \frac{[3ij+5(i+j)+8]\bar{K}^4}{(i+2)(j+2)(i+j+4)} + \frac{[3ij+4(i+j)+5]\bar{K}^5}{(i+2)(j+2)(i+j+5)} - \right. \\ &\quad \left. - \frac{(i+1)(j+1)\bar{K}^6}{(i+2)(j+2)(i+j+6)} \right]; \\ I_2(\bar{K}) &\equiv \bar{V}^{-2} \int_{\bar{K}}^1 \mathcal{W}_x^2(\bar{L}, Y)(1-Y) dY = \frac{1}{R^2(\bar{K})} \left[ \left( \frac{\eta_w}{\eta_0} \right)^2 \left( \frac{1}{24} - \frac{1}{4} \bar{K} + \right. \right. \\ &\quad \left. \left. + \frac{5}{8} \bar{K}^2 - \frac{5}{6} \bar{K}^3 + \frac{5}{8} \bar{K}^4 - \frac{1}{4} \bar{K}^5 + \frac{1}{24} \bar{K}^6 \right) + 2 \left( \frac{\eta_w}{\eta_0} \right) \times \right. \\ &\quad \left. \times \left( -\frac{1}{8} + \frac{1}{2} \bar{K} - \frac{3}{4} \bar{K}^2 + \frac{1}{2} \bar{K}^3 - \frac{1}{8} \bar{K}^4 \right) E(\bar{K}) + \right. \\ &\quad \left. + \left( \frac{1}{2} - \bar{K} + \frac{\bar{K}^2}{2} \right) E^2(\bar{K}) \right]; \\ E(\bar{K}) &= \sum_{i=0}^n b_i(\bar{K}) \left( \frac{\bar{K}^2}{i+2} - \frac{\bar{K}}{i+1} \right); \\ I_3(\bar{K}) &= \bar{V}^{-2} \int_0^{\bar{L}} \frac{\partial \mathcal{W}_x}{\partial Y}(X, 0) dX = \int_0^{\bar{K}} \frac{\bar{f}_1(K) dK}{R(K)}. \end{aligned}$$

System of equations (17), (19) serves to determine the thickness of the boundary layer at the outlet from channel  $\bar{K}$  and the dimensionless mean-flow velocity  $\bar{V}$ . It contains the four dimensionless parameters  $\text{Gz}_0$ ,  $\text{Pr}_0$ ,  $\bar{F}$ , and  $\bar{B}$ .

The values of the quantities  $\bar{K}$  and  $\bar{V}$  enable us to determine the change in the thickness of the temperature boundary layer along the channel, and then to determine the temperature and velocity fields. The characteristics of heat exchange and resistance are found from the following relationships:

$$\begin{aligned} \text{Nu}_x &= 4 \left[ 1 + \frac{2(1-K)^2}{K(2-K)} \ln(1-K) \right]^{-1}, \\ \bar{\text{Nu}} &= 2 \text{Gz}_0 \bar{V} \int_0^{\bar{K}} \bar{f}_1(K) \left[ 1 + \frac{2(1-K)^2}{K(2-K)} \ln(1-K) \right]^{-1} dK, \\ \xi_x &= \frac{16}{\text{Re}_w R(K) \bar{V}}; \quad \xi = \frac{8 \text{Gz}_0 I_3(\bar{K})}{\text{Re}_w}, \end{aligned} \quad (20)$$

where  $\text{Nu}_x = \alpha d/\lambda$ ,  $\xi_x = \Delta P/(\rho \bar{V}^2/2)$  are the local Nusselt number and the coefficient of resistance, respectively, while  $\text{Nu} = \int_0^{\bar{L}} \text{Nu}_x dx / \bar{L}$ ,  $\xi = \int_0^{\bar{L}} \xi_x dx / \bar{L}$  are integral quantities.

System (17), (19) represents a collection of transcendental equations. For its solution, we use an extension of the Pearson thermal sensitivity parameter  $\bar{F}$  in conjunction with the Newton–Kantorovich method. For the initial approximation we select the boundary-layer thickness  $\bar{K}_0$  and the velocity value  $\bar{V}_0$ , which correspond to the flow of a medium with temperature-independent

properties, i.e., when  $\bar{F} = 0$ . In this case,  $\bar{V}_0 = 1$ , while the quantity  $\bar{K}_0$  satisfies Eq. (17), which after transformation reduces to the relationship

$$\frac{\bar{K}^3}{36} \left( 1 - \frac{7}{40} \bar{K} \right) = Gz_0^{-1}. \quad (21)$$

Let us note that the case  $\bar{F} = 0$  has been examined in monograph [5]. The equation for  $\bar{K}$  derived there differs from (21) by the coefficient of the second term (in [5] it is equal to 9/40). This is a result of the fact that we kept a larger number of terms in the expansions for  $\Theta$  and  $B$  in relationships (12) and (13).

Figure 2 shows the change in the thickness of the boundary layer and the associated evolution of the profiles of temperatures and velocities, as well as of the integral Nu number along the length of a circular tube ( $d = 3 \cdot 10^{-3}$  m,  $L = 0.1623$  m,  $\Delta P = \text{const}$ ). The temperature profile, constant at the inlet to the tube, remains that way within the core of the flow. The intensity of heat exchange is significantly weakened as the flow moves through the depth of the tube. The dependence of Nu and of the boundary-layer thickness on the longitudinal coordinate is approximately linear. Comparison of results from calculations based on integral and one-dimensional methods demonstrated that the one-dimensional relationships yield acceptable results only for  $Pr_0 \geq 10^{2.5}$ , since here the Prandtl number is absent. For the integral method in this range of Prandtl numbers, its value exerts no influence on the characteristics of the flow and of heat exchange. Figure 3 shows the results from calculations of the regimes of flow and heat exchange for the ÉD-20 nonhardened resin when  $\Delta P = 5 \cdot 10^4 - 3.2 \cdot 10^6$  Pa,  $T_0 = 60^\circ\text{C}$ , derived by the one-dimensional and integral methods. The

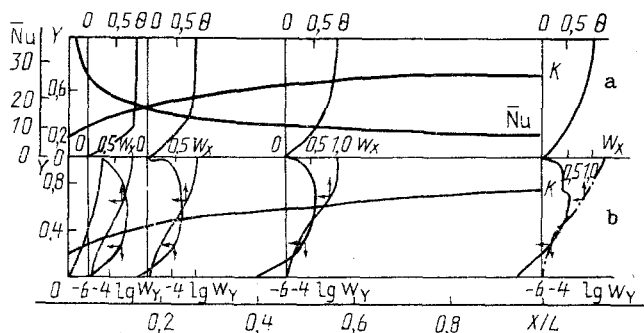


Fig. 2. Evolution of the profiles for temperature, velocities, boundary-layer thickness, and  $\bar{Nu}$  along the channel length.  $E = 84.1$  kJ/mole;  $\bar{F} = 3.245$ ,  $\bar{B} = 28.67$ ,  $\bar{\kappa} = 0.1133$ ,  $\bar{Gz}_0^{-1} = 1.4841 \cdot 10^{-3}$ ,  $T_{in} = 80^\circ\text{C}$ ,  $T_w = 40^\circ\text{C}$ ,  $Pr_0 = 554$ .

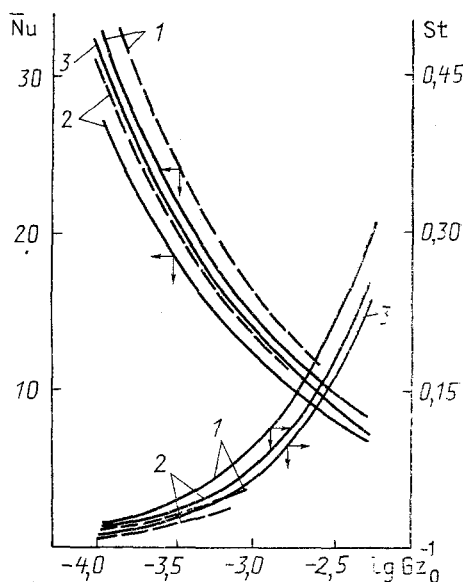


Fig. 3. Comparison of results from calculations by the integral and simplified methods for  $\bar{Nu}$  and  $\bar{St}$  when  $\bar{B} = 3039$ ,  $Pr_0 = 3100$ ,  $\bar{F} = 0.968$ : 1)  $C = 1.86$ ; 2)  $C = 1.55$ ; 3)  $A_2 \neq 0$ .

value of  $Pr_0 = 3100$  corresponds to the region in which this parameter is insignificant. Comparison of the results obtained in a calculation based on these two methods shows that the one-dimensional relationships are suitable for the calculation of the heat-exchange parameters in the region of average thicknesses in the temperature boundary layer. The  $\overline{Nu} = \overline{Nu}(\overline{Gz_0}^{-1})$  curves for  $C = 1.55$  and 1.86 yield lower and upper bounds for values calculated by the integral method. In the region of a thin boundary layer, on the basis of one-dimensional formulas, the calculation error increases. It is associated with utilization of the effective viscosity calculated for  $T = T_l$  in the formula for hydraulic resistance, i.e., the characteristic mean temperature through the boundary layer, rather than through the cross section of the channel. Acceptable in this case is the approximation in which, for purposes of calculating resistance, the effective viscosity is taken at the temperature of the inlet, while for purposes of calculating the heat exchange in conjunction with nonisothermicity, the Zider—Tate correction factor is utilized. The corresponding curves are indicated in Fig. 3 by a dashed line. The temperature  $T_l$  best characterizes the effective channel temperature in the calculation of hydraulic resistance, the thicker the boundary layer. The upper bound of the area of applicability for this simplified method is represented by the earlier-cited conditions of validity for the nonisothermal Zider—Tate correction factor.

### CONCLUSIONS

We have proposed a method to investigate the effect of rheokinetics on the thermohydraulic characteristics of flow under pressure in polymerizing liquids and for the design of an installation with space—time separation of the thermochemical and hydraulic stages. For ED-20 epoxide resin with an amine hardener it has been established that below a hardening level of  $\beta \leq 0.2$  the viscous-flow activation energy does not change. It has been demonstrated that for a partially hardened composition the exchange of heat at the inlet thermal segment is determined by the same relationships as for a Newtonian fluid. We have developed and experimentally verified methods for the calculation of nonisothermal flow in a partially hardened liquid at the inlet thermal segment of a tube in the one-dimensional and two-dimensional boundary-layer approximations.

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