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: \( \frac{d_r}{d_c} \ll 1 \) (\( d_r \) and \( d_c \) represent the diameters of the reservoir and the channel); \( t_{stay} \sim t_{kin} \), \( t_{cha} \sim t_{res} \), \( t_{res} \sim t_{kin} \) (\( t_{stay}, t_{cha}, t_{res}, t_{kin} \) 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 \( T_w = 40°C \). 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: \( \lambda = 0.153 \text{ W/(m} \cdot \text{K)} \); \( \rho = 1.14 \times 10^3 \text{ kg/m}^3 \); and \( a = 0.86 \times 10^{-7} \text{ m}^2/\text{sec} \).

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., \( \Delta P = 3.65 \times 10^4 \) and 6.547 \times 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 \((0.6-5) \times 10^{-3}\).
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; 3) 67.5.

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 \( T_{in} \) of the medium at the inlet to the channel; b) the mean mass temperature \( T_{out} \) 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

\[
\eta_0 = a \exp \left( -b \left( T - T_0 \right) \right),
\]

where \( a = 10.78 \text{ Pa} \cdot \text{sec}, b = 0.114 \text{ K}^{-1}, T_0' = 298 \text{ K} \). 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 (100-500 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 \( T \) 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 \( T(t) \) 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:

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

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