Journal of Engineering Physics and Thermophysics, Vol. 79, No. 5, 2006

MATHEMATICAL MODELING OF THE GAS-PHASE POLYMERIZATION OF BUTADIENE BASED ON THE MODEL OF INTERPENETRATING CONTINUA

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UDC 66.021.3.06

Based on the model of interpenetrating multivelocity continua, a mathematical description of the gas-phase polymerization of butadiene has been constructed, taking account of the variation in temperatures and volumes of the gas and polymer during the polymerization.

Recently, increased interest in the gas-phase polymerization of butadiene has been observed abroad (in Germany, China, and Japan). Unlike the solution polymerization, the gas-phase one is considered to be safer; structures of the devices allow a more efficient removal of the excess of heat released during the process. The operation of isolating the polymer from a solution is no longer needed, which reduces expenditures on the rubber production and decreases the environmental pollution.

Attention to the gas-phase polymerization of butadiene is also linked with the fact that it became possible to use, as a catalyst, neodymium complexes, which not only speed up the reaction but also make it possible to obtain stereoregular polybutadiene with an ~98% content of 1.4-*cis* links. Exactly such rubber is now of greatest demand in the tire industry.

In Russia, the gas-phase polymerization of butadiene is accomplished using a sodium catalyst. Consideration is given to the possibility of converting to new catalytic complexes with the application of the existing plant equipment for the gas-phase polymerization; therefore, the problem of studying hydrodynamics and heat and mass transfer in operating polymerizers is of current interest for upgrading the produced sodium-butadiene rubber and for subsequent application of the results in developing a mathematical model of the gas-phase polymerization using new catalytic complexes.

The first investigations of the gas-phase polymerization of butadiene using sodium were carried out in the early 20th century by K. Ziegler abroad and by S. V. Lebedev in Russia. In [1], the kinetic identity of the gas- and liquid-phase polymerization of butadiene using sodium was noted, and the temperature effect on the diffusion coefficient of the monomer in butadiene was described.

In industry, the gas-phase polymerization of butadiene is carried out in a periodic regime in horizontal cylindrical hollow devices with a detachable spherical cover (Fig. 1). Into the polymerizer, multiple-tier trolleys with detachable shelves are rolled, on which a catalyst paste has been preliminarily laid in the form of thin sheets. Gaseous butadiene arrives at the polymerizer, where, on the surface of the catalyst paste, polymerization begins, in which a certain temperature and pressure are maintained. Heat released during the process is removed due to the circulation of gaseous butadiene through a cooler. The gas circulation is set up by a gas blower. The total time of the polymerization is, on the average, 18 h.

The drawback of this method is that the produced sodium-butadiene polymer is not standard to some extent. Because of possible inhomogeneities of the catalyst paste and local superheating of the reactant mass, sometimes "gristles" are formed, that is, solid three-dimensional structures deteriorating the quality of the rubber. A nonobservance of the temperature mode of the polymerization can give rise to a "thermopolymer," which is prone to self-decomposition with the release of a large amount of heat and, when in contact with air, is capable of igniting.

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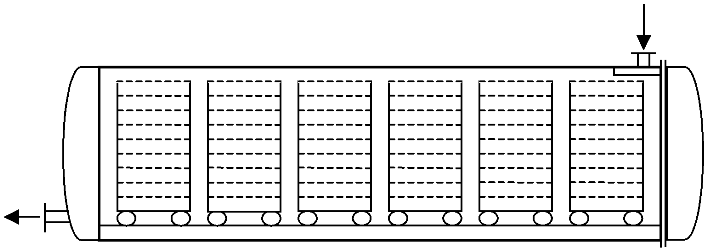

Fig. 1. Schematic of the device for the gas-phase polymerization of butadiene.

The polymerizer capacity is, on the average, 4200 kg of the polymer in an operation, and the polymer density is 920 kg/m^3; therefore, by the end of the process the device volume that is free for the motion of gaseous butadiene decreases by 4.56 m^3, which should be taken into account in modeling the gas motion in the device.

The polymerization rate and properties of the obtained rubber depend on the catalyst distribution in the reaction medium, on the temperature, pressure, and purity of the monomer, and on the structure of the polymerizer. The control of the industrial process of polymerization proceeds by technological regimes specifying the temperature of the incoming gas and the pressure in the device. These regimes have been determined experimentally. Also available is a table of the hourly increment of the amount of the polymer at prescribed pressure and temperature difference of the gas at the inlet to and outlet from the device [2].

A simplified kinetic scheme of the butadiene polymerization using a sodium catalyst incorporates the following elementary reactions [1]:

Initiation $I_0 + M \xrightarrow{k_\mathrm{i}} R^*$ (1),
Chain growth $R^*(l) + M \xrightarrow{k_\mathrm{gr}} R^*(l+1)$
Chain transfer to the monomer $R^*(l) + M \xrightarrow{k_\mathrm{t.m}} P\ (l) + R^*$ (1).

Reactions of branching of macromolecules are also observed; however, in such reactions the monomer is not expended. The rate of expenditure of the monomer during the polymerization is determined from the equation

$$r_m = mM\,(k_\mathrm{i} I_0 + k_\mathrm{p} R^* + k_\mathrm{t.m} R^*)\ .$$

In order to sufficiently accurately model the operation of the polymerizer, apart from chemical kinetics it is necessary to take into account the laws of gasdynamics, as well as heat and mass transfer between the gas and the solid phase (polymer) and inside the phases.

The shelves with catalyst sheets uniformly occupy the internal space of the polymerizer (Fig. 1); therefore, the moving gas and the layers of the growing polymer may be regarded as interpenetrating continua having different velocities. A two-phase system of the gas and polymer layers is considered under the following basic assumptions: the distances at which parameters of the gas motion vary markedly (beyond the discontinuity surfaces) are much larger than the characteristic dimension of the polymer layers (the thickness of the sheets of the catalyst paste is 0.4 mm, and the average thickness of the polymer layer in the end of the polymerization is 5 mm); and the thickness of the polymer layers is many times larger than the distances between molecules. This makes it possible to describe the behavior of a two-phase system relying on the model of interpenetrating continua. According to this model, the equations of conservation of mass, momentum, and heat for each phase involve terms characterizing the interaction between the phases and the volume fractions ε_g and ε_s occupied by the gas and polymer, which vary during the polymerization.

The proposed mathematical model of a two-phase system, in which the polymerization reaction proceeds along with the heat and mass transfer processes, which is based on the model of interpenetrating multivelocity continua [3], is of the form

$$\frac{\partial}{\partial y}(\varepsilon_\mathrm{g}\rho_\mathrm{g} w) = -J_\mathrm{g,s}\ ,\quad 0 < y < L\ ;$$

$$\varepsilon_\mathrm{g}\rho_\mathrm{g} w\frac{\partial w}{\partial y} = -\varepsilon_\mathrm{g}\frac{\partial p}{\partial y} - f\ ;$$

$$\varepsilon_g \rho_g w C_{pg} \frac{\partial T_g}{\partial y} = K (T_s - T_g) ;$$

$$\frac{\partial}{\partial \tau} (\varepsilon_s \rho_s X_{s,b}) = J_{g,s} - \varepsilon_s r_m , \quad \tau > 0 ;$$

$$\frac{\partial}{\partial \tau} (\varepsilon_s \rho_s X_{s,pol}) = \varepsilon_s r_m , \quad X_{s,b} + X_{s,pol} = 1 ; \tag{1}$$

$$\varepsilon_s \rho_s C_{ps} \frac{\partial T_s}{\partial \tau} = \lambda_s \frac{\partial^2 T_s}{\partial y^2} - K (T_s - T_g) + \varepsilon_s r_m \Delta H ;$$

$$\varepsilon_s + \varepsilon_g = 1 .$$

From the system of equations (1) it follows that the variation in the volume of phases, pressure, and velocity and temperature of the gas flow results from the decrease in the number of moles of butadiene in the polymerization reaction and from the flow heating due to heat transfer with the polymer. The system is closed using the equation

$$p = \frac{\rho_g}{m} RT . \tag{2}$$

The boundary and initial conditions are

$$\rho_g (\tau, 0) = \rho_{g0} (\tau) , \quad w (\tau, 0) = \frac{V (\tau)}{S (\tau)} ,$$

$$T_g (\tau, 0) = T_{g0} (\tau) , \quad \lambda_s \left. \frac{\partial T_s}{\partial y} \right|_{y=0} = \tilde{K} (T_s - T_g) , \quad \left. \frac{\partial T_s}{\partial y} \right|_{y=L} = 0 ; \tag{3}$$

$$T_s (0, y) = T_{s0} (y) , \quad \varepsilon_s (0, y) = \varepsilon_{s0} (y) , \quad X_{s,b} (0, y) = 0 .$$

In system (1), the equations for the gas phase are written in the quasi-stationary approximation. Difference schemes approximating the momentum equation and the equations of material and heat balance are obtained by integrating the first three equations of system (1) from $j - 1$ to j;

$$(\varepsilon_g \rho_g w)_j^n - (\varepsilon_g \rho_g w)_{j-1}^n = - J_{g,sj}^n h ,$$

$$\varepsilon_{g,j-1}^n \, \rho_{g,j-1}^n w_{j-1}^n \, (w_j^n - w_{j-1}^n) = - \varepsilon_{g,j-1}^n \, (p_j^n - p_{j-1}^n) - f_{j-1}^n h ,$$

$$\varepsilon_{s,j-1}^n \, \rho_{g,j-1}^n w_{j-1}^n C_{pg} \, (T_j^n - T_{j-1}^n) = K \, (T_{sj}^{n+1} - T_j^n) \, h , \tag{4}$$

$$\varepsilon_{sj}^n + \varepsilon_{gj}^n = 1 .$$

The system of equations (4) was solved in the following order: initially, the temperature of the polymer and the volume fraction on the $(n + 1)$th time layer were calculated using the factorization method from the difference equations

$$\left(\frac{T_{sj}^{n+1} - T_{sj}^n}{\Delta \tau} \right) = \frac{\lambda_s \left(\dfrac{T_{s,j+1}^{n+1} - 2T_{sj}^{n+1} + T_{s,j-1}^{n+1}}{C_{ps} h^2} \right) - K \, (T_{sj}^{n+1} - T_{gj}^n) + \varepsilon_{sj}^n \, r_{mj}^n \Delta H}{\varepsilon_{sj}^n \, \rho_{sj}^n C_{ps}} , \tag{5}$$

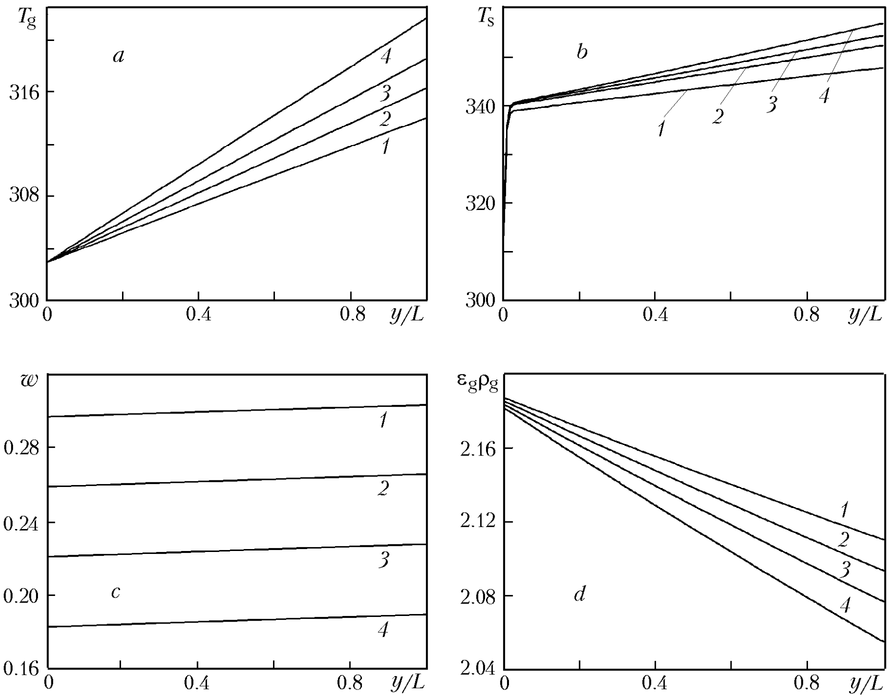

Fig. 2. Distribution of temperatures of the gas flow (a) and polymer layers (b), gas-flow velocity (c), and average gas density characterizing the gas mass in unit volume of the device (d) along the device length at time instants: 1) 900; 2) 1800, 3) 2700, 4) 3600 sec. T_g, T_s, K; w, m/sec; $\varepsilon_g \rho_g$, kg/m^3.

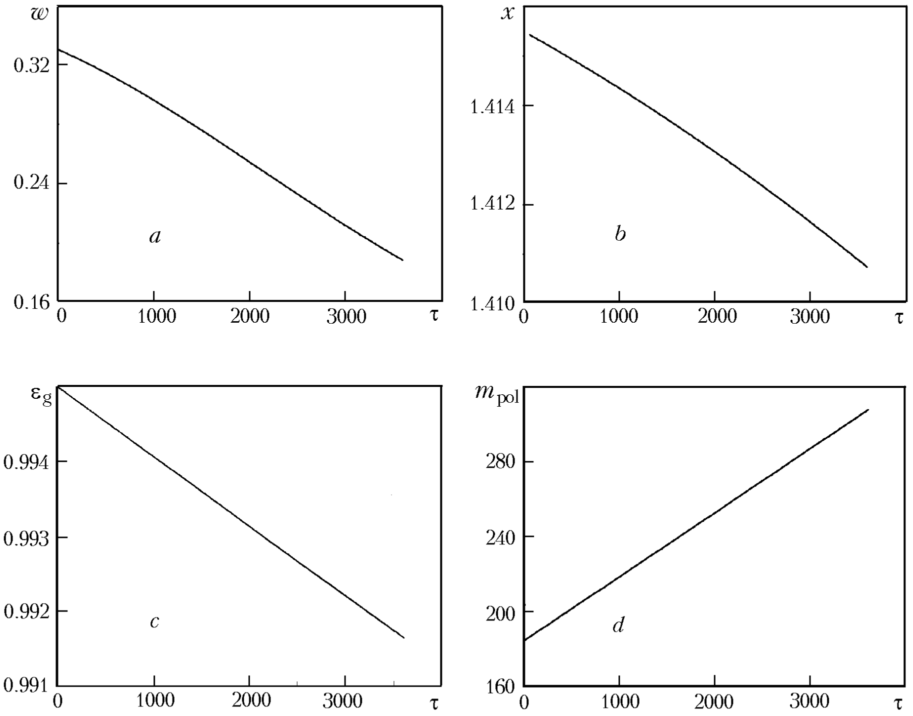

Fig. 3. Variation in the gas velocity $w(\tau, L/2)$ (a), monomer conversion (b), volume fraction of the device free for the gas motion (c), and mass of the formed polymer (d) in 1 h of the polymerizer operation. w, m/sec; x, %, m_{pol}, kg; t, sec.

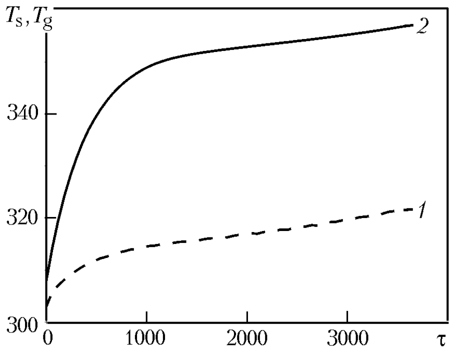

Fig. 4. Time variation of temperatures of the gas flow $T_g(\tau,\ L/2)$ (1) and polymer layers $T_s(\tau,\ L/2)$ (2). T_g, T_s, K; τ, sec.

$$\varepsilon_{sj}^{n+1}\,\rho_{sj}^{n+1}X_{s,polj}^{n+1} - \varepsilon_{sj}^{n}\,\rho_{sj}^{n}X_{s,polj}^{n} = \varepsilon_{sj}^{n}r_{mj}^{n}\Delta\tau\ ,$$

and, afterward, the values of all flow variables were determined using an algorithm, which lay in reducing the system of finite-difference equations (4) for the solid phase to the equation for the velocity w and in selecting one of the roots of this equation. When the gas velocity is known, there is no difficulty in finding the other variables. The values of the temperature of the polymer and gas flow in the penultimate equation of system (4) are taken from different time layers; therefore they are refined by means of iterations.

The calculation was carried out assuming that the polymerization reaction proceeds rapidly and the rate of growth of the polymer is controlled (limited) by the rate of transfer of the monomer, i.e., $\varepsilon_s r_m \approx J_{g,gr}$. The monomer conversion was calculated from the equation

$$x\,(\tau) = \frac{\rho_g wS\Big|_{y=0,\tau=0} - \rho_g wS\Big|_{y=L,\tau=\tau}}{\rho_g wS\Big|_{y=0,\tau=0}}\ .$$

The constructed model provides the calculation of variations in the temperature of the gas phase and polymer layers along the device length, the gas-phase velocity along the device length, the volume fraction of the device that is free for the gas motion, the polymer mass, and the monomer conversion with time. Results of the numerical experiments are presented in Figs. 2–4. The calculations have been performed with account for the return of the outgoing gas flow to the device and for the gas precooling to the initial temperature at the following parameters: $\rho_g(0.0) = 2.2$ kg/m^3; $\rho_s(0.0) = 920$ kg/m^3; $X_{s,b} = 0$; $X_{s,pol} = 1$; $J_{g,s} = 0.00085$ kg/(m^3·sec); $C_{pg} = 1600$ J/(kg·K); $C_{ps} = 1957$ J/(kg·K); $\Delta H = 1{,}342{,}351.8$ J/kg; $K = 30$ W/(m^3·K); $\lambda_s = 0.091$ W/(m·K); $\Delta\tau = 0.005$ sec; and $h = 0.055$ m.

The obtained data show that, even at constant parameters of the gas flow entering the device that is, the gas-velocity distribution in it varies with time as a result of the decrease in the device volume that is free for the gas motion, which affects the temperature distribution of the gas and polymer layers.

The program implementing this model was formed in the Fortran Power Station 4.0 environment. The work was carried out with support from the Russian Foundation for Basic Research, grant No. 03-03-96234, and a Grant of the President of the Russian Federation, "Young Doctors" (No. MD 104-2003-08).

NOTATION

C_{pg} and C_{ps}, specific heats of gas and solid phases, J/(kg·K); f, interphasic friction force, N/m^3; h, step along the device length; I_0, initial concentration of the initiator in the bulk of a solid phase (of the polymer); $J_{g,s}$, rate of transition of butadiene from a gas phase to a solid phase, kg/(m^3·sec); k_i, initiation rate constant; k_{gr}, growth rate constant; $k_{t.m}$, rate constant of transfer of the polymer chain to the monomer; K, volumetric heat-transfer coefficient, W/(m^3·K); $\tilde{K}$, heat-transfer coefficient, W/(m^2·K); L, polymerizer length, m; m, molecular mass of a gas, kg/mole; M, monomer concentration in the bulk of a solid phase (of the polymer); m_{pol}, polymer mass, kg; p, pressure in the device, N/m^2; $P(l)$, concentration of inactive macromolecules (with no active center) in the bulk of a solid phase (of the polymer) with number of links l; R, universal gas constant; $R^* = \sum_{l=1}^{\infty} R^*(l)$, concentration of active macromolecules in the bulk of a solid phase (of the polymer); r_{m}, rate of expenditure of the monomer during the polymerization; S, cross-sectional area of the polymerizer, m^2; T_{g} and T_{s}, temperatures of gas and solid phases, respectively; V, volumetric flow rate of a gas phase at the inlet to the polymerizer, m^3/sec; w, velocity of motion of a gas phase, m/sec; w_j^n, velocity of motion of a gas phase at the nth time layer at the jth point of the device; $X_{\mathrm{s,b}}$ and $X_{\mathrm{s,pol}}$, mass fractions of butadiene and the polymer in a solid phase; x, monomer conversion, %; y, spatial variable, m; ΔH, thermal effect of the reaction, J/kg; $\Delta\tau$, time step; ε_{g} and ε_{s}, volume fractions occupied by a gas and a solid phase (the polymer), which vary during the polymerization; λ_{s}, thermal conductivity of a solid phase, W/(m·K); ρ_{g} and ρ_{s}, true densities of gas and solid phases, kg/m^3; τ, time, sec. Subscripts: g, gas phase; i, initiation; j, number of the point of the device for difference equations; n, number of the time layer for difference equations; m, monomer; gr, growth; s, solid phase; b, butadiene; pol, polymer; t.m, chain transfer to the monomer.

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