Combined Processes of Polymerization and Drying of Prepolymer Grains in Double-Section Apparatus with Fluidized Bed

A. G. Lipin, S. V. Fedosov, and A. A. Shubin

Ivanovo State University of Chemical Technology, Ivanovo, Russia
Ivanovo State Architectural Academy, Ivanovo, Russia

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Abstract—The possibility of combining polymerization and drying in obtaining polymers from derivatives of methacrylic acid was revealed experimentally. A mathematical model of combined polymerization and solvent removal under conditions of a fluidized bed of the material was developed.

Water-soluble polymers based on derivatives of acrylic and methacrylic acids are used in various fields of technology as flocculants, thickeners, water-retaining agents, and substances reducing the hydraulic resistance [1].

Highly promising for manufacture of water-soluble acrylic polymers are continuous methods in which the process is carried out in a set of apparatus, e.g., reactor–extruder–granulator–drying chamber, combined in a single installation.

One of the possible ways to make the technological cycle shorter consists in combining the process of polymerization with high conversion and solvent removal from the reaction mass [2]. In addition, this reduces the power consumption, since moisture is partly evaporated by the heat of the chemical reaction. In synthesizing water-soluble polymers, water is the reaction medium. Therefore, the process of drying must not occur in advance of the polymerization. Otherwise, the reaction terminates at low conversions [3].

To reveal the possibility of combining the processes of polymerization and drying, special-purpose experiments were carried out. The initial stage of synthesis was performed in concentrated aqueous solutions. For example, in copolymerization of sodium methacrylate (SMA) with methacrylamide (MAA), the concentration of the solution of the starting monomers was 66 wt %. The copolymerization was done in the course of 1200 s at 65°C. During this time, the conversion was as high as 67%. Further, the prepolymer was ground and dried.

Selected results of the experiments are presented in Fig. 1 as dependences of the conversion and the humidity of the product on the process time. During the first 1800 s of drying, the conversion became as high as 93, 96, and 98%, and the humidity as low as 25, 23, and 20%, at temperatures of, respectively, 70, 90, and 105°C. Further drying during 13,500 s raises the conversion only slightly. In all experiments, the conversion was 99.5%. The product humidity decreased to 10, 4, and 1%.

The results of the experiments demonstrated that, in the course of prepolymer drying, the rate of the chemical process much exceeds that of solvent (water) removal. Under these conditions, the polymerization process
process goes till virtually complete exhaustion of the starting monomers. Rather effective is performing combined processes in apparatus with fluidized bed.

The performed investigations of the process of copolymerization of SMA with MAA in its final stage allowed development of a mathematical description of drying and additional polymerization of the granulated prepolymer. The description includes units related to chemical kinetics, kinetics of heat-and-mass exchange for isolated particle, and material and heat balances for the apparatus as a whole.

In developing a mathematical model of processes occurring in an isolated inclusion of the dispersed phase, the following assumptions were made: stirring of the material in the fluidized bed is intensive, heat-transfer coefficients are high, small particle size leads to absence of temperature fields, each grain is a micro-reactor operating in the quasistationary mode. The particles are spherical.

In describing the kinetics of SMA copolymerization with MAA, account is taken of the reactions of chain initiation, growth, and termination. The system of kinetic equations for the concentrations of the initiator and monomers and initial moments of the molecular weight distribution has the form [4]

\[
d/d\tau = -k_{dI},
\]

\[
dC_A/d\tau = -k_{pAA}R_AC_A - k_{pBA}R_BC_A.
\]

\[
dC_B/d\tau = -k_{pBB}R_BC_B.
\]

\[
dR_A/d\tau = f_k d + k_{pBA}R_BC_B - k_{pBA}R_BC_B - k_{tAA}R_A^2 - k_{tAB}R_AR,B.
\]

\[
dR_B/d\tau = f_k d + k_{pBA}R_BC_B - k_{pBA}R_BC_B - k_{tBB}R_B^2 - k_{tAB}R_AR,B.
\]

\[
dP/d\tau = k_{tAA}R_A^2 + k_{tAB}R_AR_B + k_{tBB}R_B^2.
\]

where \(I, C_A, C_B, R_A, R_B, \) and \(P\) are the concentrations of initiator, SMA, MAA, growing radicals with SMA and MAA end units, and inactive chains (M); \(\tau\) time (s); \(f\) the efficiency of initiation; \(k_d\) the rate constant of initiator decomposition (s\(^{-1}\)); \(k_p, k_t\) the rate constants of chain growth and termination (M\(^{-1}\) s\(^{-1}\)).

The efficiency of initiation and the rate constants of elementary reactions, which vary in the course of the process, are calculated using the formulas reported in [4]. The grain temperature is found from the heat balance equation

\[
\rho_m(c_m + \bar{U}c_w)\frac{dT}{d\tau} = 6\frac{d}{dv}(T_g - T)
\]

\[= \left(\frac{dC_A}{d\tau} + \frac{dC_B}{d\tau}\right)\Delta H + \frac{d\bar{U}}{d\tau}r\rho_m,
\]

where \(d_{\text{equiv}}\) is the equivalent particle diameter (m); \(\rho_m\) the material density (kg m\(^{-3}\)); \(\alpha\) the heat-transfer coefficient (W m\(^{-2}\) K\(^{-1}\)); \(\Delta H\) the heat effect of polymerization (J mol\(^{-1}\)); \(T\) the particle temperature (°C); \(T_g\) the temperature of the drying agent (°C); \(r^*\) the latent heat of vaporization (J kg\(^{-1}\)); \(\bar{U}\) the absolute humidity of the material (kg kg\(^{-1}\)); \(c_m, c_w\) the specific heats of dry material and water, respectively (J kg\(^{-1}\) K\(^{-1}\)).

The last term in the right-hand side of Eq. (7) accounts for the relationship between heat and moisture transfer processes. The mathematical description is supplemented with an equation characterizing the kinetics of variation of the moisture content of a prepolymer grain. As is known, in drying of materials with high diffusion resistance to moisture transfer, to which also belongs the copolymer of SMA with MAA, the equilibrium humidity is virtually instantaneously attained on the body surface [5]. In this case, the variation of the moisture-content field in a material being dried is described by a differential mass-transfer equation with a boundary condition of the first kind with variable coefficient of moisture transfer. For a spherical particle we have

\[
\frac{\partial U(r, \tau)}{\partial \tau} = \frac{k_m(\bar{U}, T)}{r} \left[ \frac{1}{r} \frac{\partial^2(rU)}{\partial r^2} \right],
\]

\[
0 \leq r \leq R, \; \tau > 0,
\]

\[
\frac{\partial U(0, \tau)}{\partial r} = 0, \; U(0, \tau) \neq \infty,
\]

\[
U(R, \tau) = U_p,
\]

\[
U(r, 0) = U_{in}.
\]

The moisture-transfer coefficient \(k_m(\bar{U}, T)\) is a complex function of the moisture content and temperature of a particle. Exact analytical solution of the problem (8)–(11) is impossible. An approximate solution to this problem will be sought for in the classical form [5] at finite number of expansion elements:

\[
U(x, \tau) = U_p + (U_0 - U_p)R \sum_{j=1}^{\infty} A_j(\tau) \sin \left( \pi \frac{r}{R} \right).
\]

Let us use the Petrov–Galerkin method [6]. We substitute a trial solution (12) into Eq. (8) and require