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VAPOR-BUBBLE GROWTH IN A SUPERHEATED POLYMER SOLUTION

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Vapor-bubble growth in a superheated polymer solution is studied. Superheating is achieved by a pressure drop at the initial time instant. The process is numerically analyzed on the basis of a model allowing for the formation of a thin surface layer with an elevated concentration of polymer around the bubble.

The use of polymer liquids in the heat treatment of metals, in thermal power plants, and in cooling systems stimulates interest in the theoretical investigation of boiling processes in binary polymer-solvent systems. A central part in these investigations, as well as for low-molecular liquids [1], is occupied by the study of the processes of interphase interaction at the level of individual bubbles.

In [2] the growth and collapse of a spherical cavity in a polymer liquid are studied with allowance for rheological effects only, and in [3] small-amplitude pulsations of vapor bubbles in solutions of high-molecular compounds are analyzed without allowance for diffusion phenomena in the liquid phase. The growth of vapor bubbles in a binary solution of low-molecular liquids was studied in [4]. Outburst boiling-up of highly superheated macromolecular systems was experimentally studied in [5, 6]. In the present paper we consider the nonlinear problem of the growth of a vapor cavity in a superheated polymer fluid on the basis of a model that allows for both heat and mass transfer and rheological effects in the liquid phase. The evolution of a bubble is considered within the framework of a spherically symmetric scheme. The parameters inside the inclusion are assumed to be homogeneous and independent of the spatial coordinate [4].

Within the framework of the assumptions adopted, the equations of state and of the change in the mass of the vapor phase have the form

$$p_1 = \frac{\rho_1 BT}{\mu}, \tag{1}$$

$$\frac{R}{3}\dot{\rho}_1 + \dot{R}\rho_1 = J. \tag{2}$$

Interphase heat and mass exchange is determined by transport processes in the liquid phase, to describe which we use the equations of heat conduction and diffusion:

$$\frac{\partial T_2}{\partial t} + v_R \frac{R^2}{r^2} \frac{\partial T_2}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(a_2 r^2 \frac{\partial T_2}{\partial r} \right), \tag{3}$$

$$\frac{\partial k}{\partial t} + v_R \frac{R^2}{r^2} \frac{\partial k}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D r^2 \frac{\partial k}{\partial r} \right). \tag{4}$$

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The boundary conditions on the phase interface and at a distance from the bubble can be written in the form

$$(T_2)_R = T_1 = T_s (p, k_R) ; \quad (k)_R = k_R ; \quad \int ! = \lambda_2 \left(\frac{\partial T}{\partial r}\right)_R ;$$
$$(1 - k_R) J = \rho_2 D \left(\frac{\partial k}{\partial r}\right)_R ; \quad (T_2)_\infty = T_0 ; \quad (k)_\infty = k_0 . \tag{5}$$

To describe the dependences of saturation temperature above the solution on pressure and concentration we use the Flori–Huggins equation obtained within the framework of the thermodynamic theory of solutions of flexible-chain polymers [7]

$$\frac{p}{\bar{p}} = \varphi_1 \exp [1 - \varphi_1 + \chi (1 - \varphi_1)^2] ; \quad \varphi_1 = k_R [k_R + (1 - k_R) K_\rho]^{-1} . \tag{6}$$

In selecting a rheological model to describe the behavior of the carrying phase one should take into account the fact that radial flows originating in oscillations of inclusions in a polymer medium refer to elongational ones. Due to this, the coincidence of the character of the dependence of longitudinal viscosity, predicted by the model, on the rate of longitudinal deformation should be one of the criteria of such a selection. To qualitatively analyze the effect of the factor of rheological nonlinearity on the dynamics of bubbles in a polymer medium one can use the following equation with one relaxation time [8]:

$$\tau = \tau^{(1)} + \tau^{(2)} ; \quad \tau^{(2)} = 2\eta (1 - \beta) e ; \quad \tau^{(1)} + \lambda \left[\frac{D\tau^{(1)}}{Dt} - \alpha (\tau^{(1)} \cdot e + e \cdot \tau^{(1)})\right] = 2\eta\beta e .$$

Here β characterizes the contribution of the Maxwellian element to the effective viscosity of the medium, and the parameter $1/2 \le \alpha \le 1$ controls the effect of nonlinear terms. In derivation of the Rayleigh equation one assumes that during the growth of a vapor bubble, due to intense evaporation of the solvent, a thin layer of fluid with an elevated polymer concentration forms around the inclusion. Since the layer thickness is very small, it can be assumed that the components of the stress tensor are approximately equal to the mean value. The contribution to the generalized Rayleigh equation of stresses arising inside a diffusion boundary layer is allowed for within the framework of a linear approximation over ε. The contribution of fluid rheology beyond the limits of the surface layer is found to be similar to [8]. As a result we have

$$\rho_2 \left(R\ddot{R} + \frac{3}{2}\dot{R}^2\right) + p_2 (\infty) - p_1 (t) + \frac{2\sigma}{R} = S ;$$

$$S = S^{(1)} + S^{(2)} + S^{(3)} ; \quad S^{(2)} = - 4\eta (1 - \beta) \dot{R} R^{-1} ;$$

$$S^{(1)} = - \frac{2\beta\eta}{\alpha\lambda R^{4\alpha} (t)} \int_0^t \exp \left[\frac{\xi - t}{\lambda}\right] \frac{R^{6\alpha} (\xi) - R^{6\alpha} (t)}{R^3 (\xi) - R^3 (t)} \times$$
$$\times R^{2(1-\alpha)} (\xi) \dot{R} (\xi) d\xi ; \tag{7}$$

$$S^{(3)} = \varepsilon (\tau_{10} - \tau_{20}) + \frac{4\beta\eta\varepsilon}{\lambda R^{4\alpha} (t)} \int_0^t \exp \left[\frac{\xi - t}{\lambda}\right] \frac{\dot{R} (\xi) d\xi}{R^{1-4\alpha} (\xi)} +$$
$$+ 2\beta\eta R^{2\alpha} (t) \lambda^{-1} \int_0^t \exp \left[\frac{\xi - t}{\lambda}\right] \dot{R} (\xi) R^{-1-2\alpha} (\xi) d\xi .$$

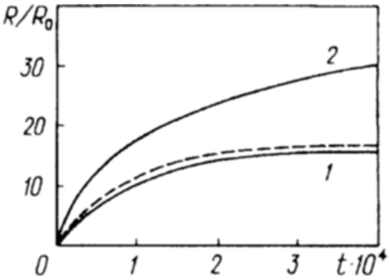

Fig. 1. The growth of vapor-bubble radius as a function of time. $R_0 = 10^{-5}$ m, $p_0 = 10^5$ Pa, $k_0 = 0.9$: 1) $p_1 = 0.8 \cdot 10^5$ Pa; 2) $0.6 \cdot 10^5$. t, sec.

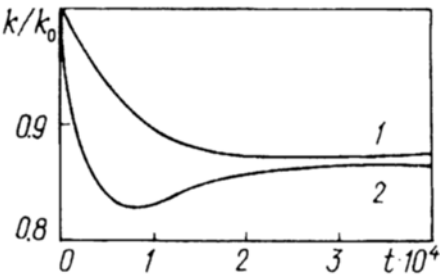

Fig. 2. Change in the relative concentration of solvent on the inclusion surface. For the notation see Fig. 1.

The terms $S^{(1)}$ and $S^{(3)}$, which characterize the effect of the non-Newtonian part of the stress tensor on the bubble evolution, can be determined from a system of first-order differential equations for the boundary values of the coefficient α, thus making it possible to considerably simplify the calculation. In particular, at $\alpha = 1/2$ we obtain the equations

$$S^{(1)} + S^{(3)} = L_1 + \varepsilon\,(\tau_{10} - \tau_{20} - L_1 + L_2)\,; \quad \dot{L}_1 + L_1\left(\frac{1}{\lambda} + \frac{2\dot{R}}{R}\right) = -\frac{4\beta\eta\dot{R}}{\lambda R}\,;$$

$$\dot{L}_2 + L_2\left(\frac{1}{\lambda} - \frac{\dot{R}}{R}\right) = \frac{2\beta\eta\dot{R}}{\lambda R}\,.$$

To perform calculations one should first determine the values of physical parameters characterizing the liquid-bubble system. The time of fluid relaxation was estimated on the basis of the Kargin–Slonimskii–Rauz molecular-kinetic theory [9] by the formula

$$\lambda = \frac{0.608\,(\eta_{\mathrm{sol}} - \eta_{\mathrm{s}})\,M}{cBT}\,. \tag{8}$$

To describe the dependence of the solution viscosity on the polymer concentration the Martin empirical equation can be used, which is valid for many polymers within a wide range of concentrations [7]:

$$\frac{\eta_{\mathrm{sol}}}{\eta_{\mathrm{s}}} = 1 + \tilde{c}\exp(k_m \cdot \tilde{c})\,; \quad \tilde{c} = c\,[\eta] = cKM^{\gamma}\,. \tag{9}$$

The influence of the liquid temperature on the rheological parameters of the system was taken into account within the framework of the theory of viscous flow, according to which

$$\eta_{\mathrm{sol}} = \eta_{\mathrm{sol0}}\exp\left[\frac{E_{\mathrm{sol}}}{BT_0}\left(\frac{T_0}{T} - 1\right)\right]; \quad \eta_{\mathrm{s}} = \eta_{\mathrm{s0}}\exp\left[\frac{E_{\mathrm{s}}}{BT_0}\left(\frac{T_0}{T} - 1\right)\right], \tag{10}$$

and the principle of the temperature-frequency superposition [9]. For the coefficient of binary diffusion, the approximation of [10] was used, which rather accurately described the experimentally found dependence of the constant of diffusion transfer on temperature and concentration for a solution of polystyrene in toluene.

System of equations (1)-(10) can be solved only numerically. Difference equations were constructed by the integro-interpolation method with the liquid around the bubble being divided to spherical layers. The variable $\xi = r/R(t)$, which "freezes" the movable boundary of phase transition, was used. Numerical calculations were performed for the example of a dilute solution of polystyrene in toluene, which is a good organic solvent for many polymers.

In Fig. 1 the radius–time dependence for various superheatings due to a pressure drop at the initial time instant is shown. The dashed curve illustrates the behavior of a vapor bubble in toluene under conditions similar to those of curve 1. It is seen that the introduction of a small amount of polymer to the liquid does not lead to a

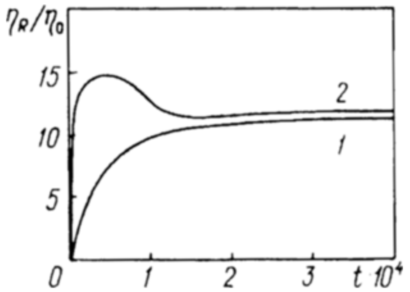

Fig. 3. The solution viscosity at the vapor bubble boundary as a function of time. For the notation see Fig. 1.

considerable decrease in the rate of vapor-bubble growth. This occurs thanks to the presence of a nearly horizontal plateau on the curve of liquid–vapor phase equilibrium in the coordinates T, k in the range of small polymer concentrations [11].

The dependence of the solvent concentration at the bubble boundary on time is shown in Fig. 2. In the case of insufficient superheating and, correspondingly, of a smooth increase in the radius of the inclusion, the drop in concentration at the boundary is monotonic. In the opposite case, diffusion transport does not compensate for the intense evaporation of solvent from the solution, and at the initial stage of the process there is a considerable decrease in k. Then, due to the retardation of bubble growth, the balance between solvent evaporation and entry from the volume is restored, and the surface polymer concentration reaches an asymptotic value corresponding to the self-similar solution of the problem at $(t \to \infty)$ [11]

$$\frac{\Delta T}{\Delta T_*} = \left[1 - c_2 l^{-1} (1 - k_R) \sqrt{\mathrm{Le}} \left(\frac{\partial T_s}{\partial k}\right)_{k=k_0}\right]^{-1}; \quad R \approx h\sqrt{t}; \quad \Delta T_* = T_{20} - T_s(k_0);$$

$$h = \sqrt{12 a_2 \pi^{-1}}\, \mathrm{Ja}; \quad \mathrm{Ja} >> 1 .$$

The calculated curves in Fig. 3 show the correspondence between the changes in concentration and viscosity of the solution on the inclusion surface. As is seen, during the growth of a vapor bubble in a superheated solution, a thin layer with a high content of polymer is formed around it, thus explaining some experimentally found effects, viz., the stabilization of a spherical shape and the reduced tendency of bubbles to coalesce in boiling solutions of macromolecules [12, 13].

Calculations similar to those considered above were also performed for concentrated systems at $k_0 \sim 0.5$. In these systems, the phenomenon of diffusional retardation of bubble growth is much stronger than in dilute solutions. At the same time, the manifestation of relaxation properties of liquid weakens, to a great extent, dissipative losses caused by the growth in the non-Newtonian viscosity of the liquid for large polymer contents.

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NOTATION

p, pressure; B, universal gas constant; T, temperature; M, relative molecular mass of polymer; R, bubble radius; ρ, density; J, rate of phase transitions; k, concentration of solvent; D, coefficient of binary diffusion; λ_2, thermal conductivity; a_2, thermal diffusivity; l, specific heat of vapor generation; v, velocity; $\bar{p}$, pressure of saturated vapors above a pure solvent; φ_1, volumetric concentration of a volatile component; χ, Flori–Huggins parameter; K_p, ratio of specific volumes of polymer and solvent; λ, relaxation time; η, solution viscosity; ε, ratio of diffusion-layer thickness to bubble radius; σ, surface tension coefficient; τ and e, tensors of excess stress and deformation rate; τ_{10} and τ_{20}, radial and tangential components of stress tensor at the bubble boundary; c, concentration of polymer in the solution; k_m, Martin constant; K and γ, constants for given solvent and temperature within a certain range of change in molecular mass; E, activation energy of viscous flow; [illegible], Lewis number for liquid phase; Ja, Jacobs number; c_2, specific isobaric heat capacity of solution; D/Dt, Jaumann derivative. Subscripts: 1, 2, correspond to vapor and liquid phases; sol and s, solution and solvent; 0, initial state of the system; R, the value at the bubble boundary.

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