

Degasification of Polymer-Composite Solutions via Ultrasonic Dispersion

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Abstract—The parameters and conditions defining liquid degasification upon ultrasonic treatment have been considered. Ultrasonic treatment has been applied to F-40 elastic polymer composite, and the effect of the ultrasonic-field parameters on the degasification efficiency is shown.

Keywords: polymer solution, filler, composite, ultrasound, cavitation, stirring, dispersion, degasification

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INTRODUCTION

The main defects in polymer coatings are the pores that initiate the coating destruction. They arise owing to gas-bubble release from a liquid polymer during its polymerization, especially at high temperature [1]. Providing the conditions for reducing the coating porosity is an important technical task [2, 3]. This study is thus aimed at determining the parameters for effective degasification of polymer-composite solutions (PCSs) via ultrasonic dispersion.

Degasification is a process accompanied by a decrease in the gas content in a liquid under ultrasonic vibrations. Ultrasonic degasification assumes the presence of nuclei in the form of stable gas bubbles in the liquid, which possess specific properties allowing their stable existence even at high hydrostatic pressure. In a liquid medium (i.e., liquid metals) containing solid nonwetted impurities, the gas phase is also present in microscopic irregularities of their surfaces [4]. In the polymer-composite solution filled with dispersed metal particles, the gas phase will be at the micro- or nanoirregularities of the nanofiller particle surfaces [5]. When the sound intensity is above the cavitation threshold, it causes the formation of new fragmentation nuclei in the liquid due to the collapse of bubbles, leading to a doubling in the total amount of nucleus bubbles.

Ultrasonic degasification consists of two stages. In the first one, the gas bubbles vibrate in the acoustic field, and their dimensions increase owing to the diffusion of the gas dissolved therein. In addition to diffusion, the augmentation of bubble sizes is due to coalescence, or merger of bubble pairs and groups under the action of hydrodynamic flows (Bernoulli forces) and acoustic jets (Bjerknes forces). At the sec-

ond gasification stage, the gas bubbles, having achieved certain sizes, rise to the liquid surface with their subsequent release into the environment. The condition of gas-bubble ascent in a liquid metal has the form [6]

$$P_{H_2} > P_0 + h\rho + \frac{2\sigma}{r}, \quad (1)$$

where P_{H_2} is the gas pressure in the bubble, P_0 is the atmosphere pressure at the bath surface with the solution, h is the solution column height above the bubble, ρ is the solution density, σ is the surface tension of the solution, and r is the bubble radius.

As follows from Eq. (1), the larger the density and the surface tension of the liquid, the higher the expected gas pressure in the bubble for its ascent. Ascent velocity v of the bubble onto the surface can be evaluated from the Stocks equation:

$$v = \frac{2}{9} g \frac{r^2}{\mu} (\rho - \gamma), \quad (2)$$

where g is the gravitational acceleration, μ is the dynamic viscosity of the melt, ρ is the solution density, and γ is the gas density.

It follows from Eq. (2) that, the smaller the liquid viscosity, the higher the ascent rate of the bubble onto the surface. The calculation of the main degasification characteristics, such as degasification rate dC/dt and quasi-equilibrium concentration C_p' (the constant gas-bubble concentration achieved in the liquid during ultrasonic treatment (UST) after a certain time interval) is a complicated problem that was significantly simplified by B.A. Agranat in [4] by considering the diffusive degasification mechanism.

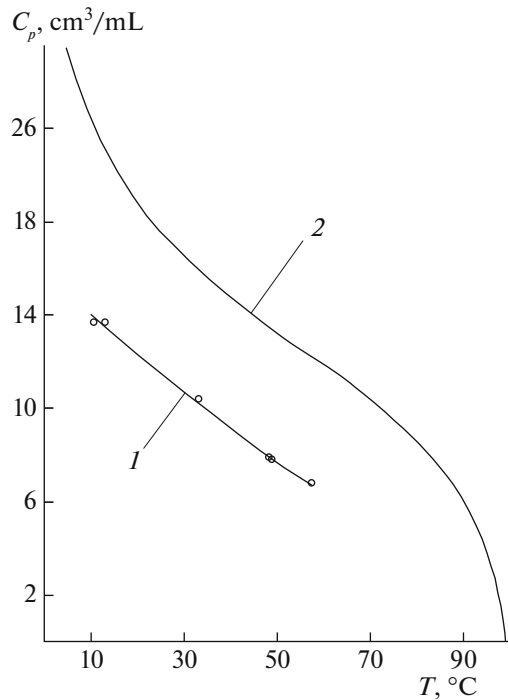


Fig. 1. Equilibrium air concentration in water as a function of temperature at static pressure of 0.1 MPa [7]: (1) US treatment of water at a frequency of 22 kHz; (2) untreated water.

True degasification is a release of solved gas with a decrease in its concentration in the liquid to values below the equilibrium ones owing to diffusion. The alteration in the gas concentration in the liquid in the acoustic field for the irradiation period is defined by the expression

$$C = C_p' + (C_0 - C_p')e^{-\beta t}, \quad (3)$$

where C_0 is the initial concentration; t is the time; β is the parameter determined by the acoustic characteristics (sound intensity I and sonic vibration frequency f); $\beta = A(E - E_0)^n$, where A and n are coefficients with values that depend on the acoustic conditions; and E_0 is the minimum density of energy E at which degasification is still observed.

There are two ultrasonic degasification modes that accompany precavitation and ultrasonic cavitation. In the precavitation mode, the rate of change in gas concentration in the liquid V_c is proportional to sound intensity I , while its empirical dependence on frequency f has the form

$$\frac{dC}{dt} = V_c = Bf^n e^{-kt}, \quad (4)$$

where B , n , and k are constants.

The experimental studies in [7] revealed that quasi-equilibrium concentration C_p' shows no dependence on frequency f and intensity I of the ultrasonic vibrations. In the liquid, independently of vibration frequency f and energy density E of the sound field, the same quasi-equilibrium concentration C_p' value is achieved over the corresponding time ranges.

In the cavitation mode, the rate of concentration change V_c rises with increasing sound intensity faster than in the precavitation mode; i.e., the cavitation accelerates the release of gas from the liquid. This dependence is nonlinear. However, at a very high sound intensity, there a cavitation bubble vibration mode is possible in which a further increase in the intensity inhibits the degasification. This concerns the pulsating second-group gas cavities, the initial sizes of which are superior to the resonance one. They are considerably larger with expansion, but have no time for impact in the cavity-compression phase, pulsating near a certain average maximum gas-cavity radius. The effective dispersion condition $2P_0 \leq \delta P_A < 10P_0$ is thus valid, being also an effective degasification condition of a polymer solution.

Gas concentration C in the liquid depends on frequency f and intensity I of the ultrasonic vibrations and on the time of UST as follows: the larger f and I at the same t , the lower C . The frequency and intensity of ultrasonic vibrations exert almost no influence on quasi-equilibrium concentration C_p' , but determine the rate of change in quasi-equilibrium concentration V_c so that the latter increases with f in accordance with Eq. (4). As follows from experiments conducted at various temperatures, the higher the temperature of the liquid, the lower the quasi-equilibrium concentration achieved under the effect of sound (Fig. 1).

Since the collapse of the third-group gas cavities in the microvolumes of solution is accompanied by the emergence of high pressures to 100 MPa and the temperature increases to 1000°C, the solution of F-40 elastomer exposed to UST is expected to increase its temperature and decrease quasi-equilibrium concentration C_p' ; i.e., the gas-bubble concentration decreases in comparison with the solution at 20°C.

It was proposed to evaluate the impact of the ultrasonic vibrations of liquid on the steady gas concentration using dimensionless parameter $\gamma = (C_p - C_p')/C_p'$, where C_p is the equilibrium gas concentration in the absence of ultrasonic vibrations. At a static pressure of 0.1 MPa and 20°C, the γ value is 0.3 (30%). With the decreasing static pressure, the γ parameter increases, attaining 0.7 (70%) at a pressure of 0.05 MPa [8].

The reducing hydrostatic pressure causes a decrease in quasi-equilibrium concentration C_p' , i.e., a

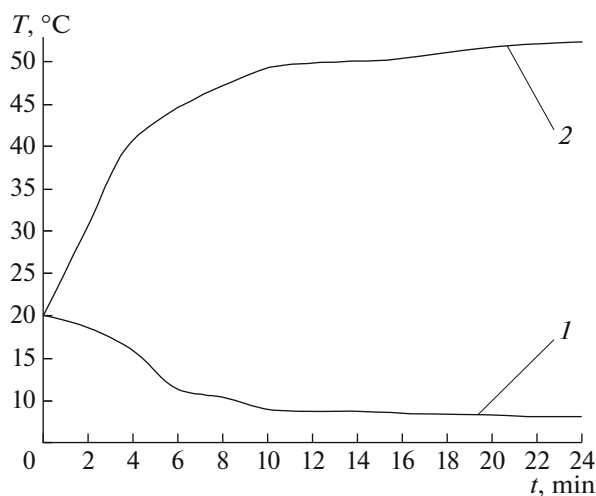


Fig. 2. Temperature T of F-40 elastomer composite as a function of stirring time t : (1) manual mechanical stirring; (2) US treatment.

decrease in the gas concentration in the solution. Nevertheless, a decrease in the hydrostatic pressure necessitates a vacuum setup, which complicates the technique and UST equipment. It is also worth mentioning that the reducing hydrostatic pressure is accompanied by a decrease in the erosion-activity criterion or with a decrease in the dispersion efficiency of fillers in the PCM solution. A UST of the PCM solution at atmosphere pressure is thus more preferable.

The correctness of the theoretical investigation results was verified by means of a control experimental study of degasification of F-40-elastomer-based PCM solution via the manual stirring of metal-filler particles with a polymer matrix and via ultrasonic dispersion. Figure 2 displays temperature T of the solution of F-40 elastomer as a function of stirring time t . As follows from Fig. 2, the temperature of solution of F-40 elastomer decreases during manual mechanical stirring. It diminishes most rapidly after first 8 min (from 20 to 9.1°C), showing a nonlinear behavior, and then stabilizes for 16 min, linearly decreasing from 9.1 to 8°C. This is probably due to the evaporation of acetone causing a refrigerating effect.

A completely different situation is observed upon ultrasonic treatment of solution of F-40 elastomer, where the temperature, it was assumed, increases. The rapidest increase in the temperature, from 20 to 48.8°C, takes place for the first 10 min of UST with respect to a nonlinear dependence. It then stabilizes after 14 min and increases linearly from 48.8 to 53.8°C. The temperature increase is here due to the above-described reasons.

Figure 3 depicts residual weight m of the solution of F-40 elastomer as a function of time of stirring t . Evi-

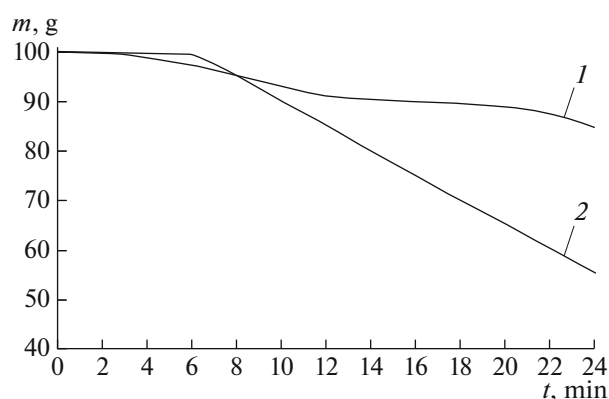


Fig. 3. Residual weight m of solution of F-40 elastomer as a function of stirring time t : (1) manual mechanical stirring; (2) US treatment.

dently, the higher the amount of evaporated acetone, the lower the residual weight of the polymer-composite solution. The weight of the evaporated acetone is almost equal for both methods of stirring after the first 4–6 min of the process, but it strongly differs in the subsequent 18–20 min, showing a decrease from 101.5 to 83.4 g upon manual stirring and to 56.8 g during UST. The amount of acetone evaporated upon UST is 2.5 times higher than after the manual stirring of solution of F-40 elastomer, which confirms the validity of the theoretical statements.

CONCLUSIONS

(i) In polymer solutions with smaller viscosity the rate of the gas-bubble ascent at the surface is higher and the conditions for degasification via the ultrasonic treatment are more favorable.

(ii) The degasification rate increases with the frequency and intensity of ultrasonic vibration, and the gas content is thus decreased in the polymer solution.

(iii) The UST of PCM solution increases its temperature and causes a decrease in quasi-equilibrium concentration C_p' due to the cavitation; i.e., the gas bubble concentration is lower than the standard temperature (20°C), and the ultrasound dispersion of PCM solutions favors their efficient degasification and shrinks the porosity of the coatings applied from the PCM solution.

(iv) The amount of acetone evaporated upon UST is 2.5 times higher than after the manual stirring of F-40 elastomer polymer composite, decreasing the porosity and improving the quality of its polymer coatings.

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