

The model of ultrasonic cavitation depolymerization

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ABSTRACT: *The paper presents the model of ultrasonic cavitation depolymerization which is destruction of polymer macromolecules under cavitation. The model is based on probability approach which is allow to reduce the task of cavitation depolymerization calculation to solve the system of self-similar equations for macromolecules with different weights concentration. The equations include probability of macromolecules destruction. The probability is determined by cross-section of collision of macromolecules pair and possibility of macromolecule destruction at contact with another molecule. The calculations have shown that the cavitation reduces the modal molecular weight up to 2 times. It causes reducing the polymer viscosity up to 10 times.*

Keywords – *Ultrasonic, cavitation, polymer, macromolecule, destruction*

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I. INTRODUCTION

The modern development of machine-building, instrument making, medicine, transport, aviation and rocket and space technology is determined by the newly created construction materials with improved mechanical properties [1]. The main task of today is the creation of new samples of materials by solving two mutually exclusive tasks, which are the simultaneous provision of low specific gravity and high strength properties of materials. A promising and successfully developing direction for solving this problem is the creation and use of polymeric materials, which turn out to be more than 5 times lighter than traditional metals and alloys. However, it is impossible to ensure the necessary strength properties of polymers without modifying their physicochemical structure [1, 2].

Among the known methods for modifying the structure of polymers, the most developed method is based on the introduction of dispersed fillers during the formation of polymer compositions. However, the threshold strength of polymer compositions, which does not cause microcracks and does not retain residual deformations, reaches no more than 150 MPa, even when carbon nanotubes are present and less than 50 nm in size [3]. This is due, both, to the insufficient interaction surface of the polymer binder and filler, and to the heterogeneity of the molecular structure of the polymer caused by a large number of monomeric units (up to 10,000). A promising way to increase the interaction surface of the binder with the filler and homogenize the high-molecular compound is the preliminary ultrasonic (US) cavitation effect on the material in the uncured state [2, 4]. The ultrasonic action in the cavitation mode allows us to concentrate the energy of the oscillations propagating in the medium into the energy of cavitation bubbles in which local temperature rises up to 5000 K, and when they explode, shock waves with a pressure amplitude up to 1000 MPa occur. This leads to the destruction of molecular bonds, ensures the homogeneity of the structure of a multicomponent material, the uniform distribution of reinforcing particles, and can enhance the strength properties of the material in all directions of deformation [2, 6]. Purposeful obtaining of a material with the necessary properties for a particular application requires selection of ultrasonic cavitation impact modes.

To date, the most fully studied influence of the ultrasonic modes of cavitation effect on the increase in the total surface of the reinforcing particles of the filler polymer material [5, 6]. While the effect of cavitation on the structure of polymer macromolecules has not been studied in detail until today. In connection with this, a model of cavitation effect on the molecular structure of a polymer should be developed. The model will make it possible to reveal the dependence of the change in the structure of molecules on the modes of cavitation influence.

The developed model is described in following section.

II. THE POSTULATES OF CAVITATION DEPOLYMERIZATION MODEL

Polymers in the uncured state are liquid media consisting of molecular chains of monomers connected by hydrogen bonds. Cavitation leads to the destruction of molecular chains (cavitation depolymerization). At the same time, the fractional composition of molecular chains by the concentration of molecules with different amounts of monomeric units determines the rheological properties of the material and the strength properties after curing. Thus, the proposed model is aimed at to determine fractional composition of molecular chains and rheological properties during cavitation depolymerization in dependency on starting viscosity, influence intensity and time. The proposed model of cavitation depolymerization based on following physical mechanism of macromolecules destruction under cavitation. The shock waves generated by cavitation cause increasing the dispersion of velocity of macromolecules, because around cavitation bubble the pressure rises sharply. Due to it the amount of molecules pairs with relative velocity more than critical (at the critical velocity one of the molecules is destroyed at collision) increases.

The assumptions used for the model development are following.

- 1) The macromolecule has a linear structure consisting of serially connected monomer units through equal distances r_e (the model of a Gaussian sub chain or "spring beads").
- 2) The distribution of macromolecules over the velocities of the centers of mass obeys a Gaussian law (the Maxwell's distribution).
- 3) The pairing of collisions of macromolecules (the probability of simultaneous collision of 3 or more macromolecules is negligible).
- 4) For each elementary act of collision of macromolecules, it is possible to destroy an individual molecule (with the number of monomer units i) by only two particles with the numbers of monomer units M and $i-M$.
- 5) The disruption of the macromolecule occurs only at the point of its contact with another molecule during the collision.
- 6) The probability of rupture of a macromolecule depends weakly on the position of its point of contact with another molecule, since the number of monomeric links $i \gg 1$.
- 7) The cavitation bubble size is much more than single macromolecule size.
- 8) The polymeric liquid is almost incompressible during the cavitation bubble expansion, because Mach's number is small:

$$v = \frac{4R_{\max}}{T} < 15 \frac{m}{s};$$

$$M = \frac{v}{c} < 0,01;$$

where R_{\max} is maximum radius achieved after expansion of bubble, m; T is period of ultrasonic oscillations, s; c is speed of sound in the liquid, m/s.

- 9) The viscosity of polymeric liquid does not influent on the cavitation bubble collapse due to large Reynolds number:

$$Re = \frac{vd\rho}{\mu} > \frac{v_{\min}d_a\rho}{\mu_{\max}} = \frac{1500 \frac{m}{s} \cdot 100 \cdot 10^{-6} m \cdot 1000 \frac{kg}{m^3}}{1 Pa \cdot s} = 150;$$

where v_{\min} is the typical speed of bubble wall during collapse, m/s; d_a is the typical of bubble size; ρ is the typical of liquid density, kg/m³; μ_{\max} is the maximum viscosity of the liquid, Pa·s.

On the presented assumptions the model is based. The model includes four stages presented on Fig. 1.

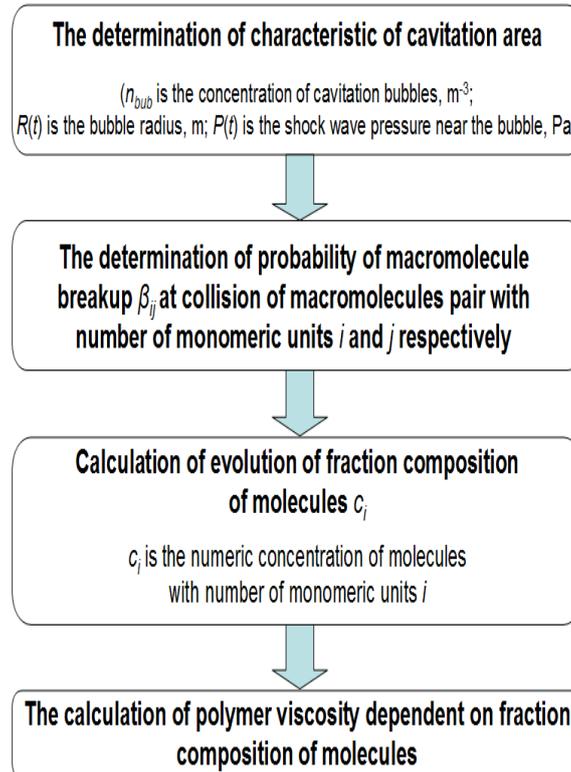


Fig. 1. The stages of theoretical analysis of cavitation depolymerization

Each stage allow to obtain own results which is input data for next stage. The first stage is for determination of characteristic of cavitation area dependent on US oscillations intensity and polymer viscosity at the current time moment. The last stage allows to determine the polymer viscosity of fraction composition of molecules and finally to determine the polymer viscosity dependency on time and intensity influence.

Further the sub model of cavitation bubbles formation realized the first stage of theoretical analysis is described in details.

III. THE SUB MODEL OF CAVITATION BUBBLES FORMATION

The characteristics of cavitation area are based on equations of cavitation bubble during expansion (1) and collapse (2):

$$R \frac{\partial^2 R}{\partial t^2} + \frac{3}{2} \left(\frac{\partial R}{\partial t} \right)^2 = H ; \tag{1}$$

$$R \frac{\partial^2 R}{\partial t^2} \left(1 - \frac{\partial R}{C} \right) + \frac{3}{2} \left(\frac{\partial R}{\partial t} \right)^2 \left(1 - \frac{\partial R}{3C} \right) = H \left(1 + \frac{\partial R}{C} \right) + \frac{\partial H}{\partial t} \frac{R}{C} \left(1 - \frac{\partial R}{C} \right) ; \tag{2}$$

$$H = \int_{p_\infty}^{p_w} \frac{\partial p}{\rho(p)} ; p_\infty = p_0 - \sqrt{2\rho c I} \sin(2\pi f t) ;$$

where H is liquid enthalpy depending viscosity, m^2/s^2 ; C is local sound speed of liquid, m/s ; p_∞ is the pressure on the large distance from bubble, Pa ; p_0 is the atmospheric pressure, Pa ; f is the frequency of ultrasonic oscillations, Hz ; t is the time, s ; c is the equivalent sound speed in the cavitating liquid, m/s ; ρ is the equivalent density of cavitation liquid, kg/m^3 ; I is the intensity of ultrasonic influence, W/m^2 ; p_w is the liquid pressure depending on viscosity near the bubble wall, Pa .

The equation (1) determine cavitation bubble radius $R(t)$ during expansion. The equation (2) determine cavitation bubble radius $R(t)$ shock wave pressure (near bubble wall) $P(t) = p_{st} \left(\frac{R_{st}}{R(t)} \right)^{3\gamma}$ (γ is the adiabatic constant for gaseous in bubble; p_{st} is the pressure in bubble interior at the radius R_{st} (m), Pa) during collapse.

For the determination of last characteristic of cavitation area which is bubble concentration n_{bub} the local area with sizes much less than US wave length but much more than cavitation bubble radius. The schematic image of the local area is presented in Fig. 2.

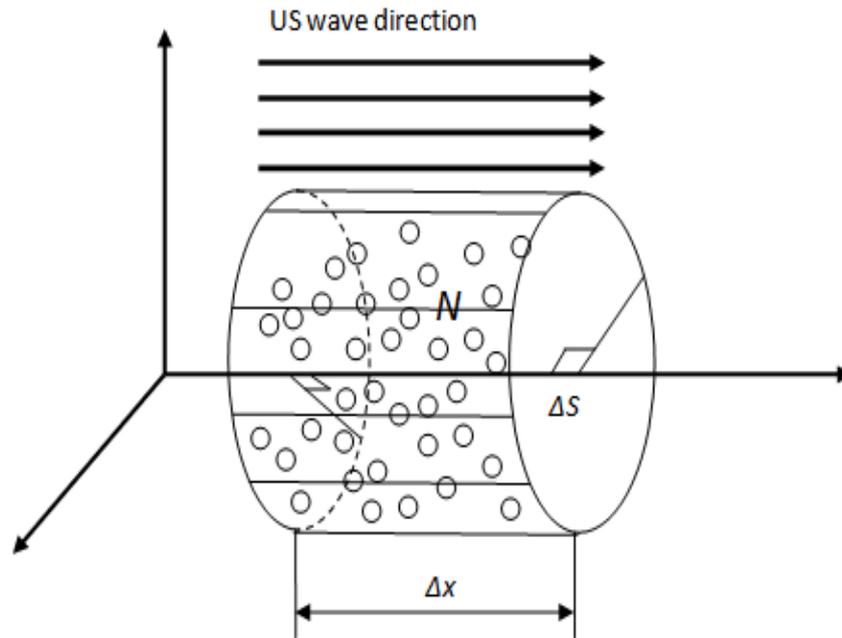


Fig. 2. The schematic image of considered local area for bubbles concentration determining

According to the scheme the concentration of bubbles is determined as (3) [7]:

$$n_{\infty} = \frac{2(j-1)}{25\pi R_{MAX}^2 i |\mathbf{d}_{12}(T) - \mathbf{d}_{12}(0)|}; \tag{3}$$

where j is the number of cavitation nuclei formed after single bubble collapse [7]; R_{MAX} is the cavitation bubbles radius determined from (1, 2), m; i is number of periods of oscillations required for single expansion-collapse of bubble cycle; T is period of US oscillations, s; \mathbf{d}_{12} is the vector of distance between centers of bubble pair, m.

The vector of distance \mathbf{d}_{12} is determined by equation of motion of interacting bubbles pair (4):

$$\begin{aligned} \frac{4\pi R_0^3}{3} \rho_G \frac{\partial^2 \mathbf{d}_{12}}{\partial t^2} = & -2 \frac{4\pi R^3}{3|\mathbf{d}_{12}|^3} \rho_L \frac{\partial \left(R^2 \frac{\partial R}{\partial t} \right)}{\partial t} \mathbf{d}_{12} +; \\ & + \frac{1}{2} \frac{\partial}{\partial t} \left(\frac{4\pi R^3}{3} \rho_L \left(-\frac{\partial \mathbf{d}_{12}}{\partial t} \right) \right) + 4\pi \eta R \left(-\frac{\partial \mathbf{d}_{12}}{\partial t} \right) \end{aligned} \tag{4}$$

where R_0 is the initial radius of cavitation bubble, m; ρ_G is the density of gaseous in the bubble at the radius R_0 , kg/m³; ρ_L is the density of liquid around bubble, kg/m³; η is the viscosity of liquid, Pa·s.

Thus, the proposed sub model allowing to determine radius of bubble, concentration of bubbles and shock wave pressure. Founded values are used for determination of macromolecules breakup probability and fraction composition evolution. The sub model for determining fraction composition evolution is described in following section.

IV. THE PROBABILITY SUBMODEL OF MACROMOLECULES FRACTION COMPOSITION EVOLUTION UNDER CAVITATION INFLUENCE

The sub model for determining fraction composition evolution is based on probability approach. According to the approach the intensity of molecules breakup is characterized by breakup probability $\beta_{ij,k,M}$ at unity concentration of molecules with weights (numbers of monomer units) i and j per unit of time. $\beta_{ij,k,M}$ is the probability of breakup of molecule with weight i on two molecules having weights k and $i-k$. The breakup occurs at collision between i -weight and j -weight molecules on points separating i -weight molecule on k -weight and $(i-k)$ -weight molecule, j -weight molecule on M and $(j-M)$ molecule.

The concentrations evolution equation including the probability is

$$\frac{\partial c_i}{\partial t} = \frac{1}{2} \sum_{j>i, k>i} \left(\sum_{M_2=1}^{k-1} \beta_{jk,i,M_2} + \sum_{M_2=1}^{k-1} \beta_{jk,j-i,M_2} + \sum_{M_1=1}^{j-1} \beta_{kj,i,M_1} + \sum_{M_1=1}^{j-1} \beta_{kj,k-i,M_1} \right) c_j c_k + \sum_{j>i, k \leq i} \left(\sum_{M_2=1}^{k-1} \beta_{jk,i,M_2} + \sum_{M_2=1}^{k-1} \beta_{jk,j-i,M_2} \right) c_j c_k - \sum_{l, M_1=1 \dots i-1, M_2=1 \dots l-1} \beta_{il, M_1, M_2} c_i c_l \quad ; \quad (5)$$

where c_i is number concentration of i -weight molecule, mol/m³.

At the large average molecular weight the $\beta_{ij,k,M}$ is independent on k and M (assumption 6 in section II) and equals to β_{ij} . According to it the equation (5) is reduces to (6):

$$\frac{\partial c_i}{\partial t} = \sum_{j>i, k>i} (k + j - 2) \beta_{jk} c_j c_k + 2 \sum_{j>i, k \leq i} (k - 1) \beta_{jk} c_j c_k - \sum_l (i - 1)(l - 1) \beta_{il} c_i c_l \quad (6)$$

The probability included in equation (6) is determined by the analysis of pair molecules collision, presented in following section.

V. THE DETERMINING OF PROBABILITY OF MACROMOLECULES DESTRUCTION

The determining of probability of macromolecules destruction is proportional to intersection during relative motion of macromolecules probability and to i -weight macromolecule breakup at collision.

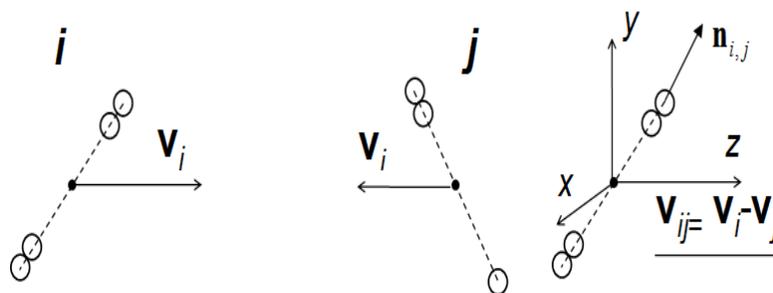


Fig. 3. The schematic image of considered local area for bubbles concentration determining

Each macromolecule orientation is characterized by vector n :

$$\mathbf{n}_{i,j} = \begin{pmatrix} n_{i,jx} \\ n_{i,jy} \\ n_{i,jz} \end{pmatrix} = \begin{pmatrix} \sin \theta_{i,j} \cos \varphi_{i,j} \\ \sin \theta_{i,j} \sin \varphi_{i,j} \\ \cos \theta_{i,j} \end{pmatrix}; \quad (7)$$

Using the expression (7) the expression for probability was obtained (8). The expression (8) considers collision at different orientation of each molecule.

$$\beta_{ij} = N_A \frac{n_{bub}}{T} \int_0^T \int_{R(t)-1}^{\infty} \int_0^{\pi} \int_0^{\pi} 8r^2 r_e^2 \sin^2 \theta_i \sin^2 \theta_j \times$$

$$\times \frac{\sqrt{2\delta_i^2 + 2\delta_j^2} e^{-\frac{v_{min}^2(i,j,\theta_i,\theta_j,\alpha)}{2\delta_i^2 + 2\delta_j^2}} \left[\frac{v_{min}^2(i,j,\theta_i,\theta_j,\alpha)}{2\delta_i^2 + 2\delta_j^2} + 1 \right]}{\sqrt{\pi}} d\theta_i d\theta_j d\alpha dr dt ; \tag{8}$$

$$\alpha = \cos(\varphi_i - \varphi_j); \delta_i = C_i \sqrt{\frac{P(t)R(t)}{p_0 r}}$$

where C_i is proportionality coefficient determined by thermodynamically conditions in the polymer liquid, m/s; r_e is equilibrium distance between monomer units, m; N_A is number of Avogadro, mol^{-1} ; n_{bub} is cavitation bubbles concentration determined in section III, m^{-3} ; v_{min} is minimal relative macromolecules pair velocity necessary for macromolecules breakup, m/s; $P(t)$ is the shock wave pressure determined in section III, Pa; $R(t)$ is the radius determined in section III, m. The minimal relative macromolecules pair velocity v_{min} obeys energy conservation law (summa of molecules kinetic energy and hydrogen bonds potential energy is constant) and can be determined empirically by indirect methods (approximation of viscosity dependence of time at fixed cavitation energy). The substitution of probability (8) in equation (6) allows to calculate macromolecules fraction composition evolution.

VI. THE RESULTS OF CALCULATION OF MACROMOLECULES FRACTION COMPOSITION EVOLUTION

The calculated mass fractions of molecules with different monomer units are presented in Fig. 4.

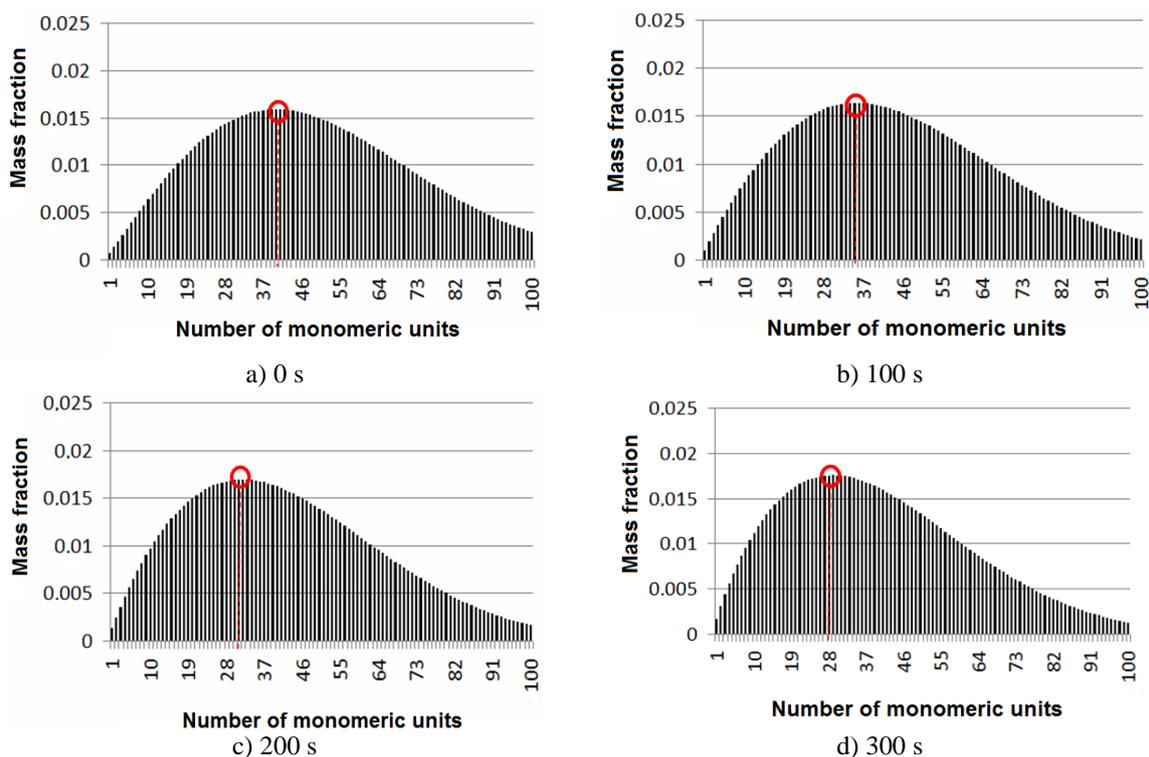


Fig. 4. The fraction composition of molecules at different times (US intensity is 10 W/cm^2 ; US frequency is 22 kHz; initial viscosity is $0.4 \text{ Pa}\cdot\text{s}$)

According to the presented histograms, at the intensity 10 W/cm^2 the modal number of monomer units is reduced up to 40%. It is enough to reduce viscosity up to more than 3.5 times. The analogical distributions for intensity 25 W/cm^2 is presented in Fig. 5.

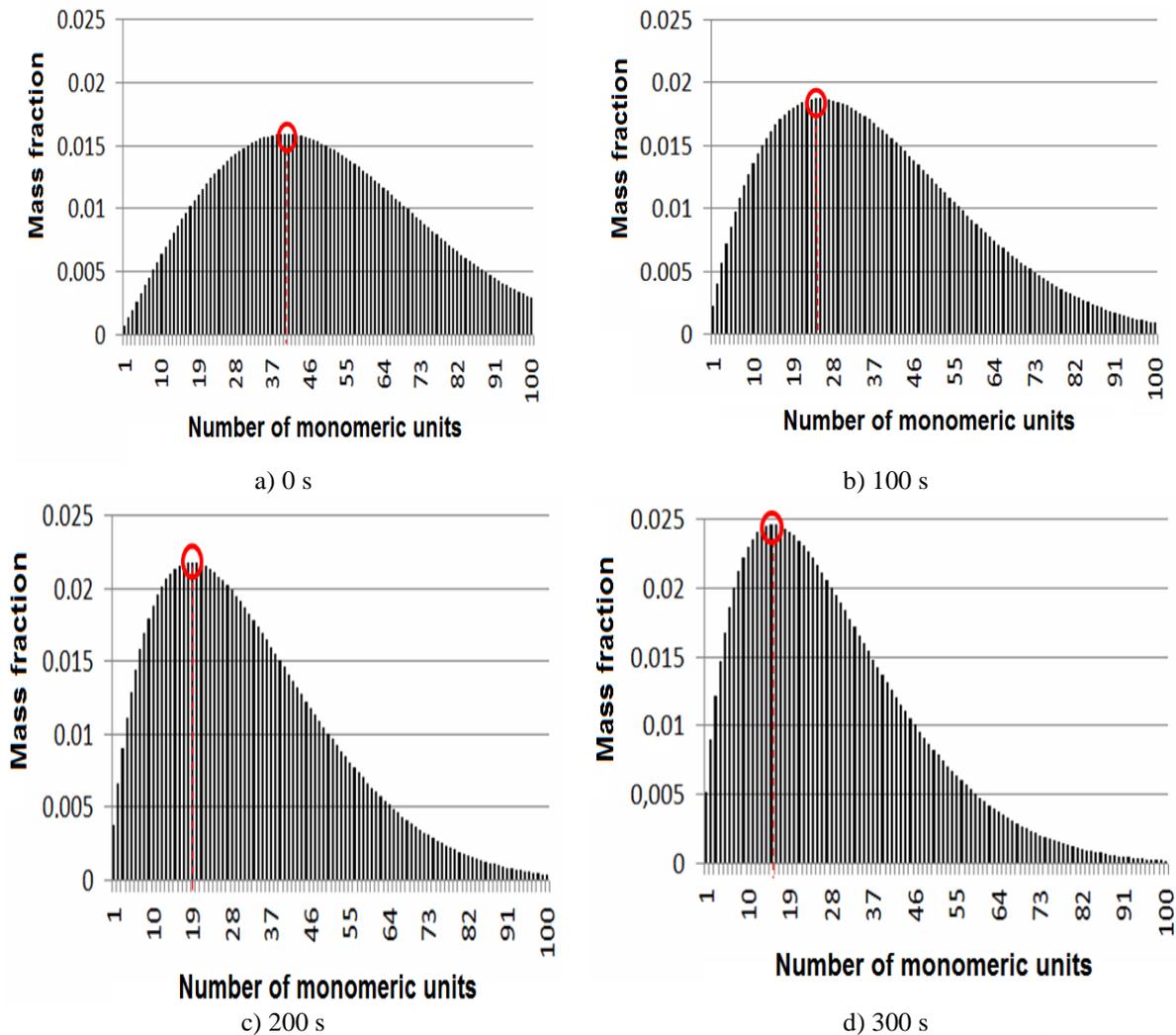


Fig. 5. The fraction composition of molecules at different times (US intensity is 25 W/cm²; US frequency is 22 kHz; initial viscosity is 0.4 Pa·s)

According to the distributions, higher intensity causes the faster maximum shift. For example, through 300 s, the modal number of monomer units reduces up to more than 2 times. It causes viscosity reducing up to more than 10 times. In the following section the results of calculation of polymer viscosity changing were presented.

VII. THE RESULTS OF CALCULATION OF POLYMER VISCOSITY CHANGING

The polymeric liquid viscosity is calculated by empirical law, obtained by Rouse P.E., Khokhlov A.R., Pyshnograï G.V. [8–10]:

$$\eta(t) = \eta(0) \frac{\sum_{i=1}^{\infty} c_i^{2\delta+1}(t) i^{3\delta+2}}{\sum_{i=1}^{\infty} c_i^{2\delta+1}(0) i^{3\delta+2}}; \tag{9}$$

where t is time, s ; δ is empirical parameters which equals to 2.4 for most part of polymers.

According to expression (9) and equation (6) for concentrations c_i , the dependences for viscosity on time was obtained (Fig 6.)

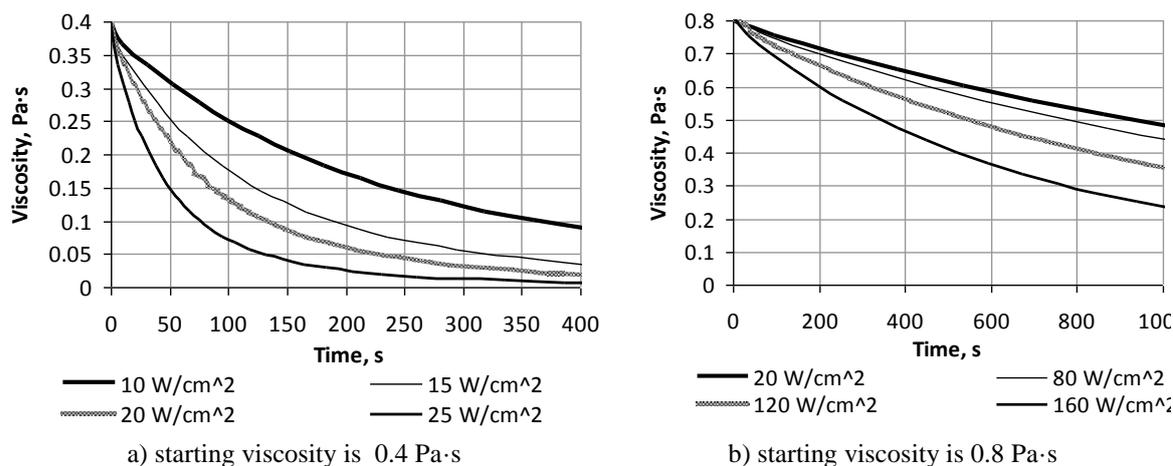


Fig. 6. The dependences of viscosity on time at different US intensities and starting viscosities

According to the dependences, the ultrasonic with intensity 25 W/cm^2 reduces the viscosity up to 10 times and more (for polymer with starting viscosity $0.4 \text{ Pa}\cdot\text{s}$). As well as, the possibility of ultrasonic cavitation depolymerization of high viscous polymers ($0.8 \text{ Pa}\cdot\text{s}$) was shown. Ultrasonic cavitation influence can reduce viscosity up to 3.5 times during 1000 s at starting viscosity $0.8 \text{ Pa}\cdot\text{s}$ (US oscillations intensity is 160 W/cm^2). For ultrasonic depolymerization of high viscous polymers the larger intensities is required due to viscosity prevents cavitation. Obtained results can be used for choose the operating modes of industrial ultrasonic equipment for cavitation depolymerization.

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