Numerical calculation of intermolecular bonds under the action of ultrasonic cavitation

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Abstract. The linear model of macromolecules was proposed. Expression for probability of macromolecules breakup under ultrasonic cavitation action was obtained. The fractional composition and viscosity of uncured polymer were calculated. As a result of the calculations, it was evaluated that the cavitation-acoustic effect for a time of no more than 1 min at an vibration intensity of at least 6 W/cm² and an initial viscosity of 0.2 Pa·s reduces the viscosity of polymers by at least 8 times. At the same time, it was theoretically revealed that the cavitation-acoustic effect is also capable of reducing the viscosity of polymers with an initial viscosity of more than 1 Pa·s up to 4 times.

1. Introduction
To date, the problem of controlling the properties of polymers is mainly solved by introducing additional chemical additives – hardeners, plasticizers, dispersed fillers, UV stabilizers, etc. [1–3] However, additional chemical additives, primarily, are consumables that negatively affects the cost of the final product, are aggressive media that makes the resulting target material harmful to humans and the environment, as well as leading to corrosion of metal parts and components of the technical system. Moreover, chemical additives often make both production and operation of the material harmful. Another disadvantage of chemical additives is that they can improve some of the target properties and degrade other properties. For example, the addition of 2- (2'-hydroxy-3 ', 5'-ditretamylphenyl) benzotriazole (UV stabilizer) to a liquid epoxy binder can increase the UV resistance of the composite material, but at the same time reduce the mechanical material strength by 15%.

A promising area of research that can potentially serve as a basis for creating an effective technology for controlling the properties of polymers is the impact of mechanical vibrational disturbances on a high molecular weight medium. In real uncured polymers, mechanical vibrational disturbances, as a rule, represent a cavitation-acoustic effect, i.e. linear sinusoidal oscillations created in the medium initiate a secondary phenomenon – cavitation bubbles. During cavitation-acoustic impact, bubbles periodically expand and collapse forming microshock waves. Thus, mechanical vibrational disturbances have two components – linear sinusoidal and nonlinear shock-waves.

Mechanical vibrational disturbances will allow controlling the properties of polymers due to the fact that the energy of such disturbances is sufficient for the destruction or formation of new hydrogen and carbon bonds in polymers, and by varying the parameters and shape of disturbances, one can smoothly change the properties of materials and thereby receive materials with certain predetermined properties.
[4–10]. For example, it has been experimentally proven that the cavitation-acoustic effect on an epoxy binder with a filler increases the strength of the composite material up to 70%, which can compensate with a large margin for the decrease in strength caused by the addition of a UV stabilizer. All this is achieved by increasing the frequency of interactions of macromolecules of substances with each other in a cavitation-acoustic field, the destruction of existing chemical bonds and the formation of new bonds, etc. Another feature of mechanical vibrational disturbances is that they are able to control individual properties of the target material (you can smoothly change properties by selecting modes and duration of exposure) without the use of consumables. For example, such an effect makes it possible to effectively reduce the viscosity of uncured polymers (up to 5 times or more in a time of 1...2 min) without the use of chemical additives and liquids insoluble in the polymer (for example, without adding water to oil to obtain an oil-water emulsion, which less viscous than the original oil). At the same time, for certain types of polymers (for example, phenol-formaldehyde resin), a delayed effect is observed - the viscosity increases by more than 20% relative to the original uncured polymer after removal of the impact.

To determine the degree of change in the properties of polymers, depending on the parameters of the cavitation-acoustic effect, it is necessary to create a numerical model that will reveal how the restructuring of molecular bonds in the medium occurs, the number of acts of destruction of bonds and the final properties of the material.

2. Description of model and results
As is known, 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. In this case, the fractional composition of molecular chains by the concentration of molecules with different amounts of monomer units determines the rheological properties of the material, which ultimately determine the strength of a product based on a polymer with an added hardener, the impregnation ability and uniformity of the material structure.

The performed theoretical analysis of the effect of cavitation on the structure of polymer macromolecules was based on the following assumptions:

- All monomeric units of macromolecules have the same mass equal to \( m_0 \).
- Each molecular chain is a linear structure (figure 1), characterized by the number of monomer units \( N \), a unit orientation vector \( n \) (\( ||n|| = 1 \)), the velocity of the center of mass \( v \), and intrinsic angular momentum \( l \) (the angular momentum of the macromolecule in frame of reference of its center of mass).

![Figure 1. Schema of linear model of macromolecule.](image-url)
The state of the polymer medium is uniquely characterized by the distribution function of macromolecules over the number of monomer units, orientation vectors, velocities, and intrinsic angular momentum \( f(N, n, v, l, t) \) (\( t \) is the time instant). The distribution function is normalized to the density \( \rho \) of the uncured polymer as follows.

\[
\rho = \sum_{N} \int \int \int \int \int f(N, n, v, l, t) dS(n) dl dv .
\]

- The density of the polymer remains unchanged over time.
- The disintegration of macromolecules is possible only with the appearance of a shock wave arising from the collapse of cavitation bubbles. In the absence of cavitation, the disintegration of macromolecules does not occur.
- The disintegration of a molecule occurs if and only if the collision rate of molecules exceeds a certain threshold value at which the potential field of the forces of hydrogen or carbon bonds is overcome.

Visualization of the process of disintegration of macromolecules is shown in figure 2.

Figure 2. Visualization of the disintegration process of a pair of macromolecules (the shape of a macromolecule is approximated by a linear chain of monomer units) as a result of collision.

To determine the fractional composition of macromolecules as a result of their disintegration, an expression was obtained for the probability of disintegration of an individual molecule:

\[
P = H\left( |v_i - v_j| - v_{\text{min}}(n_i, N_i, n_j, N_j) \right) C_{N_i, v_i, n_i} C_{N_j, v_j, n_j} \Delta V \Delta t |v_i - v_j| \times \\
\times Sdv_i dv_j d\Omega(n_i) d\Omega(n_j) = 1/2 H\left( |v_i - v_j| - v_{\text{min}}(n_i, N_i, n_j, N_j) \right) \times \\
\times C_{N_i, v_i, n_i} C_{N_j, v_j, n_j} N_i N_j r_c^2 |v_i - v_j| \times \\
\left( |n_i - (\frac{n_i \cdot v_{ij}}{|v_{ij}|^2}) v_{ij}| \right) \times \left( |n_j - (\frac{n_j \cdot v_{ij}}{|v_{ij}|^2}) v_{ij}| \right) \times \Delta V \Delta t dv_i dv_j d\Omega(n_i) d\Omega(n_j)
\]

where \( P \) is number of molecules pairs destructed in volume \( \Delta V \) during time \( \Delta t \), \( C_{N, v, n} \Delta V dv d\Omega(n) \) is
number of macromolecules in volume $\Delta V$, which have velocities from range $(v_x; v_x + dv_x) \times (v_y; v_y + dv_y) \times (v_z; v_z + dv_z)$, orientations in solid angles range $d\Omega(n)$ and number of monomeric units $N$; $H(v)$ is Heaviside’s function, which equals 1, if $v \geq 0$, and 0 if another case; $n_j$ is vector of orientations of $i$-th macromolecule; $N_i$ is number of monomeric units in $i$-th macromolecule; $v_{\text{min}}(n_i, N_i, n_j, N_j)$ is minimum velocity, which is necessary for destruction of $i$-th macromolecule at its collision with $j$-th macromolecule, $\text{m}\cdot\text{s}^{-1}$.

Using the expression for the probability of decomposition on the basis of the obtained kinetic equation, the fractional composition of macromolecules was further calculated, which made it possible to determine the viscosity of the polymer as a result of ultrasonic cavitation action.

As a result of the calculations, it was established that the cavitation-acoustic effect for a time of no more than 1 min at an vibration intensity of at least $6 \text{ W}\cdot\text{cm}^{-2}$ and an initial viscosity of $0.2 \text{ Pa}\cdot\text{s}$ reduces the viscosity of polymers by at least 8 times. At the same time, it was theoretically revealed that the cavitation-acoustic effect is also capable of reducing the viscosity of polymers with an initial viscosity of more than 1 Pa·s up to 4 times.

These obtained results indicate the effectiveness of the use of cavitation-acoustic impact for the intensification of the process of mechanical destruction of macromolecules.

**Acknowledgements**

The reported study was supported by the Grant of the President of Russian Federation No. MK-5387.2021.1.1.

**References**

[1] Nikafshar S, Zabihi O, Ahmadi M, Mirmohseni A, Taseidifar M and Naeebe M 2017 *Materials (Basel)* 10(2) 180

[2] Ozhogin A V, Lenskiy M A, Korabelnikov D V and Novickiy A N 2019 *Plastics* 1-2 57-9

[3] Ozhogin A V, Lenskiy M A, Korabelnikov D V and Novickiy A N 2018 *Polymer composite materials and production technologies of a new generation: Proceedings of the III All-Russian Scientific and Technical Conference* 262-70

[4] Huang Y D, Liu L, Qiu J H and Shao L 2002 *Composit. Sci. Techn.* 62 2153

[5] Mullakaev M S, Volкова G I and Gradov O M 2015 *Theoretical Foundations of Chemical Engineering* 3 49 287-96

[6] Volкова G I, Prozorova I V, Anufriev R V, Yudina N V, Mullakaev M S and Abramov V O 2012 *Refining and petrochemicals* 2 3-6

[7] Prachkin V G, Mullakaev M S and Asylbaev D F 2015 *Chemical and Petroleum Engineering* 9-10 50 571-5

[8] Mohapatra H, Kleiman M and Esser-Kahn A P 2017 *Nature Chemistry* 9 135-9

[9] Cass P, Knower W, Pereeia E, Holmes N P and Hughes T 2010 *Ultrason Sonochem* 17(2) 326-32

[10] Magsumova A F, Amirova L M and Ganiev M M 2005 *Bulletin of KSTU named after A.N. Tupolev* 2