

DISTINCTIVE FEATURES OF FORMATION OF THE PROPERTIES OF CERTAIN POLYMER COMPOSITE MATERIALS UNDER THE INFLUENCE OF WAVE ACTION

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Consideration has been given to the influence of vibrowave action on polymer dispersions (styrene-butadiene and acryl latexes and their blends), solutions of gelating polymers (polyacrylic acid, gelatin, and starch) with fillers (activated carbon and zeolite), and emulsions of the motor oil/water type. An increase in the degree of dispersity and the aggregative stability of disperse systems after their vibrowave treatment has been noted. An algorithm of calculation of a possible way of optimizing one method of intensification of mass transfer in the case where wave technology is used has been proposed.

In solving technological problems associated with processing of polymers and production of polymer composite materials (PCMs) and caused by the intensification of such processes that are underlied by the phenomena of heat and mass transfer, it becomes necessary to describe the dynamic behavior of polymer systems. The problem of describing of the dynamic behavior of PCMs as multiphase, multicomponent systems in a wide viscosity range — from low-viscosity materials (of the type of paintwork materials) to high-viscosity ones (of the type of rubber blends, which may be considered by analogy with highly concentrated dispersions) — seems significant. For the most part, these are heterogeneous disperse systems whose properties are determined by the efficiency of mixing and the size of distributed particles.

If polymer dispersions are considered as PCM models containing a liquid phase, it is necessary to note their sensitivity to external action. Fundamental is the ambiguous character of mechanical action (on the one hand, it may induce coagulation of colloidal system of the latex type, on the other, it is one way of producing artificial latexes). Intensification of mass exchange in the case where certain new technologies are used is a factor contributing to the overcoming of interphase instability. Among these technologies is a wave one whose theoretical foundations are based on studying the problems of wave mechanics which are associated with nonlinear vibrations and the stability of motion. It has been noted that specific features of the dynamic behavior of multiphase systems reveal themselves under vibrowave action on such systems in the audio-frequency band; these features are accompanied by the intensification of heat and mass exchange, the acceleration of relaxation processes and phase and chemical transformations, cavitation phenomena contributing to the processes of dispersion, the turbulization of the processes of mixing, and others. It is significant that the radical transfer of the energy of vibrations and waves to the energy of other forms of mechanical motion in a multiphase medium occurs in the resonant mode, and this considerably reduces the energy consumption [1].

In the present work, vibrowave action has been used as the factor accelerating relaxation processes in PCMs. We considered, as the objects of investigation, latexes based on polymers of rigid-chain (styrene-butadiene) and flexible-chain (acryl) natures and their blends, latex films, filled latex systems, aqueous solutions of gelating polymers (polyacrylic acid, starch, and gelatin) with fillers (activated carbon and zeolite), and a model system: a motor oil/water (5 vol. %) emulsion. The polymer systems were subjected to vibrowave action on a VEDS-400A- and an EDVK-250-type shaker, whereas the model systems were treated using a hydrodynamic generator on a setup whose technological

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TABLE 1. Influence of the Vibroaction on the Dispersity of Emulsions and Suspensions

| Disperse system | Vibroaction parameters | | d , μm | Fraction of particles with d , % | N | $S \cdot 10^{-4}$, m^2 |
|--------------------------------|------------------------|------------------|---------------------|------------------------------------|------------------------|----------------------------------|
| | t_v , min | Δp , atm | | | | |
| Oil/water | 0 ¹⁾ | — | 3.0 | 60 | 10^7 | 33 |
| | 10* | 10 | 1.6 | 80 | $7 \cdot 10^8$ | 148.6 |
| | 20* | 10 | 0.8 | 80 | $0.185 \cdot 10^{12}$ | 900 |
| | 10* | 15 | 0.7 | 100 | — | — |
| | 10* | 25 | 0.62 | 100 | $44 \cdot 10^{12}$ | 1240 |
| | 10** | — | 1.14 | 97 | — | — |
| | 3*** | — | 0.7 | 92 | — | — |
| | 5*** | — | 0.5 | 100 | — | — |
| Chalk/water | 0 ¹⁾ | — | 80 | >50 | — | — |
| | 10* | 10 | 55 | >50 | — | — |
| | 20* | 10 | 25 | >50 | — | — |
| Polymer/water (latex blend) | 0 ¹⁾ | — | 0.18 | 83 | $0.645 \cdot 10^{14}$ | 16 000 |
| | 5*** | — | 0.15 | 82 | $1.67 \cdot 10^{14}$ | 22 000 |
| | 10** | — | 0.13 | 96 | — | — |
| Carbon/water + gelatin | 0 ¹⁾ | — | 2.82 | 94 | $0.017 \cdot 10^{12}$ | 1060 |
| | 5** | — | 1.57 | 100 | $0.0985 \cdot 10^{12}$ | 1911 |

1) The compositions were prepared by mechanical mixing, * the compositions were subjected to vibroaction on a setup with a hydrodynamic generator, ** the compositions were subjected to vibroaction on a shaker, and *** after mechanical mixing, the compositions were exposed to ultrasound.

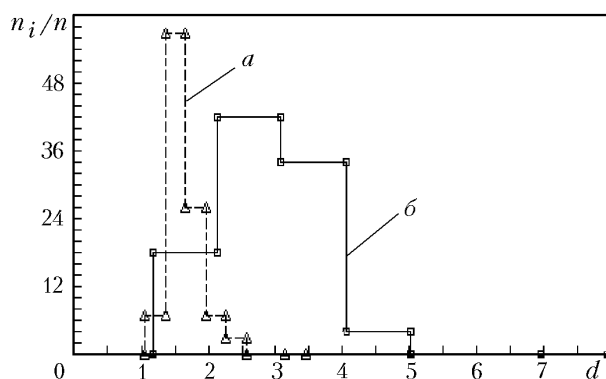


Fig. 1. Particle distribution: a) vibrowave mixing; b) mechanical mixer. n_i/n , %; d , μm .

diagram is given in [1]. For the sake of comparison, certain compositions were subjected to ultrasonic action using a UZDN 2 generator (frequency 22 kHz and maximum intensity $30 \text{ W} \cdot \text{cm}^{-3}$).

Table 1 gives data on the influence of vibrowave action on the dispersity of emulsions and suspensions, which has been evaluated using a light microscope and by the method of laser autocorrelation spectroscopy. A decrease in the average most probable diameter of dispersed-phase particles and a narrowing of the particle-diameter distribution (PDD) in passage from the compositions prepared by mixing using a mechanical mixer to compositions subjected to vibrowave action are observed in all the systems. This is clear from Fig. 1, where PDD histograms are presented for oil/water emulsions prepared in different ways.

TABLE 2. Influence of the Wave Action on the Aggregative Stability of Disperse Systems

| Formula of Composition | t_v , min | $t_{b.layer}$ |
|-----------------------------------|-------------|---------------|
| Oil/water (5 vol. %) | 0 | 10–15 min |
| | 10* | 5–7 days |
| Chalk/water (30 wt. %) | 0 | 1–2 h |
| | 20* | >3 months |
| Latex + zeolite (30 wt. %) | 0 | 10–15 min |
| | 10 | 2–3 h |
| Carbon + PAC solution (0.02%) | 0 | 20–25 min |
| | 5 | 3.5 h |
| Carbon + gelatin solution (0.02%) | 0 | 18–20 min |
| | 5 | 3 h |

*The compositions were subjected to wave action on a setup with a hydrodynamic generator.

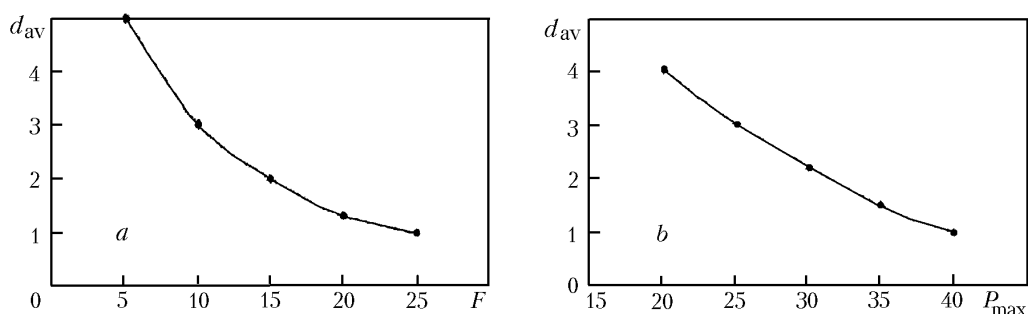


Fig. 2. Particle size vs. frequency (a) and amplitude of pressure (b). d_{av} , μm ; F , kHz; P_{max} , atm.

The dispersity of emulsion droplets grows with vibration intensity, which is seen in Fig. 2, where the average diameter of oil droplets in the emulsion is given as a function of the vibration frequency and the pressure amplitude.

Based on the data on the dispersity of particles in the systems studied, we have calculated the interfaces whose values, naturally, sharply grow in passage from the mechanical mixer to vibrowave action [2].

We should note an increase in the aggregative stability of all the disperse systems after their vibrowave treatment (Table 2). The increase is the most substantial (of several orders of magnitude) in the oil/water emulsion and the chalk/water suspension (Table 2).

The influence of wave vibration action on the properties of PCMs is illustrated by the data of Table 3, where the physicochemical indices of the properties of films from styrene-butadiene and acryl latexes are given using these latexes as an example. We should note that vibrowave action in the resonant mode of vibromixing has enabled us to produce transparent homogeneous elastic films from the blends of such latexes throughout the range of the component ratios, which was impossible to attain using traditional mechanical mixing. A deviation of the composition-breaking stress curve from additivity may be considered as evidence of the enhancement of the interaction in the interphase layer in polymer blends, resulting from the nonlinear vibrations. It is characteristic that the effect of nonmonotony of this dependence is more pronounced in compositions with the dominant content of a rigid-chain polymer whose relaxation characteristics determine its higher sensitivity to vibrowave action. The enhancement of the interaction in the interphase layer of latex films subjected to vibrowave action is also demonstrated by the data of IR spectroscopy (appearance of bands in the region $3440\text{--}3238\text{ cm}^{-1}$ and broadening of the 670-cm^{-1} and $1000\text{--}1300\text{-cm}^{-1}$ bands) [3]. This manifests itself in the noted improvement of the strength of the latex films. Furthermore, we observe the effect of strengthening of such PCMs as unwoven materials produced by the method of impregnation of fiber linens (lavsan/kapron, lavsan/viscose, 70/30) with latex binders subjected to vibrowave action.

The results of consideration of the interrelationship between the structural-mechanical, rheological, and technological properties of polymers and PCMs enable us to infer that the process of their processing may be described by a complex function of many variables: $\Pi = f(\mu, \gamma, \tau, G, \rho \dots)$ [4].

TABLE 3. Physicomechanical Indices of Latex Films

| Volume ratio of the latexes I:II | t_v , min | P , MPa | ϵ , % |
|----------------------------------|-------------|-----------|----------------|
| 80:20 | 0 | 2.0 | 360 |
| 80:20 | 4 | 2.5 | 550 |
| 80:20 | 8 | 4.0 | 650 |
| 60:40 | 0 | 1.0 | 550 |
| 60:40 | 4 | 2.4 | 750 |
| 60:40 | 8 | 3.8 | 900 |
| 40:60 | 0 | 0.6 | 800 |
| 40:60 | 4 | 0.9 | 1030 |
| 40:60 | 8 | 1.1 | 1110 |

Note. I, polystyrene latex; II, polybutyl acrylate latex; polymer concentration 20 wt. %.

TABLE 4. Influence of the Order of Mixing of the Components on the Properties of Vulcanizates

| Property | Amount of TGM-3, wt. parts per 100 w. parts of rubber* | | | | | |
|--|--|---------|---------|-------|-------|-------|
| | 0.5/0.5 | 1.0/5.0 | 5.0/1.0 | 1.0/0 | 0/5.0 | 0/0 |
| P , MPa | 20 | 23 | 15 | 18 | 17 | 16—17 |
| M_{300} , MPa (300%) | 11 | 14 | 8 | 9 | 9 | 8—10 |
| ϵ , % | 550 | 500 | 400 | 450 | 500 | 500 |
| Energy consumption,** arbitrary units | 0.9 | 0.7 | 0.6 | 1.2 | 0.7 | 1.0 |

*The numerator, introduction into the rubber; the denominator, introduction into the soot-filled blend. **The energy consumption by the mixing of the rubber with PM-50 without TGM-3 has been taken to be 1.

In describing the properties of polymer dispersions, it is significant that the parameter t_r , i.e., the relaxation time, which may be considered to be equal to the ratio of the viscosity of the system μ to its modulus (of rigidity) G , possesses a distinctive feature combining the properties of liquids and solids [5]. Nonetheless, despite the fundamental generality noted for the properties of solid and liquid disperse systems, the quantity t_r for stresses τ lower than the ultimate strength may be used as the criterion for separation of systems into solid- and liquid-plastic ones. Depending on the relation between the time of action and the relaxation time, the rheological properties of polymer systems may change and a system will act as a solid or liquid one. The unusualness of the rheological properties of polymers and their melts and solutions is known to be a consequence of the fact that these materials are simultaneously characterized by the distinctive features of both solid and liquid bodies. The rheological properties of polymer systems are related to the manifestation of viscosity anomaly, normal stresses, and thixotropic and other nonlinear effects caused by the change in the relaxation spectrum. With allowance for the determining character of the relaxation spectrum and the relaxation nature of viscosity anomaly, it seems significant to establish a generalizing criterion, characterizing the efficiency of the processing, and the interrelationship between this criterion and the relaxation factors and characteristics determining the hydrodynamic and rheological features of technological processes of processing of PCMs. It is well known that the processes of mixing and dispersion associated with the formation and shaping of a new surface in multiphase compositions are the most general in processing on both high-viscosity PCMs and low-viscosity polymer dispersions containing a liquid phase. In the case of high-viscosity blends where strain and shear stress may be considered as the criterion of efficiency of mixing, the work of dispersive mixing is determinable from the Reh binder equation [5]. Increase in the shear stress contributes to a better distribution of the components and hence to an improvement of the quality of mixing. It is significant that we are dealing with the optimization of the process, not with its intensification. Decrease in the viscosity does not necessarily contribute to the creation of the best conditions for dispersion and may lead to an agglomeration of particles in the process of mixing.

For example, it has been established [6] for rubber blends that the optimum distribution of filler particles in the volume of a rubber matrix, which must ensure the maximum strength for vulcanization, is only attained in a certain range of the values of rubber plasticity where the agglomerates of commercial-carbon particles are destroyed in

their mixing with the rubber and the possibility of nodulizing is eliminated. The transfer of a filler from one phase to the other is carried out in the process of mixing, and the mixing conditions and the order of introduction of the filler exert a decisive influence on its distribution [7].

With allowance for these circumstances, it has been proposed [8] that mixing be carried out in steps and fractions with the use of the effect of abnormal growth in the viscosity of rubbers in the presence of prescribed amounts of oligomer plasticizers and without changing the strain modes of mixing. In the first step, a plasticizer in an amount necessary for a certain plasticity level to be attained is introduced into the rubber, then a filler is introduced into this blend with an increased viscosity; the agglomeration of particles is substantially reduced. Next, an excess plasticizer is added to the system with the aim of compensating for the energy consumption. Thus, one carries out further dispersion of the filler in highly plasticized filled systems, ensuring the necessary level of physicochemical properties of rubbers. In Table 4, the efficiency of this technique is shown using the blend *cis*-polyisoprene rubber (SKI-3)-PM-50 commercial carbon (30 wt. parts)-TGM-3 oligoester acrylate (viscosity regulator) as an example. It is difficult to create high shear stresses ensuring the destruction of particles in disperse systems with a low viscosity. Nonetheless, evaluation of the dispersion energy must involve the determination of the size of the newly formed interface ΔS in the corresponding systems. The shear stress on the interface in formation of an emulsion in the presence of surfactants is 10^{-3} MPa [9]. In liquid-phase, chemical-engineering processes, mass transfer may be accompanied by the phenomena of interphase instability generated by hydrodynamic and hydrochemical interactions [10].

Thus, the given examples demonstrate the increase in the intensity and efficiency of mass-exchange processes under the influence of vibrowave action and may be associated with the nonlinear effects occurring in different processes of processing and production of PCMs. At present, there is no adequate physical model describing the dependence of the degree of dispersity of a multiphase, multicomponent system on the parameters of vibrowave action. Based on the premise that the first reaction of a polymer material to a change in the temperature-mechanical field is strain, the rheological properties are considered as the most informative factor of the dynamic behavior of polymer systems, and the rheological equations of state are a theoretical substantiation of the processes of processing of polymers [11]. Investigation of the above parameters of vibrowave action along with the use of formula-technological techniques contributes to the development of the technology of production of materials with prescribed properties.

We have proposed an algorithm of calculation of a possible way of optimizing one method of intensification of mass transfer in the case where wave technology is used [13] with the aim of constructing a simplified model for understanding of the qualitative character of the dynamics of the processes in question based on the phenomenological description of certain processes of processing of polymers (mixing and dispersion) with the use of the similarity method and the elements of system analysis [12]. Expressions for the destruction criteria and the grinding functions (destruction probability $A(r)$ and the distribution function $B(r, \gamma)$) have been obtained. If the process of dispersion (dispersive mixing) in a multiphase system subjected to either mechanical (shear) or wave action is represented, from the analytical expressions obtained, it may be inferred that the destruction probability in the first case, where it is determined mainly by the shear stress (wave effects may be disregarded) is lower than that in the second case, where the parameters of wave action are determining.

In closing, we may note that apart from the traditional, most popular view of PCMs as reinforced materials, in this work, emphasis is on the colloidal-chemical approach to PCMs, where they are considered primarily as disperse distributed systems with their multiphase and multicomponent character, instability, nonequilibrium, multilevel inhomogeneity, and an appreciable sensitivity to mechanical and other external actions. Another confirmation of the legitimacy of such an approach are trends noted at present in the field of the technology of processing of such a typical composite and structural material as rubber. It is well known that up to now most technological processes of processing of rubber blends and other elastomer materials have been based on energetically imperfect processes of intense multiple high-temperature mechanical straining accompanied by the destruction of the initial structure of the materials and the release of volatile destruction products. In creating new, environmentally sound and energy-conserving technologies, it is necessary to reduce mechanical forces and the level of temperature action. The technologies of processing of polymer materials in the disperse state — powder thermoelastoplastics (TEPs) and PVC dispersions — are promising in this respect [14].

NOTATION

$A(r)$, destruction probability; $B(r, \gamma)$, distribution function (r and β are the particle volumes); d , particle diameter, μm ; d_{av} , average particle diameter, μm ; F , frequency, kHz ; G , shear modulus, MPa ; M , tensile modulus, MPa ; N , number of particles per ml of the composition; n , number of particles, %; n_i/n , fraction of particles with a diameter d_i ; P , conventional tensile strength, MPa ; P_{max} , amplitude of pressure oscillations, atm ; S , size of the total interface, m^2 ; t_v , time of vibroaction, min ; $t_{\text{b.layer}}$, time before phase layering, min , h , and days ; t_r , relaxation time, sec ; ΔP , pressure difference, atm ; $\dot{\gamma}$, rate of shear strain, $\text{m}\cdot\text{sec}^{-1}$; ε , relative elongation at the instant of breaking, %; μ , viscosity, $\text{Pa}\cdot\text{sec}$; Π , processability; ρ , density, kg/m^3 ; τ , shear stress, MPa . Subscripts: v, vibration; b.layer, beginning of phase layering; r, relaxation; av, average; i , any component of a mathematical series; max, maximum.

REFERENCES

1. R. F. Ganiev (Ed.), *Wave Technology and Techniques* [in Russian], Logos, Moscow (1993).
2. R. F. Ganiev, A. M. Kashnikov, E. B. Malyukova, V. N. Fomin, and A. A. Berlin, Influence of wave action on dispersed polymer composite materials, *Lakokras. Mater. Ikh Primenen.*, No. 12, 25–28 (2003).
3. J. Dechant, R. Darz, W. Kimmer, and R. Schmolke (Eds.), *Ultrarot spektroskopische Untersuchungen an Polymeren* [Russian translation], Khimiya, Moscow (1976).
4. E. G. Vostroknutov and G. V. Vinogradov, *Rheological Principles of Processing of Elastomers* [in Russian], Khimiya, Moscow (1998).
5. Yu. G. Frolov, *A Course in Colloidal Chemistry* [in Russian], Khimiya, Moscow (1982).
6. A. I. Lukomskaya and V. F. Evstratov, *Principles of Predicting the Mechanical Behavior of Rubbers* [in Russian], Khimiya, Moscow (1975).
7. V. N. Kuleznev, *Polymer Mixtures (Structure and Properties)* [in Russian], Khimiya, Moscow (1988).
8. S. M. Mezhikovskii, E. I. Vasil'chenko, and Sh. A. Shaginyan, Anomalies of increase of viscosity in binary polymer systems, *Usp. Khim.*, **57**, No. 11, 1867–1887 (1988).
9. I. A. Gritskova, E. B. Malyukova, G. A. Simakova, and V. P. Zubov, Influence of the mechanism of formation of polymer-monomer particles on the kinetic regularities of emulsion polymerization of acrylic monomers, *Vysokomolek. Soed. A*, **32**, 14–19 (1990).
10. Yu. A. Buevich, A. V. Vyaz'min, and D. M. Rabinovich, Mass transfer in interphase hydrochemical convection, *Dokl. Akad. Nauk SSSR*, **312**, No. 4, 904–908 (1990).
11. R. V. Turner, *Theoretical Fundamentals of Polymer Processing* [Russian translation], Khimiya, Moscow (1977).
12. V. V. Kafarov and I. N. Dorokhov, *System Analysis of the Processes of Chemical Technology* [in Russian], Nauka, Moscow (1976).
13. V. N. Fomin, E. B. Malyukova, and A. A. Berlin, Concerning the optimization criteria of the processes of processing and obtaining polymer composite materials, *Dokl. Ross. Akad. Nauk*, **394**, No. 6, 778–781 (2004).
14. V. S. Al'tzitser and V. A. Berestnev, Main concepts of new energy-conserving environmentally safe processes of processing elastomers, in: *Ext. Abstr. of Papers presented at Int. Conf. on Rubber* [in Russian], 1–4 June 2004, OAO VNIIEMI, Moscow (2004), pp. 33–34.