ON COLLOID-CHEMICAL PROPERTIES
OF SOME POLYMER COMPOSITES

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The influence of the vibrowave action on the properties of some disperse systems used in the textile industry has been considered. It has been noted that excitation of nonlinear oscillation in the audio band under resonant conditions leads to an increase in the degree of dispersion of distributed systems and an increase in their colloid stability.

The last few years have seen an enhanced interest in polymer composites (PC) as multiphase disperse (distributed) systems along with their traditional consideration as strengthened materials [1, 2]. This is in accord with the general tendency in chemical technology largely oriented toward processes of obtaining products and materials in which the determining role is played by the degree of dispersion of distributed systems, the surface phenomena, the rheological properties of dispersions, the interphase interactions, etc. [3]. The urgency of investigating the dynamic behavior of multiphase, multicomponent disperse systems characterized by a multilevel inhomogeneity is connected with their appreciable sensitivity to external factors. Since heat and mass transfer is the basis of most processes of obtaining and processing polymers and PCs, new technologies that make it possible to intensify the heat and mass transfer along with restraining or decreasing power consumption seem to be the most promising.

One of them is the wave technology based on effective conversion of vibrational and wave energy into energy of other kinds of motion [4]. In [5, 6], it was shown that the use of nonlinear vibrations in the sound range of frequencies will make it possible to considerably intensify the processes of vibroagitation and dispersion in such liquid-phase disperse systems as paintwork materials, dispersion of polymers (latexes and their mixtures), etc.

The present paper considers the influence of the vibrowave action on multiphase composites used in manufacturing textile materials. As objects of investigation, we used: water and froth printing inks and dye solutions (with an original viscosity from 5 to 30 P) containing stiffeners of the type of starch, carboxylmethyl cellulose (CMC), and sodium alginates intended for printing cotton and cotton-lavsan cloths, mixtures of butadiene-styrene and acrylic latexes, as well as composites with activated carbon and aqueous solutions of polymers (polyacrylic acid, starch, gelatin) used for impregnating fibrous bases in obtaining nonwoven materials (lavsan/viscose). Since the aim of the investigation, along with intensification of the technological processes of coloring and printing fabrics as well as the impregnation of nonwoven materials, was improvement of the functional properties of the materials obtained, the estimation of the degree of dispersion of distributed particles, the stability of disperse systems, the quality of textile materials (colorability and color uniformity of fabrics, physicochemical properties of nonwoven cloths, and their sorption and filtering properties), and the decrease in the specific consumption of dyes and binder components were of paramount importance. The influence of the vibrowave action was compared to the preparation of composites with the help of a mechanical mixer. We also used model mixtures: motor oil (5 volume %)/water and chalk (30 mass %)/water.

Preliminary experiments have shown that the vibrowave effect on liquid-phase-containing multiphase systems, including those based on PCs, can be produced in two ways: in a closed volume on facilities of the type of an electrodynamic stand (EDVK-250, VEDS-400A, etc.) and in a flow by means of a pump and a hydrodynamic generator

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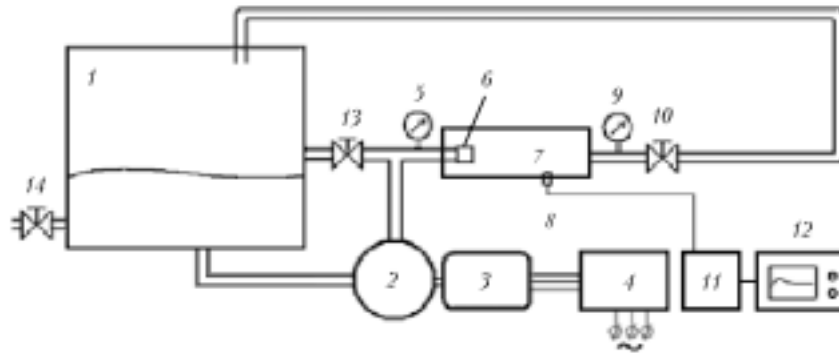
Fig. 1. Flow diagram of the experimental wave facility: 1) intake tank; 2) pump; 3) electric motor; 4) frequency converter (inverter); 5) pregenerator manometer; 6) hydrodynamic generator; 7) working chamber; 8) piezoelectric pressure transducer; 9) manometer after the working chamber; 10) ball cock on the working line; 11) signal amplifier; 12) oscilloscope; 13) ball cock on the bypass line; 14) drain cock.
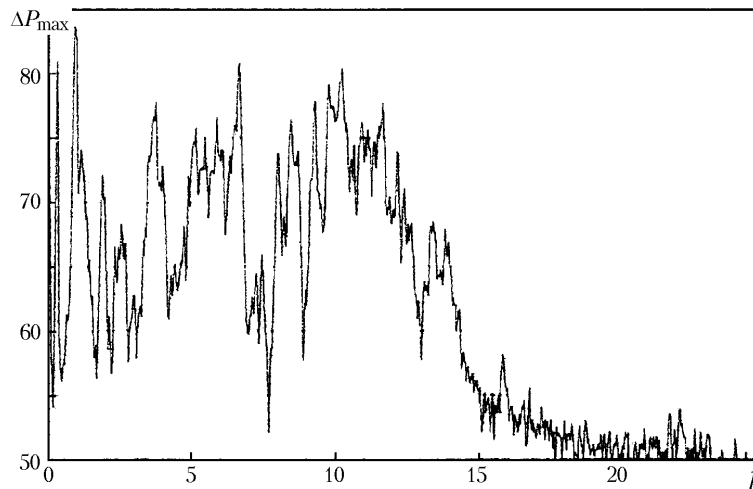

Fig. 2. Spectrum of the cavitation generator (disperser).

(the flow diagram of such a facility is given in Fig. 1). Some composites were subjected to the wave action in the ultrasound frequency range with the aid of a UZDN 2 generator (frequency 22 kHz, maximum intensity 30 W·cm^{-3}). It should be noted that the way of exciting vibrations in a multiphase medium in realizing the basic principles of the wave technology is of no significance. At the same time, the intensity of the wave action determined by the supplied energy of sound vibrations and expressed in terms of the amplitude-frequency characteristics depends on the particular equipment. The range of frequencies realized in shakers is between ~40 Hz and 1 kHz and the attained amplitude values correspond to vibroaccelerations of the order of 20–25 g. In the typical wide-band frequency spectrum of the vortex-type hydrodynamic generator (disperser) with clearly defined harmonics, two regions connected with different mechanisms of wave excitation can be distinguished (Fig. 2). The amplitude and frequency of these generators are determined by the conditions for the appearance and collapse of a cavitation cavity (ratio between the geometric dimensions of the generator, pressure, and flow rate, as well as the physicochemical properties of the liquid medium pumped through the generator). Vibrations in the 0–5-kHz range are associated with the cavitation-cavity motion in the generator cavity, and in the 5–30-kHz range they are due to the collapse of the cavitation bubbles separating from the cavity. The pressure pulse amplitude depends on the physical processes that take place in the process of collapse of bubbles and can be very large. Importantly, the wave technology is realized in the resonant mode, which determines minimal energy expenditures.

138

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

Disperse system	Vibroaction parameters		d, μm	Proportion of particles with d, %
	t_{v}, min	Δp, atm		
Oil/water	0*	—	20.5	>50
	10	10	5.2	>50
	20	10	0.8	>50
	10	15	0.7	100
	10	25	0.62	100
	10	—	1.14	97
	1***	—	3.0	80
	3***	—	0.7	92
	5***	—	0.5	100
Polymer/water (latex)	0*	—	0.18	83
	5**	—	0.15	82
	10**	—	0.13	96
	1***	—	0.15	97
Carbon/water + PAA	0*	—	3.5	60
	5**	—	2.1	94

The composites were: * prepared by mechanical mixing, ** subjected to vibroaction on a vibroplatform (vibration-testing machine), *** subjected to the action by ultrasound.

Table 1 presents the data on the influence of the vibrowave action on the dispersion of emulsions and suspensions. The particle size was determined by means of a microscope and by the method of laser autocorrelation spectroscopy [7]. It was tempting to compare the experimental and calculated data by the dependence of the size of dispersed droplets on the energy dissipation rate. In the works of Kolmogorov, Hinze, and Thomas [8–10], the size of dispersed droplets in emulsion is associated with the energy dissipation rate E in a unit mass of the liquid, with $E = E_1 + E_2$, where E_1 characterizes the energy dissipation due to the liquid-flow turbulization; E_2 — the same, due to the vibration action. S. A. Kostrov [10] presents the empirical dependences for $E_1 \approx u^3/l$, where u is the turbulence flow intensity, which for a flow system is taken to be between 5% (for the boundary layer) and 25% (for vortices and jets) of the change in the mean velocity in the flow section, and l is the scale factor, which is assumed to be 10% of the turbulent-flow diameter. E_2 is given in the following form: $E_2 \approx P_{max}\omega/\rho$, where P_{max} is the pressure oscillation amplitude at a given point of a two-phase medium; ω is the oscillation frequency of pressure waves in the liquid; ρ is the density of the liquid in which the internal phase is dispersed. According to the Kolmogorov–Hinze theory, a liquid droplet will collapse if the Weber number reaches a value of the order of one; $\rho\Delta^2 d/\sigma \geq 1$. The quantity Δ can be given in the form $\Delta \approx (Ed)^{1/3}$; then $d_{max} \approx (\sigma/\rho)^{3/5}E^{-2/5}$. Comparing the power consumption of electric motors, we have calculated the energy expended in the preparation of equal quantities of emulsions by the wave and traditional methods. The estimate has shown that the specific power consumption in treating 1 liter of emulsion on the wave facility is about one order of magnitude lower than in the laboratory agitator (0.046 and 0.330 kW), and the degree of dispersion attained thereby is higher. In the case of estimating d_{max}, substitution into the above formula of the existing and obtained values yields $d_{max} \approx (21.46/10^{-10})^{3/5}\cdot(93)^{-2/5} \approx 1.027\cdot10^{-6}$ m, which can be considered to be in good agreement with the experimental data (0.7–1.1 μm). In the above-mentioned investigation [10], there is also the expression for $d_{min} \approx 2.4(\sigma^2 h^2/\mu\rho E)^{1/4}$, where μ is the dynamic viscosity of liquid droplets; h is the thickness of the liquid-droplet surface film. Estimation of d_{min} under the conditions of our experiment, where the amplitude of oscillations generated by the hydrodynamic generator was varied from 600 to 2800 Pa, the rate of liquid flow through the generator was varied from $2.5\cdot10^{-4}$ to $3.5\cdot10^{-4}$ m³/sec, and the circular frequency of oscillations was 4500–5600 rad/sec, can also be done by varying over a wide range of the energy dissipation rate E_2 producing the strongest effect on the total dissipation energy E. In so doing, the motor oil density $\rho = 950$ kg/m³, the dynamic viscosity $\mu = 500$ Pa·sec, the surface tension $\sigma = 5.2\cdot10^{-2}$ N/m, and the turbulence intensity $u = 3.5$–4.5 m/sec. The scale factor was assumed to be equal to $L = 10^{-3}$ m, and the surface-film thickness was taken to
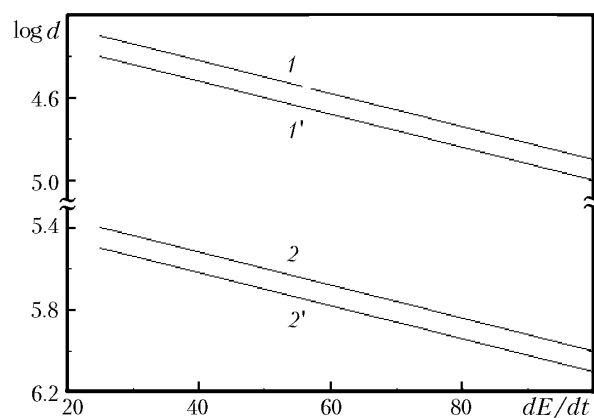
Fig. 3. Maximal (1, 1′) and minimal (2, 2′) sizes of emulsion droplets as a function of the vibrowave action intensity.

TABLE 2. Viscosity of the Initial and Final States of the Printing Ink Mass Being Mixed as a Function of the Number of Rotations per Minute of the Reotest-2 Viscosimeter Attachment

Number of rotations per minute	μ, cP (10^{-3} Pa·sec)	
	thick mass (before agitation)	froth (after agitation)
5/18	15768.0	—
0.5	13629.4	1378.6
5/6	11972.0	1240.5
1.5	10552.2	1209.4
2.5	8081.2	1102.4
4.5	6489.4	1041.8
7.5	4541.8	917.8
13.5	3603.6	663.3
40.5	2712.8	520.7
67.5	1531.4	340.9
121.5	1092.1	272.3

Note. The rotational velocity of the Reotest-2 viscosimeter motor is 1500 rpm.

be equal to $h = 5 \cdot 10^{-8}$ m. Figure 3, in which curves 1 and 2 represent the experimental data, confirms the adequacy of the corresponding calculations (curves 1′, 2′).

The above examples demonstrating that the intensity of the mass-exchange processes increases under the vibrowave action were obtained on a model system motor oil/water. Analogous effects associated with an increase in the degree of dispersion under the action of nonlinear oscillations are also noted in other disperse systems. A decrease in the internal-phase particle size under the vibrowave action was also observed in chalk/water and titanium-dioxide/water systems [11]. An increase in the vibrowave intensity promotes a further increase in the degree of dispersion accompanied by an increase in the aggregative stability. In the chalk/water system treated with the aid of the hydrodynamic generator, a paste preserving the three-phase structure for several months was obtained. It should be noted that under the influence of nonlinear oscillations excited in multiphase media not only are the physical processes associated with the mass transfer (phase transitions, diffusion, dispersion, etc.) intensified, but an increase in the rate of chemical transformations [5] and mechanochemical destruction can occur. It cannot be excluded that under the influence of the developing cavitation in the above chalk/water system the reactions proceed according to the scheme $CaCO_3 \leftrightarrow CaO + CO_2$, $CaO + H_2O \rightarrow Ca(OH)_2$.

A decrease in the viscosity of polyacrylic acid upon vibrowave treatment was noted in [11] and can be indicative of the mechanochemical destruction of the polymer.

TABLE 3. Physicomechanical Properties of Nonwoven Materials

Ratio of latexes DL-940: AK-252 B	t_v, min	R_{sp}, N·m/g	ε, %
4:1	0	0.21	30.6
4:1	4	0.32	78.3
4:1	8	0.50	135.00
3:2	0	0.22	38.9
3:2	4	0.05	68.0
3:2	8	0.28	90.6
2:3	0	0.08	60.0
2:3	4	0.12	110

TABLE 4. Physicomechanical Characteristics of Nonwoven Materials Obtained with the Use of Carbon-Containing Composites Based on Various Polymers (fiber–kapron)

Polymer	Polymer concentration, mass. %	t_v, min	R_{sp}, N·m/g	ε, %
PAA	0.2	0	17.72	70
		5	23.57	75
PAA	0.4	0	14.46	60
		5	15.85	70
PAA	0.6	0	16.6	25
		5	17.05	20
		10	17.35	25
Gelatin	2	0	15.76	50
		5	24.75	70
Starch	1	0	24.57	100
		5	29.62	75

Table 2 presents the results on the dependence of the printing-ink viscosity on the time of vibrotreatment in a Reostat-2 viscosimeter. The decrease in the froth viscosity as a result of the vibroaction is likely to be due to the change in its structure, which leads to an increase in the rate of impregnation and improves the uniformity of the color of fabrics.

The vibrowave action promotes the formation of composites with a uniformly distributed filler, which permits obtaining stable impregnating compositions and nonwoven materials with improved service properties based on them. Tables 3 and 4 present the results of the physicomechanical testing of the nonwoven materials obtained by the method of impregnation of fibrous linen with binders based on mixtures of latexes, as well as aqueous solutions of gel-forming polymers (polyacrylic acid, starch, gelatin) filled with activated carbon and subjected to preliminary vibrowave treatment. It is seen that even in the absence of the coupling agent the elastostrength characteristics of composites upon the vibrowave action are higher than in the corresponding materials obtained by the traditional technology.

In conclusion, it may be noted that in estimating the strengthening effect in the considered composites one should take into account not only the influence of the mass-exchange intensification in the process of vibrowave treatment on the formation of morphological features of the polymer composite structure but also the colloid-chemical aspect of the elastostrength properties of composites associated with the change in the interface.

NOTATION

d, particle diameter, μm; E, energy, $m^2 \cdot g \cdot sec^{-2}$; dE/dt, energy dissipation rate in a liquid mass unit, $m^2 \cdot sec^{-3}$; g, gravitational acceleration, $m \cdot sec^{-2}$; h, film thickness, m; l, scale factors, m; ΔP, differential pressure, atm; P_{max}, pressure oscillation amplitude, Pa, rel. units; R_{sp}, specific breaking load, N·m(g); t_v, vibroaction time, min; u, flow tur-

bulence intensity, m·sec^{-1}; Δ, change in the rate, m·sec^{-1}; ε, relative elongation at the moment of breaking, %; μ, dynamic viscosity, Pa·sec; ρ, density, kg·m^{-3}; σ, surface tension, N·m^{-1}; $\omega = 2\pi f$, oscillation frequency, rad·sec^{-1}. Subscripts: v, vibroaction; sp, specific; max, maximal; min, minimal.

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