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PROCESSES AND EQUIPMENT OF CHEMICAL INDUSTRY

Effect of a Hydroacoustic Treatment on the State of Chitosan Solutions Containing a Solid Filler

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Abstract—Fundamental aspects of the hydroacoustic dispersion of solid fillers, fractionated quartz sand and aerosil, in chitosan solutions were studied.

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The steady expansion of the possible areas of practical application of chitosan, polyglucosamine of natural origin, is due to the set of its unique properties, such as biocompatibility, biological activity, sorption activity, and film- and gel-forming capacity. Finely dispersed solid fillers may serve as practically and scientifically interesting modifiers for chitosan-based materials (films, sponges, granules, capsules). Use of fillers makes it possible not only to lower the cost of materials based on the expensive chitosan [1], but also to impart to these materials new properties by using insoluble functional ingredients [2].

A rather successful way to obtain finely dispersed suspensions in water and other solvents is the hydroacoustic treatment in high-speed rotary-pulsatory apparatus (RPAs) [3]. The basic design feature of these apparatus is the presence of alternating immobile and rotating cylinders with slits. The most important factors of treatment of liquid-phase materials in apparatus of this kind are ultrasonic vibrations and, accordingly, cavitation, as well as the strong shear stresses to which the fluid is subjected in narrow (0.1–0.5 mm) gaps between the rotor and stator members. The action of these factors on suspensions in which polymer solutions serve as a dispersion medium causes a number of mutually related effects, including mechanically initiated chemical processes both in the polymer and on the surface of solid particles being disintegrated.

The aim of this study was to determine the fundamental aspects of dispersion of a solid filler in chitosan solutions under a hydroacoustic treatment and to analyze the effect of this treatment on the film-forming capacity of the suspensions obtained. Fractionated quartz sand with various initial particle sizes was chosen as a model crystalline filler, and aerosil, amorphous analog of quartz sand, as an amorphous filler.

EXPERIMENTAL

As objects of study served suspensions of quartz sand (0.16, 0.1, 0.05, and 0.03 mm fractions), GOST (State Standard) 22551–77, and aerosil of A-380 brand, GOST 14922–77, in solutions of chitosans with MM 87 (Kh-87), 120 (Kh-120), and 520 kDa (Kh-500), with degrees of deacetylation equal to 0.82, 0.78, and 0.68, respectively.[1] Starting solutions with chitosan concentrations of 0.5–5 wt % in 2% acetic acid were used. The content of the solid phase in the suspension was varied from 0.5 to 10 wt %.

Chitosan solutions were treated in a laboratory RPA in the recycle mode. The thermostated working chamber of the apparatus is formed by the rotor and stator, whose cylindrical rings have rectangular channels. When the rotor rotates, the fast alternation of channel coincidence/nocoincidence gives rise to mechanical vibrations in the fluid in a wide range of frequencies, including ultrasonic vibrations. The average gap between the rotating and immobile

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[1] Chitosan samples were provided by Bioprogress Private Company.

Change in the average particle size and specific surface area upon a mechanical treatment in RPA of quartz sand suspensions in a chitosan solutions (Kh-120, *c* = 0.5 wt %)

Quartz sand fraction	Average particle size, μm		Degree of dispersion *D*/*d*	Extent of decrease in the viscosity of the medium[b]	Specific surface area *S*, cm^2 g^{-1}		Gain in the specific surface area, Δ*S*, cm^2 g^{-1}
	initial, *D*	after treatment in RPA, *d* [a]			initial	after treatment in RPA[a]	
1	30	16.2	1.85	0.18	909.1	1683.5	774.4
2	50	20.3	2.46	0.21	545.5	1343.5	798.0
3	100	25.9	3.86	0.30	272.7	1053	780.3
4	160	28.7	5.57	0.41	170.5	950.3	779.8

[a] Solid phase concentration 0.5 wt %.

[b] Calculated for the dispersion medium separated from the solid phase by centrifugation by the formula (μin – μA)/μin

members of the working chamber is 0.3 mm. The rotor rotation rate is 5000 rpm, to which corresponds a shear rate gradient of 17.4 104 s^{-1}; the treatment duration is 10 s.

The average size of dispersed particles was measured with an ANALYSETTE 22 COMPACT laser diffraction analyzer of particle sizes, with statistical processing of the micrographs obtained.

The dynamic viscosity of chitosan solutions was determined with Brookfield DV-E rotation viscometer with a cylindrical rotor (6 rpm) at 25±0.5°C, with shear rates in the range 0.1–132 s^{-1}.

Films of mechanically activated and untreated suspensions were formed by the dry method. The suspensions (10–20 ml) were poured into planar organic glass cuvettes and kept in air at room temperature for 24 h to complete drying. The film thickness was 30–50 μm.

The mechanical properties of the films were studied under uniaxial tension conditions on an RM-3 tensile-testing machine, with a 5-g load applied at a rate of 100 mm min^{-1}.

In the mechanical treatment of suspensions in RPAs, the cavitation and collisions of particles with one another and apparatus walls result in their diminution. Figure 1 shows histograms of particle size distributions, plotted using the data obtained using ANALYSETTE 22 analyzer for the untreated and mechanically activated suspension of quartz sand in a 0.5% chitosan solution. For mechanically treated quartz sand suspensions, a characteristic narrowing of the histogram and its shift to smaller particle sizes are

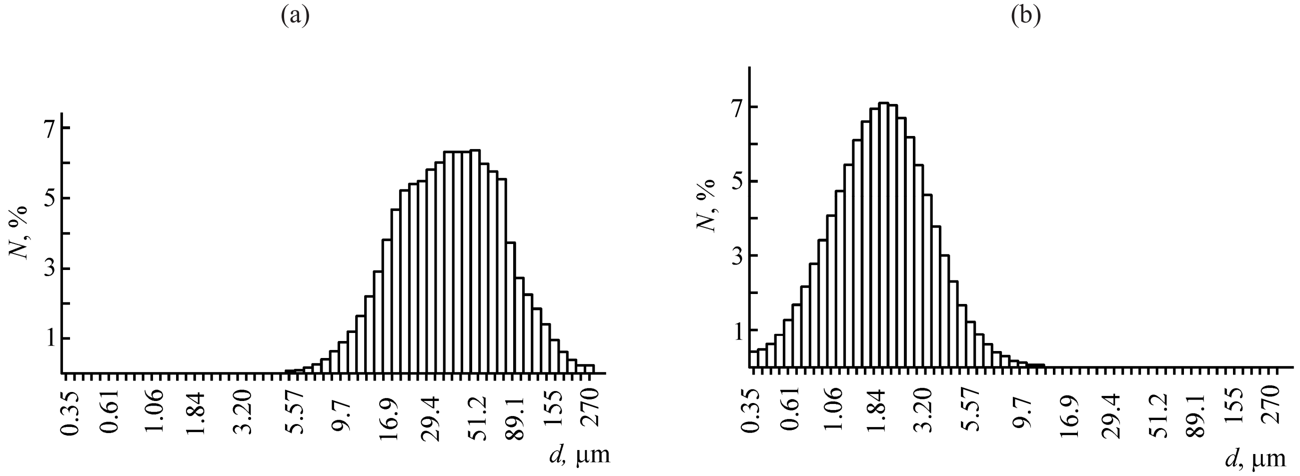
(a) (b)

Fig. 1. Histograms of particle size distribution for (a) untreated quartz sand and (b) that treated in an RPA. (*N*) Content of quartz sand particles and (*d*) particle size.

observed. The fraction of the solid phase in the suspensions being treated is 0.25–4.5 vol %, and, therefore, the role of particle collisions is insignificant because of the damping action of the medium. The key factor in the hydroacoustic treatment is the ultrasonic cavitation [3]. In the case of cavitation, particles mostly disintegrate under the action of shock waves and fluid microjects generated by collapsing cavitation bubbles.

The predominance of some mechanism in acoustic dispersion is determined by relative sizes of cavitation bubbles and particles of the dispersed phase [4]. The size of cavitation bubbles in aqueous media for frequencies on the order of several tens of kilohertz is several tens of micrometers [5]. If a particle is larger than a bubble, the initial spherical shape of the bubble is distorted and the collapsing process is accompanied by formation of fluid microjets with a high flow velocity. In this case, the mechanism of wedging at weakened intermolecular bonds predominates. It can be assumed that this mechanism is operative in mechanical treatment of quartz sand suspensions.

When particles are smaller than bubbles, particles are not split into fragments and upper layers of a particle are kind of exfoliated under the action of shock waves. Presumably, this mechanism is operative in mechanical treatment of suspensions of aerosil, whose particles have initial sizes of 0.5–1.5 μm.

According to the results of microscopic measurements and data furnished by ANALYSETTE 22 laser diffraction analyzer, the size of aerosil particles remains almost unchanged upon treatment. Particles of the untreated aerosil are aggregates, which follows from the pronounced mismatch between the size of particles well discernible under an optical microscope and the specific surface area given in the sample label. It can be assumed that this experimental result is a consequence of the parallel occurrence of disaggregation and formation of new aggregates from mechanically activated particles. In any case, the experimental data give no way of concluding that juvenile planes are opened in mechanical treatment of aerosil suspensions.

The goal of the first stage of the study was to determine the most important factors affecting the efficiency of hydroacoustic diminution of quartz sand particles in chitosan solutions. As demonstrated by the experimental results, such decisive factors at a given treatment intensity are the initial particle size of the filler, content of the solid phase in suspensions, and chitosan concentration in the solutions used. The efficiency of mechanical diminution of particles was evaluated by the degree of dispersion, D/d, numerically equal to the ratio between the average particle sizes of the starting suspension and that treated in an RPA. As indicated by the data in the table, the dispersion efficiency of solid particles increases with the initial particle size. This result is in agreement with the known pattern according to which coarser particles are subjected to mechanical disintegration in the first place and with a higher probability [3]. The table also lists values of the gain in the specific surface area of particles, ΔS, as a result of mechanical diminution, calculated by the formula [6]

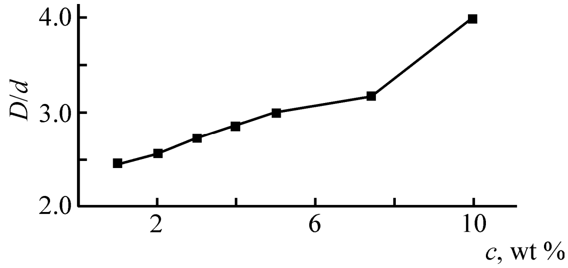

Fig. 2. Degree of dispersion of quartz sand, D/d, vs. the content c of the solid phase in mechanically treated suspensions. Dispersion medium, 0.5% solution of Kh-120 chitosan.

$$\Delta S = \frac{6}{\rho d} - \frac{6}{\rho D},$$

where $\rho = 2.2$ g cm^{-3} is the density of quartz sand; D and d, initial and final particle sizes (cm); and 6, coefficient that accounts for the particle shape.

Noteworthy is the fact that the values of ΔS are close for all the quartz sand fractions used in the study. It is known that the mechanical energy imparted to the system in the course of dispersion is expended for formation of a new surface [7]. In experiments, suspensions of the same substance were treated under identical conditions, and, therefore, to the same amount of imparted energy corresponds the same (within the experimental error) amount of dispersion work. This correspondence takes place when the mechanoacoustic efficiency [7] remains constant for a given series. If, however, the experimental conditions are strongly modified, as in the case of a change in the concentration of the solid phase or concentration of the polymer in the dispersion medium, then the efficiency of mechanical dispersion may change. For example, it is shown in Fig. 2 that the dispersion efficiency grows

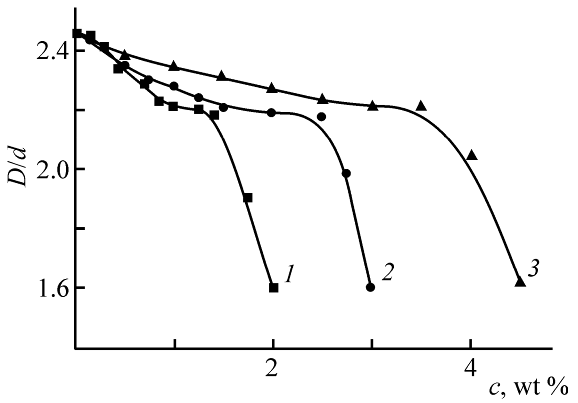

Fig. 3. Degree of dispersion of quartz sand (50 μm fraction), *D*/*d*, vs. the chitosan concentration *c* in solution in mechanical treatment in an RPA. (*1*) Kh-500, (*2*) Kh-120, and (*3*) Kh-87.

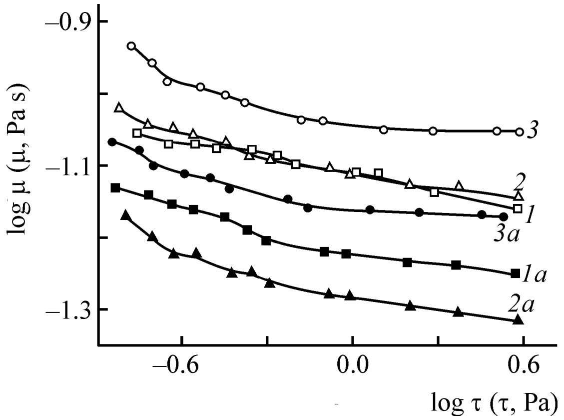

Fig. 4. Flow curves log μ–log τ for 0.5% solutions of Kh-120 chitosan (*1, 1a*) without filler and those containing 0.5 wt % filler: (*2, 2a*) quartz sand and (*3, 3a*) aerosil. (*1a*–*3a*) Mechanically treated systems.

with the content of the solid phase in suspensions. This is presumably accounted for by the increased role of particle collisions with one another and apparatus walls.

As the chitosan concentration in the dispersion medium increases, the dispersion efficiency falls, first only slightly and then, after a certain critical concentration is reached, sharply (Fig. 3). The monotonic fall of the dispersion efficiency is due to an increase in the energy dissipation and decrease in the collision energy because of the damping effect of the medium. In addition, the solution viscosity grows as the concentration increases, and, after a certain critical concentration is reached, the cavitation starts to be suppressed. The critical polymer concentrations corresponding to a sharp decrease in the dispersing effect became higher as the molecular mass decreased in the chitosan series Kh-500, Kh-120, and Kh-87 (1.5, 2.5, and 3.5 wt %, respectively).

As shown previously [8], treatment of chitosan solutions in an RPA leads to a substantial decrease in their viscosity, which an overall consequence of the simultaneous occurrence of mechanically initiated structural and chemical processes. It was of interest to find out how presence of disintegrating solid particles changes the state of chitosan solutions subjected to mechanical treatment. Figure 4 shows flow curves of Kh-120 chitosan solutions, obtained upon their treatment in an RPA in the presence of fillers and subsequent separation of the solid phase by centrifugation. The same figure shows analogous curves for chitosan solutions without a filler before and after a mechanical treatment.

All the flow curves shown in Fig. 4 are similar, i.e., it can be stated that presence of solid particles during treatment does not change the nature of the viscous flow of a solution after separation of the filler. In the case of solution treatment in the presence of aerosil, the extent to which the viscosity decreases is close that for solutions without the filler. In treatment of a solution in the presence of quartz sand particles being disintegrated, a stronger decrease in the viscosity is observed, compared with a solution treated without the filler.

It follows from the data in the table that the extent to which the viscosity decreases grows with the degree of dispersion, *D*/*d*. As already noted, the decrease in the viscosity is a consequence of the overall mechanical degradation of the solutions, which includes both a decrease in the size of supramolecular formations and destruction of macromolecules with rupture of skeletal bonds.

To evaluate the influence exerted by presence of disintegrating particles on the extent of mechanical destruction of macromolecules, the characteristic viscosity of chitosan solutions separated by centrifugation from the solid phase before and after mechanical treatment of suspensions was measured. In the process, no significant effect of the presence of the solid phase during treatment on the extent of mechanical destruction of the polymer was observed. Both in mechanical treatment of pure solutions and in treatment of the same solutions in the presence of a filler, the characteristic viscosity of chitosan changes only slightly. For example, for sample Kh-120, the characteristic viscosity decreased upon 10 s of treatment from 4.55 to 4.00 in treatment of a pure solution, and to 3.9 for a solution treated in the presence of 0.5 wt % quartz sand. Possibly, an additional degrading influence on the solution structure may appear because of changes in the nature of hydrodynamic phenomena in cavitation-induced disintegration of particles and high-velocity motion of sharp-edged fragments.

The physicomechanical properties of filler-containing polymeric materials are determined both by the size of particles of the dispersed phase and by interphase energies. In other words, the type of deformation and disintegration of a filled polymer is determined, at the same dispersity, by the interaction of the polymer with the filler surface. In a review [9], methods for reducing the interphase tension energy in fabrication of composite materials from synthetic polymers and inorganic fillers were considered. One of methods of this kind is grafting of a monomer to the surface of filler particles, initiated chemically or by various physical treatments. In the present study, in which an aqueous solution of a linear polysaccharide is subjected to an intensive mechanical treatment in the presence of an inorganic filler, chemical bonds can be formed at phase boundaries when macroradicals of the polymer being destructed recombine with active centers on the particle surface.

As already noted, no particle diminution was observed upon a mechanical treatment of aerosil suspensions in an RPA. It is known that, in treatment of suspensions under the action of ultrasonic cavitation, activation may occur because of the appearance of microscopic defects on the surface of particles even in the absence of their disintegration [10]. Thus, mechanically initiated grafting of chitosan is possible in this case, too, via appearance of active centers on the particle surface eroded by cavitation.

In formation of films from untreated and mechanically activated suspensions, the choice of the chitosan concentration in the starting solutions was based on the following. On the one hand, as already noted, the efficiency of the mechanical activation is higher in more dilute, with respect to the polymer, solutions. On the other hand, as the chitosan concentration and, accordingly, the viscosity of the solutions decrease, the sedimentation stability of the suspensions becomes lower, which may lead to a nonuniform distribution of particles over the film cross-section in drying. Therefore, a Kh-87 chitosan solution with a concentration of 2.5 wt % was chosen as the base solution for studies of the film-forming capacity of the suspensions, and quartz sand of the finest fraction (30 μm) and aerosil were used as fillers.

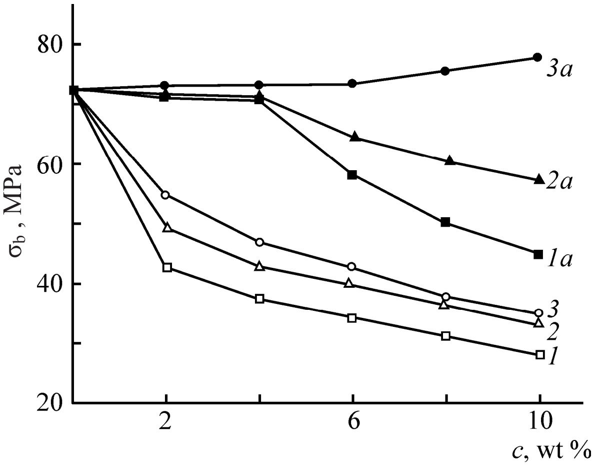

Fig. 5. Breaking load σ_b of films produced from suspensions based on a 2.5% solution of Kh-120 chitosan vs. their content c of the solid phase. Quartz sand prepared by (*1, 1a*) method 1 and (*2, 2a*) method 2; (*3, 3a*) aerosil. (*1a*–*3a*) Suspensions treated in an RPA.

Quartz sand suspensions were prepared in two ways. In method 1, quartz sand suspensions based on a 2.5% chitosan solutions were subjected to mechanical treatment, with the content of the solid phase varied. In method 2, mechanical activation was applied to quartz sand suspensions (10 wt % solid phase) in a 0.5% chitosan solution. After the activation, these suspendsions were used for introduction into a more concentrated chitosan solution so as to obtain a set of suspensions with the same concentration of chitosan in the dispersion medium (2.5%) and a varied content of the solid phase.

Figure 5 shows dependences of the breaking load for films produced from untreated and activated suspensions. In all cases, a sharp decrease in the film strength was observed as the filler content of the films increased. For quartz sand suspensions subjected to a mechanical activation, the breaking load also decreased as the filler content was raised, but did so to a lesser extent than that for films produced from untreated suspensions. It should be noted here that a stronger activating effect was observed, as it would be expected, for suspensions produced by method 2. For films formed from these suspensions, raising the filer content up to 4 wt % did not impair their strength (Fig. 5, curve *2a*). This result can be accounted for by the stronger dispersion of the filler in its treatment in an RPA in a dispersion medium with a lower viscosity.

The strongest activating effect was obtained with aerosil used as a filler. Introduction of the filler, followed by mechanical treatment, not only did not diminish the mechanical strength of the films, but even improved this parameter. The key role is presumably played in this case by the small size of aerosil particles (0.5–1.5 μm). As reported previously [6, 7], in hydroacoustic treatment of polysaccharide solutions, disintegration of the initial structure of a solution and formation of a new structure occur simultaneously under the action of high shear stresses. In the case of treatment of aerosil suspensions in an RPA, the dynamic structuring in the dispersion medium, i.e., in the chitosan solutions, occurs in the presence of particles whose sizes are comparable with those of structural elements of the solution itself. It can be stated that the solution structure incorporates solid particles, which hinders appearance of coarse supramolecular formations in the solution and thereby reduces the degree of the intrinsic microheterogeneity of the polymeric matrix.

CONCLUSIONS

(1) The efficiency of the hydroacoustic dispersion of a solid crystalline filler, fractionated quartz sand, in chitosan solutions increases as the concentration and initial size of filler particles grow and decreases as the concentration of chitosan in the dispersion medium becomes higher.

(2) The mechanical activation of chitosan solutions containing a dispersed solid filler in a rotary-pulsatory apparatus can markedly improve the strength of films formed from these solutions.

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