ISSN 1070-4272, Russian Journal of Applied Chemistry, 2008, Vol. 81, No. 12, pp. 2112–2117. © Pleiades Publishing, Ltd., 2008.
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PROCESSES AND EQUIPMENT OF CHEMICAL INDUSTRY

Effect of Hydroacoustic Treatment on Chitosan Dissolution in Aqueous Acetic Acid Solutions

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Received May 13, 2008

Abstract—Effect of a hydroacoustic treatment in a rotary-pulsatory apparatus on the dissolution rate and the achievable limiting solubility of chitosan in aqueous acetic acid solutions of various concentrations was studied. The rheological properties of solutions produced by the conventional method and with mechanical activation were compared.

DOI: 10.1134/S1070427208120136

Chitosan is an ionogenic polysaccharide with a set of rather valuable properties. The technological convenience of chitosan, related to its solubility in weakly acid aqueous media, makes it possible to produce from this polymer microspheres, microcapsules, coupling agents, and membranes, as well as carrier matrices in manufacture of medicinal preparations. Many structurally sensitive properties of these materials and articles are preset already in the stage of preparation of starting solutions from commercial chitosans manufactured in the form of powders or scales.

The properties of chitosan solutions have been described more than once [1–4], but either the method of solution preparation was not mentioned at all, or only the dissolution duration was specified. The solvent most frequently used for chitosan is 2% acetic acid. The duration of dissolution in this solvent under laboratory conditions is 4–16 h for different samples, depending on their molecular mass and degree of deacetylation [3, 4]. It was found in a study of the solubility of various brands of chitosan [5] that all the samples studied dissolve in 1% acetic acid; however, complete dissolution was reached for some of these samples only in 24 h. In addition, we found that solutions of chitosan with a molecular mass exceeding 400 kDa are inhomogeneous because of the presence of a gel fraction, which adversely affects the quality of films formed from these solutions. With the expansion of the field of industrial application of chitosans, the problem of fast preparation of their solutions without additional filtration becomes increasingly pressing.

A rather effective method for intensification of various technological processes performed in liquid media is hydroacoustic treatment in high-speed rotary-pulsatory apparatus [6]. The main distinctive design feature of these apparatus is the presence of alternating immobile and rotating cylinders with slits. In these apparatus, the most important factors activating the liquid media being treated are ultrasonic vibrations and, accordingly, cavitation, and also high shear stresses to which the liquid is subjected in narrow (0.1–0.5 mm) gaps between the rotor and stator elements.

The aim of our study was to examine the effect of a hydroacoustic treatment in rotary-pulsatory apparatus on the dissolution rate and achievable limiting solubility of chitosan in aqueous acetic acid solutions of various concentrations. In addition, we intended to compare the rheological properties of solutions produced in the conventional way and those obtained with mechanical activation.

EXPERIMENTAL

As objects of study served three chitosan samples with M = 360 (Kh-360), 470 (Kh-470), and 500 kDa (Kh-500).[1] The degrees of deacetylation (DD) of the chitosans were 0.82, 0.79, and 0.60, respectively. In the air-dry state, the chitosans were in the form of flat scales 0.5–2 mm in size.

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

We used as solvents aqueous acetic acid solutions with an acid concentration varied within the range 0.2–2 wt %. Weighed portions of chitosans (1 g dl^{-1}) were dissolved in the aqueous acetic acid solutions at a temperature of 25°C under agitation until the process termination was analytically determined.

The thus obtained suspensions were mechanically treated in a laboratory rotary-pulsatory apparatus (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. The average gap between the rotating and immobile members of the working chamber was 0.3 mm. The rotor rotation rate was 5000 rpm, to which corresponds a shear rate gradient of 17.4×10^4 s^{-1}. The treatment duration was varied within the range 4–40 s.

The dissolution rate of chitosans was determined by sampling the dispersion medium of the suspensions under study at regular intervals of time. The samples, transparent solutions, were analyzed for the content of chitosan by performing the reaction with Ninhydrin dye by the procedure described in [7], with the optical density of the resulting stained solutions measured on a Specol 11 spectrophotometer at a wavelength of 565 nm. Taking into account that the result of the analysis depends on the degree of deacetylation, a separate calibration plot was measured for each sample.

The content of the gel fraction in the chitosan solutions was found gravimetrically. A weighed portion of a solution was passed through preliminarily weighed sieves with 0.8×0.8-mm mesh, after which the sieves with the gel fraction they retained were again weighed and the volume fraction of the gel fraction was calculated, with the solution density taken to be 1 g cm^{-3}.

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

The characteristic viscosity of dissolved chitosan samples was determined at 25°C in an Ubbelohde viscometer (capillary diameter 0.73 mm) by successive dilution with 2% acetic acid. A 0.2 M solution of sodium acetate was introduced as a supporting electrolyte.

Chitosan is a polyaminosaccharide having an apparent dissociation constant of a conjugated acid, pK_a = 6.3–6.7, and dissolving in water only at pH < 6. As solvents can be used dilute solutions of monobasic organic and inorganic acids. The dissolution is preceded by protonation of NH_2 groups to give a salt adduct. Solutions are most frequently prepared using acetic acid with a concentration of 2 wt %, with the solution pH taking values of 3.3–3.6 upon complete dissolution. The so low pH values are undesirable in some cases and, in particular, in use of chitosan for immobilization of proteins and certain medicinal preparations. However, the decrease in the acid concentration strongly hinders the dissolution.

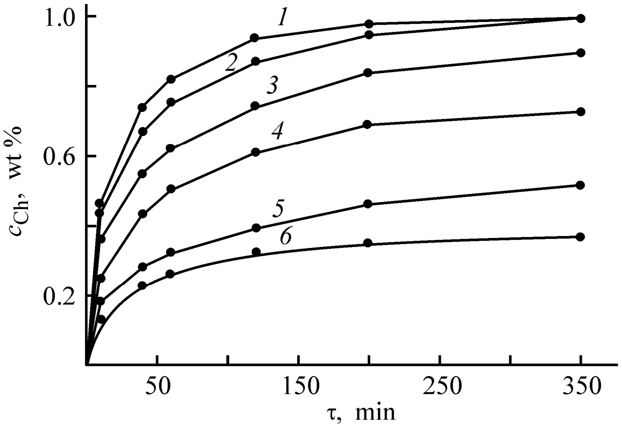

Fig. 1. Concentration c_{Ch} of Kh-360 chitosan in solution vs. the dissolution duration τ at a hydromodulus of 1 : 100. Acid concentration in solution (wt %): (*1*) 2, (*2*) 1, (*3*) 0.8, (*4*) 0.5, (*5*) 0.3, and (*6*) 0.2.

In this study, we used acetic acid solutions with concentrations of 0.2, 0.3, 0.5, 0.8, 1, and 2% as a medium for chitosan dissolution. Kinetic curves of Kh-360 chitosan dissolution in these media under ordinary conditions are shown in Fig. 1. The run of the kinetic curves indicates that the dissolution rate steeply decreases as the process duration becomes longer and the kinetic curves take a nearly horizontal position, although, according to analytical data, the process continues for several more hours until its completion.

Such a nonuniform course of the dissolution process is presumably due to structural inhomogeneity and molecular polydispersity of chitosan. The time in which the limiting concentration of chitosan is reached steadily increases as the acid concentration in the solvent decreases. For example, as indicated by analytical data and visual inspection, the process was complete in 5–6 h at acid concentrations of 1 and 2%, whereas at concentrations of 0.2 and 0.4%, the chitosan concentration in samples of the dispersion medium ceased to increase 20–22 h after introduction of chitosan into the solvent and, in this case, the solution contained a noticeable amount of undissolved particles.

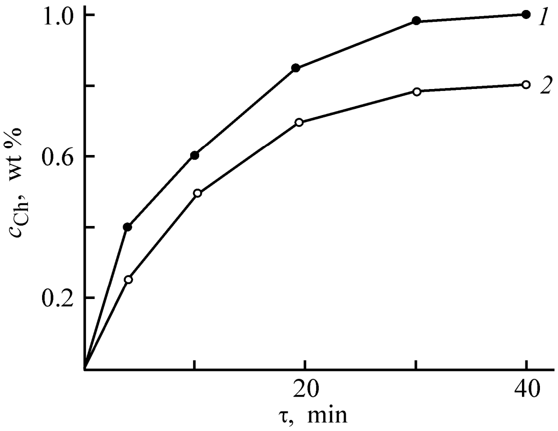

Fig. 2. Concentration c_{Ch} of Kh-360 chitosan in solution vs. the dissolution duration τ for the process performed in an RPA at a hydromodulus of 1 : 100. Acid concentration in solution (wt %): (*1*) 1 and (*2*) 0.8.

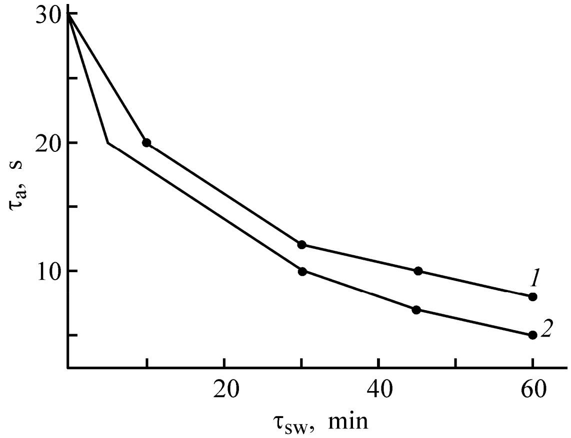

Fig. 3. Effect of the preliminary swelling time τ_{sw} on the dissolution duration τ_a of (*1*) Kh-470 and (*2*) Kh-360 chitosans in 2% acetic acid under mechanical activation in an RPA.

In the case of chitosan dissolution directly in the working chamber of RPA, sampling during treatment is impossible because of the too short process duration. To measure the rate of mechanically activated dissolution of chitosan, we prepared as many starting suspensions as the number of points to be obtained in the kinetic curve. The suspensions were activated one after another, with the treatment duration increasing each time, after which the undissolved fraction was separated and the solutions were analyzed for the content of chitosan. The kinetic curves obtained for the process of Kh-360 chitosan dissolution under hydroacoustic treatment are shown in Fig. 2 (curves *1*, *2*).

Comparison of the data in Figs. 1 and 2 points to a high efficiency of RPA application to intensification of the chitosan dissolution in the aqueous media under study. For example, a 80% dissolution of chitosan is reached under ordinary agitation by a mechanical stirrer at acid concentrations of 1 and 0.8% in 90 and 210 min, respectively, whereas in dissolution in an RPA, the same occurs in 17 and 35 s, respectively. The efficiency of mechanical activation in dissolution substantially increases if a suspension is treated in an RPA after a certain time, i.e., after a preliminary swelling of particles in the solvent, rather than immediately upon its preparation. Figure 3 shows how the time of mechanical treatment of a chitosan suspension (samples Kh-360 and Kh-470) in an RPA, necessary for complete dissolution of the polymer, becomes shorter as the time of preliminary swelling of the chitosan suspension increases.

It should be noted that, even with thermostating of the working chamber of the RPA, the solution warmed-up to 30–32°C. The heat released because of the internal friction in media being processed is apparently an additional factor that intensifies the dissolution. In this study, the duration of treatment in RPA did not exceed 40 s, because at longer durations it was impossible to preclude a considerable warming-up of the media being processed and a noticeable destruction of the polymer [8]. For Kh-500 chitosan, treatment in an RPA of a suspension without preliminary treatment does not lead to complete dissolution in 40 s. A total visually indicated dissolution is achieved only in activation of the suspension after a preliminary swelling for 2 h. In this case, too, the total process duration is substantially shorter than that in dissolution without activation. In addition, a solution obtained with mechanical activation is more homogeneous and contains no gel fraction.

The achieved effect of accelerated dissolution is accounted for by the simultaneous action of a number of factors on suspensions being processed under hydroacoustic treatment. The dissolution of solid particles in a liquid under treatment in RPA occurs simultaneously with the dispersion and, consequently, with the development of the phase-contact surface. The particles being dissolved are subjected to a multifactor treatment including turbulent pulsations of the liquid flow velocity, spherical shock waves in pulsations of cavitation bubbles, and cumulative action upon the collapse of these bubbles. Chaotic turbulent fluctuations of various layers of the liquid create strong shear stresses on the surface of a solid particle, which favors a decrease in the thickness of the diffusion layer, enhances its mobility, and provides an inflow of a fresh liquid to the surface of a particle being dissolved.

It was of interest to find whether it is possible to raise the limiting solubility of chitosan at low acetic acid concentrations by hydroacoustic treatment. According to the data of [9], the chitosan dissolution occurs at a degree of protonation equal to 0.5, i.e., 50% of amino groups are to be ionized for a macromolecule to pass into solution. According to the results of the same study, the 0.5–0.7 degree of protonation is reached only at the equimolar CH3COOH : chitosan ratio. The authors of [10] found that, irrespective of the acid concentration in the starting solutions, the residual amount of acetic acid in films formed from chitosan solutions in aqueous acetic acid is 24–27%, which corresponds to an approximately equimolar ratio between the acid and amino groups of the polymer. Upon introduction of 1 wt % chitosan into a solution, the equimolar ratio between the acid and amino groups is reached by the system at an acid concentration as low as 0.4%.

Thus, the complete dissolution can theoretically be reached at acid concentrations substantially lower than 2%, or even 1%, relative to the solution mass. As, however, follows from the experimental data obtained, only 73% of Kh-360 chitosan is dissolved even on raising the process duration to 24 h if the acid concentration is lowered to 0.5%. This result indicates that the solubility of chitosan is determined not only by the acid concentration of a solution, but, apparently, also by the degree of chemical and structural nonuniformity of a sample, i.e., by the quality of the raw material used.

Chitosan is produced by alkaline deacetylation of chitin. The incomplete course of this process is due to the presence of residual acetyl groups whose distribution in chitosan depends on the degree of crystallinity or on the relative amounts of the crystalline and amorphous regions of the starting chitosan, because the deacetylation reaction more easily proceeds in amorphous regions. The nonuniform distribution of the residual acetyl groups presumably predetermines that less soluble blocks are present in the chitosan structure, which alternate with regions of a nearly completely deacetylated polysaccharide. These latter cause a strong swelling of structural units in protonation in solution via electrostatic repulsion [11].

Under a hydroacoustic treatment, the combination of the above-mentioned factors must lead to disintegration of strongly swollen particles and to rupture of hydrogen bonds, which, in turn, must favor transfer of macromolecules with a sufficient degree of protonation to the solution. Figure 4 shows how the limiting solubility depends on the acetic acid concentration in an aqueous solution for the cases of conventional chitosan dissolution and that in the working chamber of RPA in the course of 40 s. It can be seen that, at low acid concentrations, the effect of the mechanical activation is manifested in that the limiting solubility increases, on average, by 25–45%.

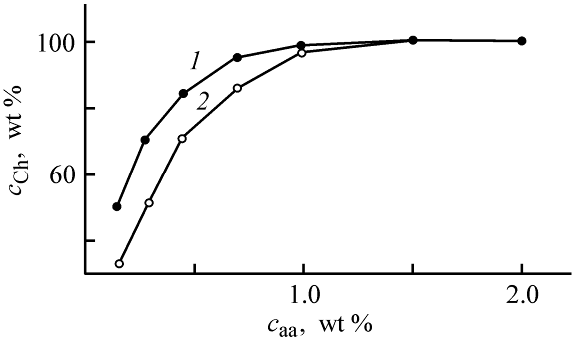

Fig. 4. Limiting solubility c_{Ch} of Kh-360 chitosan at a hydromodulus of 1 : 100 vs. the acetic acid concentration c_{aa} for the process performed (*1*) with mechanical activation in RPA and (*2*) with a mechanical stirrer at 25°C.

In mechanically activated dissolution with the use of RPA, not only the process duration changes, but also the quality of the solution obtained; in particular, the content of the gel fraction substantially decreases. Numerous publications concerned with properties of chitosan solutions do not mention presence of a gel fraction. We found that, after centrifugation of visually homogeneous solutions produced by prolonged dissolution in 2% acetic acid, their lower part with a higher viscosity can be separated by decantation. When these solutions are sieved, a viscous, gel-like part of the solution, in which spherical transparent particles (“gellites”) can be seen, remains on the sieve. This primarily refers to samples with high molecular mass and low degree of deacetylation. For example, on keeping a Kh-500 sample (DD 0.6) in 2% acetic acid under periodic agitation for 18 h, complete dissolution was visually observed. However, an analysis demonstrated that the content of the gel fraction at the instant of complete visual dissolution was 11 vol %. On further keeping of the solution for additional 4 and 8 h, the content of the gel fraction decreased to 8.5 and 6.2 vol %, respectively, but it did not disappear completely even on keeping the solution for two days.

The gel fraction is present because the polymer incompletely passes into solution even at acid concentrations and process durations at which complete dissolution must occur according to published data. The rea-

Effect of hydroacoustic treatment on the duration of chitosan dissolution in 2% acetic acid and properties of the solutions obtained (c_{Ch} = 1 wt %)

Parameters of a solution	Kh-360		Kh-470	
	without activation	with RPA	without activation	with RPA
Dissolution duration	5 h	20 s	8 h	30 s
Dynamic viscosity, mPa s^{-1}	580	370	780	410
DSS	11.3	18.6	12.7	20.7
[η], dl g^{-1}	7.2	6.8	8.2	7.6
Huggins constant	0.62	0.48	0.72	0.55

sons for such a behavior are apparently related to the prehistory of a sample and to the presence of fractions with a lower degree of deacetylation. As a result, strongly swollen transparent agglomerates remain, although visual observation shows complete dissolution. Films formed from these solutions have an uneven, hummocky surface. In solutions prepared using RPA, no gel fraction was found by the method used in this study. Films formed from mechanically treated solutions are homogeneous and have a smooth surface.

It has been found previously that hydroacoustic treatment on chitosan solutions leads to a decrease in their viscosity because of the occurrence of mechanically initiated structural and chemical transformations, with a certain contribution to the observed decrease in the viscosity made by activated hydrolytic destruction of the polymer, whose extent increases with temperature [8]. In this context, a goal of the present study was to compare the rheological properties of solutions prepared by the conventional method and with mechanical activation. To evaluate the extent of mechanically initiated destruction, we measured in parallel the characteristic viscosity related to the molecular mass of the polymer. The data obtained are listed in the table.

It can be seen from the table that solutions produced by the mechanical method have a lower viscosity and are less structured than solutions prepared by ordinary dissolution. The decrease in the characteristic viscosity, indicative of the mechanical destruction of the polymer, is 5–7%. The decrease in the degree of structuring of the mechanically treated solutions is indicated by an increase in the dynamic stability of their structure (DSS), whose values were calculated using rheological data by the formula

$$\mathrm{DSS} = (90 - \alpha)/(\alpha - 45),$$

where α is the slope rate of the linear portions of the dependences of the shear rate on shear stress, plotted in log–log coordinates.

The degree of structuring of the solutions presumably decreases via disintegration of stable aggregates of associated chitosan macromolecules in the mechanical field. The decrease in the Huggins constant, which characterizes the interaction of the polymer with the solvent, also points to a less important role of polymer–polymer contacts and increased role of polymer–solvent interactions in mechanically treated solutions. In other words, it can be stated that mechanical activation favors a more complete dissolution of chitosan.

Thus, it was shown that hydroacoustic treatment can diminish the duration of chitosan dissolution from several hours to several seconds. Solutions produced using mechanical activation are distinguished by lower viscosity and by better structural uniformity as compared with solutions of the same concentration, prepared in the conventional way. A decrease in the viscosity of chitosan solutions without any change in its concentration may be of practical interest in some cases and, in particular, for deposition of uniform films by spilling, synthesis of composite materials and impregnating solutions, and thin-layer dressing of various surfaces, and for other purposes.

CONCLUSIONS

(1) Use of hydroacoustic treatment in a rotary-pulsatory apparatus for intensification of chitosan dissolution in aqueous acetic acid solutions diminishes the process duration from several hours to 20–40 s.

(2) Mechanical activation of chitosan suspensions in acetic acid solutions with concentrations lower than 1% raises the limiting solubility of the polymer by 30–45%.

(3) Solutions produced using mechanical activation are distinguished by lower shear viscosity and molecular mass and by better structural uniformity, compared with solutions of the same concentration, prepared by the conventional method.

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