

# Rheological Properties of Cellulose–Chitosan–Phosphoric Acid Systems in Different Phase States

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**Abstract**—Rheological properties of 7.0–9.1% cellulose–chitosan suspensions, solutions, and gels in aqueous phosphoric acid were examined in various modes of shear flow in the range 0.15–100 s<sup>-1</sup> at 268–323 K. During steady state flow, the appearance of a quasi-Newtonian region was detected at shear rates between 20 and 40 s<sup>-1</sup> owing to orientational ordering of macromolecules in the stream. Under the conditions of transient shear flow at a constant shear rate, rheopexy was observed in both cellulose solutions and cellulose–chitosan solutions. The thixotropic behavior of cellulose–chitosan suspensions, spinning solutions, and gels was characterized during a sharp drop of shear rate from 0.15 to 10 s<sup>-1</sup>, that is, under conditions modeling the processes of transport and extrusion of spinning solutions.

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## INTRODUCTION

The combination of the two most widespread biopolymers in nature, cellulose and chitosan, is of great interest from the standpoint of production of composite filaments, fibers, films, membranes, and other polymeric materials with a unique set of properties. In particular, the combination of the sorption activity and hydrophilicity of both polymers with the high mechanical resistance of cellulose and the antibacterial properties of chitosan makes it possible to substantially extend their fields of application. The similarity of the chemical structures of the macromolecules provides conditions for the kinetic compatibility of the polymers in the same solvent, thus preventing the negative effect of phase separation on physical and mechanical properties of composite materials.

In recent years, investigations in the field of the combination of cellulose and chitosan have been intensive. However, an effective method of mixing the polymers to produce materials with a specified phase morphology still has not been found. Therefore, it is of great importance to study the rheological behavior of mixed solutions of cellulose and chitosan in phosphoric acid, which has been proposed as an environmentally friendly solvent for the production of regenerated cellulose fibers [1].

Phosphoric acids have recently again attracted attention from researchers. The renewal of interest in this cellulose solvent is due to the discovery of solution-preparation conditions that exclude intense polymer destruction [2]. There have been studies on the preparation of highly concentrated anisotropic spinning solutions of cellulose and its mixtures with other

polymers in anhydrous superphosphoric acids (mixtures of phosphoric and polyphosphoric acids) and on the formation of highly oriented fibers and filaments from these solutions and mixtures [3, 4]. The process of regenerated cellulose fiber preparation with the use of superphosphoric acids possesses obvious ecological advantages over the traditional viscose process; however, there have been no reports of industrial use of the former process. This circumstance is due to the necessity to use acetone as the main component of the coagulation bath, with the high flammability of acetone being a serious obstacle to execution of the process on an industrial scale. The factors limiting the wide spread of this method include also the high levels of corrosiveness of superphosphoric acids and their unsafe synthesis [5].

In [2], highly concentrated (5–12 wt %) solutions of cellulose in aqueous phosphoric acid were obtained for the first time. They proved to be suitable for use as spinning solutions, a circumstance that under laboratory, pilot, and experimental–industrial plant conditions allowed spinning of fibers with the following physical and mechanical properties: strengths of 22–30 cN tex<sup>-1</sup> at elongations of 8–15%, elastic moduli of 700–1200 cN tex<sup>-1</sup>, and degrees of cellulose polymerization in fibers of 400–500.

The advantages of the use of phosphoric acid as a cellulose solvent are primarily due to its nontoxicity and low corrosiveness. In combination with the possibility to recycle coagulation-bath components, this use has opened a real prospect to build a closed environmentally friendly process of producing regenerated cellulose fibers and filaments under industrial condi-

**Table 1.** Compositions of the studied cellulose–chitosan suspensions in phosphoric acid

Sample number	Cellulose-to-chitosan mass ratio	Concentration of cellulose in suspension, %	Total concentration of polymers in suspension, %
1	100 : 0	7.0	7.0
2	90 : 10	7.0	7.7
3	80 : 20	7.0	8.6
4	75 : 25	7.0	9.1

tions. In addition, aqueous solutions of phosphoric acid are capable of dissolving not only cellulose but also such polymers as chitosan, PAN, PVA, and starch, a circumstance that is of great interest for the preparation of modified regenerated cellulose fibers with improved properties.

Among the above-mentioned polymer pairs, the combination of cellulose with chitosan is of particular interest. However, despite numerous variations suggested by various researchers [6, 7], the technology allowing combination of these polymers at the molecular level has not yet been developed on an industrial scale. Thus, the surface modification of cellulose fibers and films with chitosan is under quite extensive investigation. For example, biologically active cellulose–chitosan fibers have been obtained via the treatment of oxidized Lyocell fibers with a chitosan acetate solution [6]. On the other hand, there have been attempts to introduce microcrystalline chitosan into a viscose solution [7].

In addition, studies on the combination of chitosan with cellulose in such dissolving systems as NaOH–thiourea and trifluoroacetic acid are known. Mixtures of cellulose and the *O*-carboxymethylated chitosan derivative in a LiCl–*N,N*-DMAA dissolving system have been obtained also [8]. However, in none of the cases was there achievement of a uniform distribution of polymers in a solution or in the corresponding products made from such a solution.

The combination of cellulose with chitosan in *N*-methylmorpholine-*N*-oxide was reported in [9] to make it possible to prepare homogeneous solutions only at chitosan contents no greater than 5 wt %. An increase in the amount of dopant resulted in a sharp deterioration of physical and mechanical properties and in an increase in the irregularity of the surfaces of the film samples formed from these solutions.

The problems of preparation of homogeneous solutions of cellulose and chitosan in ionic liquids at different cellulose-to-chitosan ratios were described in [10–13]. It was established [10] that mixed solutions of cellulose and chitosan in 1-ethyl-3-methylimidazolium acetate are pseudoplastic fluids. The higher

the chitosan content, the lower the viscosity. Highly viscous chitosan solutions with up to a 10% concentration were obtained in 1-butyl-3-methylimidazolium chloride [11]. In addition, the possibility of reducing the viscosities of cellulose–chitosan solutions after the addition of a cosolvent to the ionic liquid was shown [12]. The use of a mixture of two ionic liquids, such as glycine hydrochloride and 1-butyl-3-methylimidazolium chloride, made it possible to prepare composite fibers with improved characteristics (in comparison to those of pure cellulose fiber) via both a wet spinning process and a dry jet wet spinning process [13].

The aim of the present study is to examine the rheological properties of mixed solutions of cellulose and chitosan in aqueous phosphoric acid, which are useful as spinning solutions for the production of composite fibers. From a practical point of view, it seems reasonable to estimate the rheological properties of cellulose–chitosan suspensions in phosphoric acid as well, because their formation is the first step of the preparation of spinning solutions. In addition, gels were studied because, at  $T < 273$  K, the transition of the solutions of cellulose and chitosan into the gel state occurs, and it is these temperatures that should be maintained during storage to avoid destruction of the polymers.

## EXPERIMENTAL

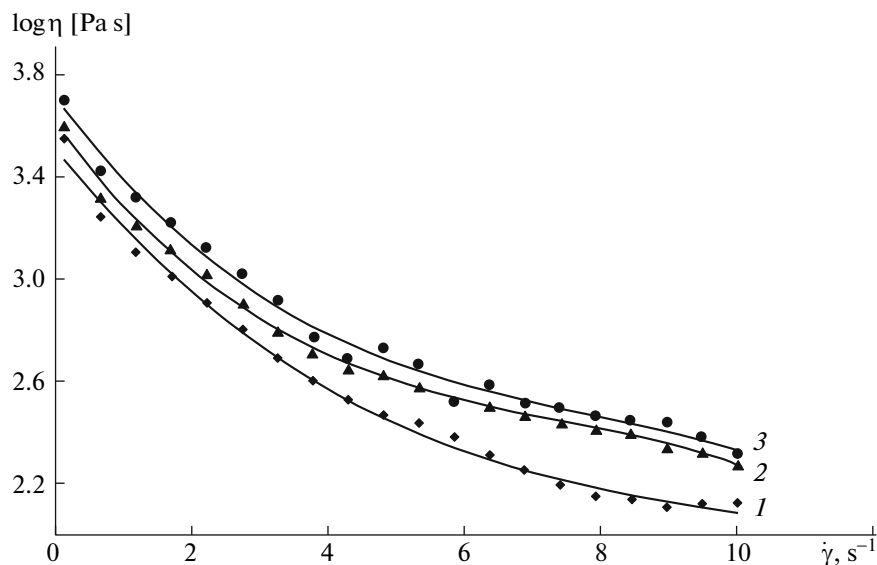
### *Initial Polymers*

To prepare suspensions and spinning solutions, industrial air-dried samples of wood sulfate cellulose produced by OAO Baikalsk Pulp and Paper Mills (Baikalsk, Russia) with a polymerization degree of 900 and an  $\alpha$ -cellulose content of 92%, as well as food-grade chitosan manufactured by ZAO Bioprogress (Shchelkovo, Russia) with a deacetylation degree of 70% and a molecular mass of  $2 \times 10^5$ , were utilized.

The initial reagent for preparation of the polymers solutions was concentrated (86 wt %) orthophosphoric acid of the high-purity grade with a density of  $1.69 \text{ g cm}^{-3}$ . The phosphoric acid contents in the aqueous solutions of phosphoric acid used for cellulose and chitosan dissolution were no more than 83 wt %.

### *Preparation of Mixed Solutions of Cellulose and Chitosan*

Before the dissolution procedure, cellulose sheets were cut into  $1 \times 1$  cm squares, while chitosan was ground in an ZM 200 ultracentrifugal mill ZM 200 (Germany) into a homogeneous powder with particles no larger than 1 mm. The ground polymers were introduced into an aqueous solution of phosphoric acid with an acid concentration not exceeding 83 wt % and were dispersed to obtain a homogeneous suspension.



**Fig. 1.** Dependences of viscosity on shear rate for cellulose and cellulose–chitosan solutions in phosphoric acid at 303 K: (1) cellulose solution, (2) 90 : 10 cellulose–chitosan, (3) 75 : 25 cellulose–chitosan.

Table 1 shows the ratios and total concentrations of the polymers that were employed to produce cellulose–chitosan suspensions and spinning solutions. The choice of solutions that were equimolar with respect to cellulose concentration was due to the requirements on the strength of a freshly prepared fiber, which must be sufficient to provide for stable spinning under laboratory, pilot, and experimental–industrial plant conditions. Because it is the cellulose that determines the strength of a fiber during its spinning from the polymer blend solution, it is the cellulose concentration, rather than the total concentration of both the polymers, that is maintained constant. In addition, the chitosan solutions (0–2%) in phosphoric acid may be considered the solvent.

The prepared suspensions were transformed into gels under cooling to temperatures no less than 273 K, and under these conditions, the complete dissolution of the polymers occurred. The determination of the completeness of dissolution was evaluated according to the presence of insoluble particles that were fixed in a thin layer of the solution in polarized light with the use of an Amplival binocular polarization microscope (Germany) at various magnifications. The final cellulose–chitosan spinning solutions in aqueous phosphoric acid looked like highly viscous transparent gels without any mechanical impurities; when heated above 293 K, the gels became fluid and, thus, suitable for fiber spinning. The obtained solutions showed no visible signs of phase separation during storage at  $T < 273$  K as well as during heating.

In addition to the fibers, films were prepared from the studied solutions. These films were likewise observed in polarized light with the use of the Amplival optical microscope (Germany).

### *Rheological Properties*

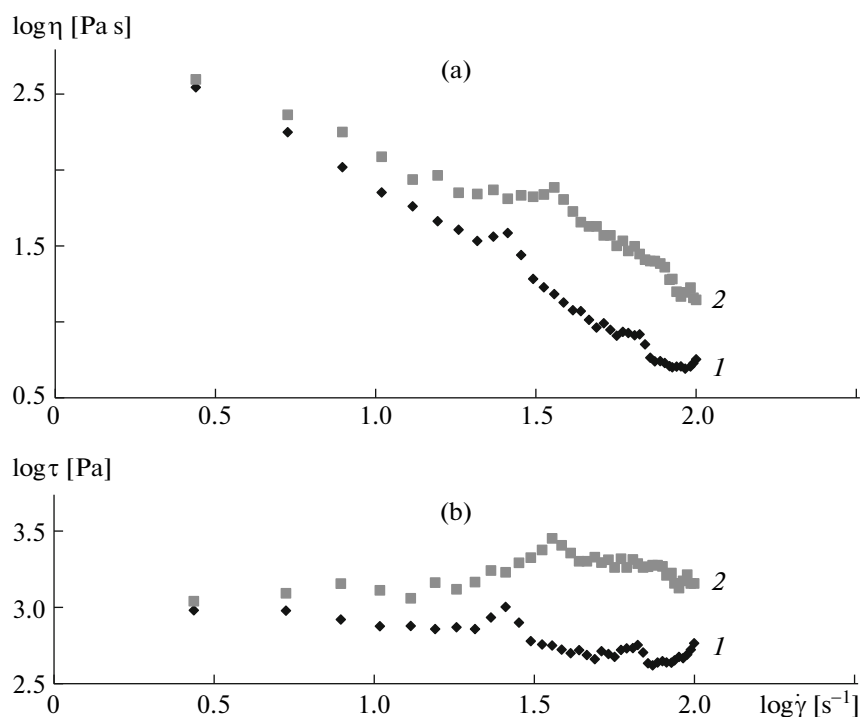
Rheological studies of the suspensions, spinning solutions, and gels were performed with an R/S Brookfield rheometer in the constant-shear-rate mode (in the range from 0.15–100  $s^{-1}$ ) with the use of a CC8 coaxial-cylinder measuring system. In addition, the evaluation of the thixotropic properties of suspensions was performed with a CC25 coaxial-cylinder system. The transition to the other measurement system in the latter case was due to the lower viscosities of suspensions in comparison to those of cellulose–chitosan solutions of similar compositions. The temperatures in the measurements of suspensions, spinning solutions, and gels were 323, 303, and 268 K, respectively.

## RESULTS AND DISCUSSION

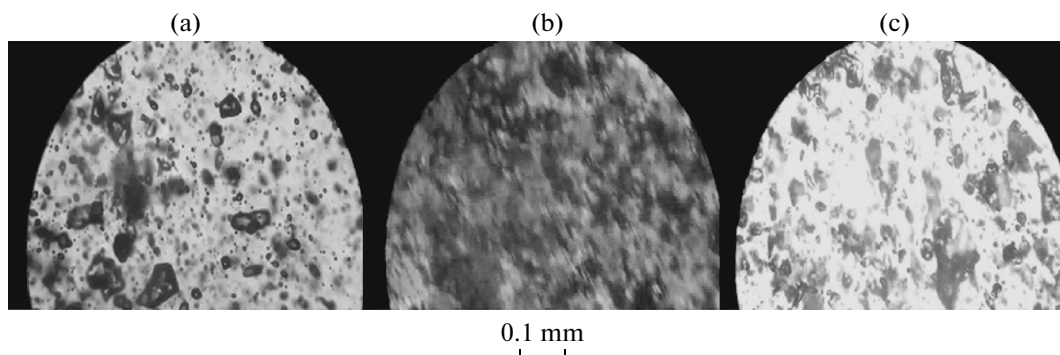
### *Steady-Shear-Flow Mode*

In the mode of steady shear flow at low shear-rate values, the solutions of cellulose and its mixtures with chitosan at 80 : 20 and 75 : 25 ratios demonstrate pseudoplastic behavior. This result is confirmed by the data in Fig. 1, which shows the dependence of viscosity on shear rate in semilogarithmic coordinates. With an increase in the chitosan content, the character of the curves does not change, whereas viscosity increases owing to an increase in the total concentration of the polymers in solution.

The higher the shear rate (up to 100  $s^{-1}$ ), the more complex the rheological behavior of the investigated systems. This result is illustrated in Fig. 2 by the dependences of viscosity and shear stress on shear rate plotted in logarithmic coordinates; these dependences are usu-



**Fig. 2.** Dependences of (a) viscosity and (b) shear stress on shear rate for spinning solutions in phosphoric acid at 303 K: (1) cellulose solution, (2) 90 : 10 cellulose–chitosan.

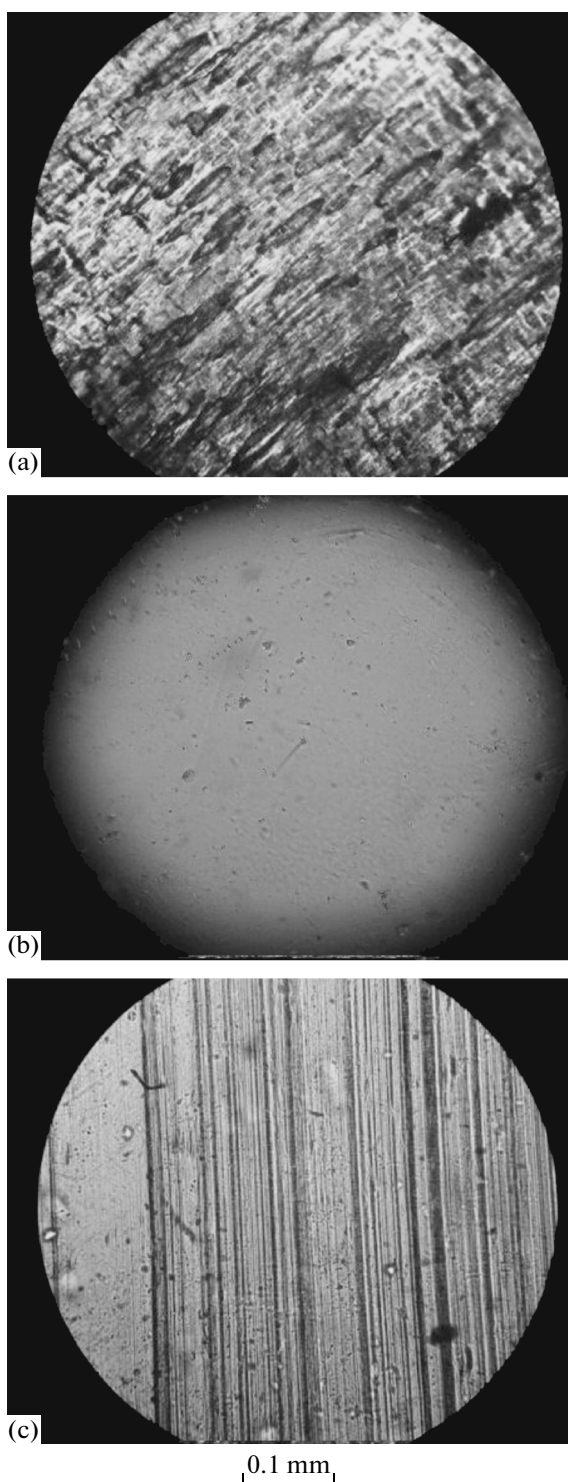


**Fig. 3.** Micrographs (in crossed polarizers) of a drop of a 7% cellulose solution in phosphoric acid (a) before shear-force application, (b) during flow, and (c) 1 s after the termination of flow.

ally regarded as rheological fingerprints of the studied samples [14, 15]. On the basis of the data in Fig. 2a, it may be concluded that, for both cellulose and cellulose–chitosan solutions, the regions of minimum and maximum Newtonian viscosities are not achieved under the experimental conditions. This outcome is likely due to the fact that, in the low-shear-rate region, the relaxation times of disclinations of the structural networks of viscous solutions substantially exceed the deformation times; even the maximum effort (at the maximum possible shear rate for the instrument,  $100 s^{-1}$ ) proved to be insufficient for destroying the whole structure. In the case of shear stresses between 15 and  $40 s^{-1}$ , a practically straight intermediate section appears on

the given curves; its length increases after the transition from the pure cellulose solution (Fig. 2a, curve 1) to the cellulose solution containing 10 wt % chitosan (Fig. 2a, curve 2). This peculiarity of the flow of the examined solutions differentiates them from classic pseudoplastic fluids and indicates the possible formation of ordered (anisotropic) structures in the shear-deformation mode.

The results agree well with the previously studied rheological behavior of cellulose solutions in phosphoric acid in the mode of constant shear stress [16]. In [16], the appearance of an intermediate quasi-Newtonian region on the viscosity–shear-stress curve was



**Fig. 4.** Micrographs (in crossed polarizers) (a, b) of films prepared from a 7% cellulose solution in phosphoric acid (a) during shear and (b) without shear and (c) of cellophane film.

detected for the first time; its presence may be attributed to the orientation of macromolecules in flow.

The assumption of orientationally ordered structure formation under dynamic conditions is confirmed also

by other experimental data. For example, all studied solutions demonstrate shear-induced birefringence, which can be clearly seen in the color pattern observed in the field of view of a polarizing microscope. Figure 3 shows micrographs of a solution drop placed between two parallel glass plates before and after shifting of the top plate relative to the bottom plate. The birefringence recorded with a digital video camera disappeared within 0.1–0.5 s after shear cessation.

In order to fix the structural ordering that appeared under shear conditions [17], the films were cast through a slit spinneret on a laboratory facility with the use of an aqueous solution of phosphoric acid salts as a precipitant. The same precipitating bath was employed for fiber molding. Texturing occurs in the films of all examined cellulose–chitosan compositions. Figure 4a presents a black-and-white shot of cellulose film with a birefringent texture well distinguishable in a color image. Cellulose–chitosan films cast from the same aqueous phosphoric acid solutions but without shear deformation (in particular, when the layer of solution is applied with a special scraper onto a glass substrate followed by immersion into the coagulation bath) have no birefringent structuring. Figure 4b shows a micrograph of such a film.

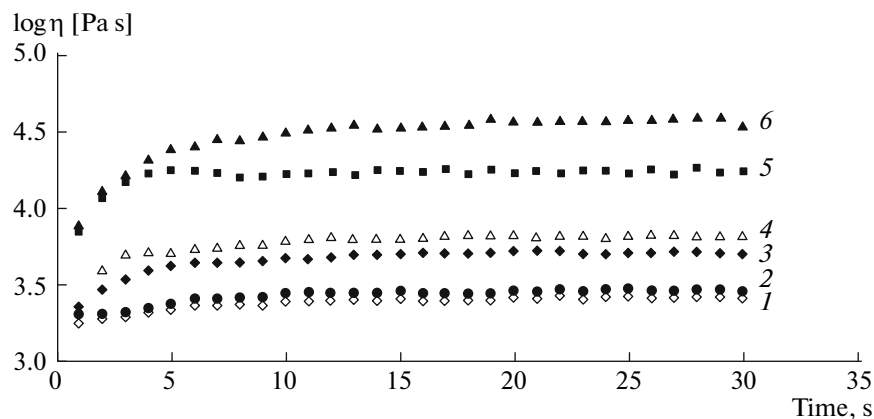
For comparison, a micrograph of uniaxially oriented commercially available cellophane film likewise produced in the mode of shear deformation is shown in Fig. 4c. However, there are no visible signs of the formation of LC ordering. This result may be explained by the fact that, if, in the initial solution, there is no orientational ordering of macromolecules, it likewise does not appear during the casting process.

Thus, for concentrated solutions of cellulose and its mixtures with chitosan in aqueous phosphoric acid, the appearance of LC ordering is typical only in the shear-deformation mode. For comparison with the literature data, cellulose solutions in anhydrous superphosphoric acids undergo transition into an orientationally ordered state with an increase in polymer concentration [3], a result that is typical of lyotropic solutions of cellulose and its derivatives in other solvents [18, 19].

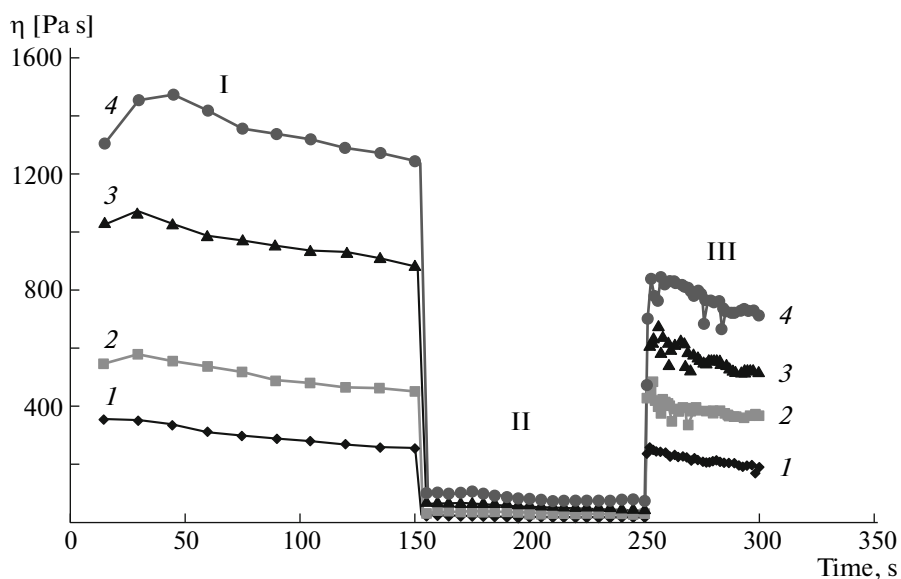
#### *Transient-Shear-Flow Mode*

The examination of solutions of cellulose with chitosan in the mode of transient shear flow indicated that the transition to steady shear flow occurs over time. Such behavior is typical of structured systems with spatial networks of links and differentiates them from Newtonian fluids, which begin to flow immediately at any shear rate.

The dependences of the logarithm of viscosity on time at constant shear rates (0.15 and 0.5 s<sup>-1</sup>) for cellulose and cellulose–chitosan solutions are shown in Figs. 5 and 6. At a constant shear rate, the viscosity increases with time within the first 10–20 s of expo-



**Fig. 5.** Changes in viscosity over time for spinning solutions in phosphoric acid at different temperatures and shear rates: (1, 3) cellulose solution and (2, 4, 6) 80 : 20 cellulose–chitosan solution;  $T = (1-4)$  303 and (5, 6) 268 K;  $\gamma = (1, 2, 5)$  0.5 and (3, 4, 6)  $0.15 \text{ s}^{-1}$ .



**Fig. 6.** Dependences of viscosity on deformation time at shear rates  $\gamma = (I)$  0.15, (II) 10, and (III)  $0.15 \text{ s}^{-1}$  for the suspensions of cellulose and chitosan in phosphoric acid at 323 K: (1) cellulose solution, (2) 90 : 10 cellulose–chitosan, (3) 80 : 20 cellulose–chitosan, and (4) 75 : 25 cellulose chitosan.

sure. The higher the shear rate, the less intense the increase in viscosity with time (Fig. 5, curves 1–4).

The behavior of spinning solutions of cellulose and its mixtures with chitosan in phosphoric acid revealed in Fig. 5 should be characterized as a rheopexy, that is, an increase in viscosity that occurs with time at a constant deformation rate owing to the structuring in the system. The main cause of the rheopexy, in turn, is that, when the shear force is applied, the macromolecules of both cellulose and chitosan take more straightened conformations, while the number of bonds between functional groups of different chains increases. This phenomenon is what leads to the vis-

cosity increase; the process rate increases with an increase in temperature (see Fig. 5, curves 2, 4–6).

The rheopexy of spinning solutions is of great interest because the rheological conditions of solution flow through the spinneret determine the stabilities of fiber-molding processes and the physical and mechanical properties of the fibers.

In addition, to predict the behavior of spinning solutions during the process of fiber spinning, it should be taken into account that the solutions in the production scheme are exposed to significant changes in shear rate during their transport through pipelines and extrusion through a spinneret. Such shear conditions cannot be modeled via conventional rheological mea-

**Table 2.** Degrees of structural recovery of suspensions and spinning solutions versus chitosan contents

Sample number	Cellulose-to-chitosan mass ratio	Degree of recovery, %
Suspensions		
1	100 : 0	85
2	90 : 10	80
3	80 : 20	65
4	75 : 25	60
Spinning solutions		
5	100 : 0	45
6	90 : 10	65
7	80 : 20	70
8	75 : 25	65

suring techniques, for instance, via obtainment of rheological curves in the mode of a gradual increase and decrease of the deforming force. At the same time, knowledge of the features of the thixotropic behavior of suspensions and solutions during sharp changes in shear rate is necessary to completely characterize their behavior during the production process.

In addition to the thixotropy of solutions, the thixotropy of cellulose and chitosan suspensions, which formed at the activation step that preceded the dissolution process (before the transportation into the reactor–dissolver), was investigated. The thixotropic behavior of the suspensions was examined at 323 K, that is, at the temperature modeling the activation step. The rheological-parameter measurements were performed according to the following scheme: state of rest → high shear force → state of rest. The state of rest

was simulated by a very small but constant shift of  $0.15 \text{ s}^{-1}$  in the rate. The simulation conditions were chosen so that viscosity values did not change within the range of measurement times. Then, the viscosity was determined at a constant shear rate of  $10 \text{ s}^{-1}$ . At the third step, the viscosity of the system was measured again under conditions similar to those at the first step. The degree of structural destruction of a suspension or solution was evaluated as the ratio between the viscosity of a suspension or solution measured at a shear rate of  $0.15 \text{ s}^{-1}$  rate and that measured after shear deformation for 50 s.

To perform the steps of the thixotropy test, the following conditions were used.

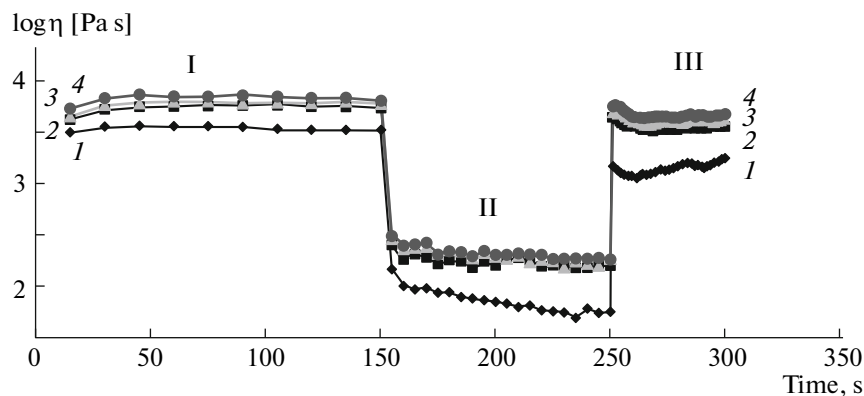
The 1st step: a shear rate of  $\gamma = 0.15 \text{ s}^{-1}$ , a measurement duration at each point of 15 s, and a number of measurement points of 10.

The 2nd step: a shear rate of  $\gamma = 10 \text{ s}^{-1}$ , a measurement duration at each point of 5 s, and a number of measurement points of 20.

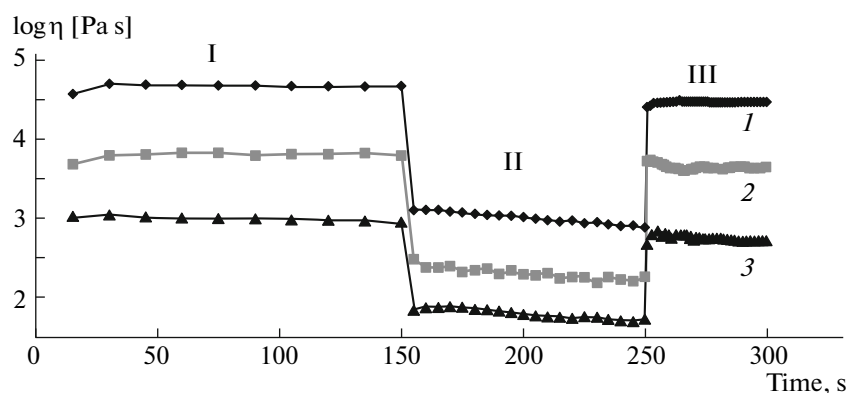
The 3rd step: a shear rate of  $\gamma = 0.15 \text{ s}^{-1}$ , a measurement duration at each point of 1 s, and a number of measurement points of 50.

Figure 6 demonstrates the results of examinations of the cellulose suspension and mixed cellulose–chitosan suspensions in phosphoric acid at 323 K. In the region of the low shear rate ( $\gamma = 0.15 \text{ s}^{-1}$ ) the suspension viscosities are almost constant. The higher the chitosan content in a sample, the greater the initial viscosity, that is, the viscosity in a state close to the state of rest. The structural strength of the pure cellulose suspension after the impact of a high-shear-rate force turned out to be almost completely recovered (Fig. 6, curve *I*). This outcome may be explained by the fact that cellulose possesses a structure that is rapidly recovered under the experimental conditions.

Cellulose–chitosan suspensions, in contrast, did not recover their structures completely, not even at relatively long test periods. The degrees of initial-viscos-



**Fig. 7.** Dependences of viscosity on deformation time at shear rates  $\gamma =$  (I) 0.15, (II) 10, and (III)  $0.15 \text{ s}^{-1}$  of the solutions of cellulose with chitosan in phosphoric acid at 303 K: (*I*) cellulose solution, (*2*) 90 : 10 cellulose : chitosan, (*3*) 80 : 20 cellulose–chitosan, and (*4*) 75 : 25 cellulose–chitosan.



**Fig. 8.** Dependences of viscosity on deformation time at shear rates  $\gamma =$  (I) 0.15, (II) 10, and (III) 0.15  $\text{s}^{-1}$  of the 80 : 20 cellulose–chitosan system in phosphoric acid at (1) 268 K (gel), (2) 303 K (solution), and (3) 323 K (suspension).

ity recovery diminished with increases in the chitosan content. According to the data in Fig. 6, the 75 : 25 cellulose–chitosan suspension is the most thixotropy-labile system. The dependence of the degree of suspension–structure recovery on chitosan content for the samples is shown in Table 2. The data should be taken into account for the design of activation-step equipment.

The thixotropic behavior of spinning solutions was studied at 303 K; thus, the conditions of solution supply to the spinneret were modeled. The results of investigations of spinning solution thixotropy are shown in Fig. 7. The regularities observed for the solutions are different from those for suspensions. The process of destruction and recovery of the cellulose solution, in contrast to solutions of cellulose mixtures with chitosan, is very slow and not full, despite the lower viscosity of the pure cellulose spinning solution. This behavior appears to be due to the higher structuring of the cellulose solution than that of the suspension. A nonmonotonic change in the degree of structural recovery of a cellulose–chitosan solution with an increased chitosan content may be due to an increase in the solution viscosity because of an increase in the overall polymer concentration on one hand, and a decrease of the solution structuring induced by an increased content of the second polymer on the other hand.

Moreover, supramolecular structures of the polymers in the solution can influence the degree of recovery. In the case of the presence of both polymers in the solution, a supramolecular structure can appear in the form of alternating layers, which are known to form in the solutions of two polymers in a common solvent [20]. The dependence of the degree of spinning–solution structural recovery on chitosan content for the samples is shown by the data in Table 2.

Because, during the preparation of a solution, its storage, and its supply to the spinneret, the cellulose–chitosan–aqueous phosphoric acid system undergoes transitions between a series of phase states, namely,

suspension–gel–solution, it was of particular interest to compare their thixotropic properties. The results of this examination for the system with the 80 : 20 cellulose–to–chitosan ratio are presented in Fig. 8. From such data, a conclusion important for practical purposes can be drawn: During the transition from the gel state to the fluid–solution state, the viscosity of the system decreases by almost an order of magnitude. This circumstance should be taken into consideration during the design of equipment for use at the step of supplying gel to the spinning unit and the subsequent step of supplying solution to the spinneret.

## CONCLUSIONS

It has been found that 7% cellulose solutions and 7.7–9.1% cellulose–chitosan spinning solutions in aqueous phosphoric acid behave as pseudoplastic fluids under steady–shear–flow conditions at shear rates between 0.15 and 100  $\text{s}^{-1}$ . On the curves of viscosity versus shear rate, the appearance of a quasi-Newtonian region is observed in the range 20–40  $\text{s}^{-1}$ , a result that may be explained by the LC ordering of the macromolecules of the system during shear flow. For all the examined solutions, shear-induced birefringence was detected; it persists in the films formed from the solutions in the water–saline precipitating bath.

In the transient–shear–flow mode at a constant shear rate, the spinning solutions of cellulose and chitosan in phosphoric acid typically exhibit rheopexy. This is due to the fact that, in the low–shear–rate region, a certain time is required for the orientation of macromolecules in the deformation direction.

The thixotropic properties of cellulose–chitosan suspensions and spinning solutions were estimated from the degrees of structural recovery of suspensions and spinning solutions after their destruction to be different. The degree of structural recovery decreases after the transition from the suspensions to the solutions. In addition, at a higher chitosan content, the degree of structural recovery of a suspension



decreases, whereas, in the case of a spinning solution, the change is nonmonotonic. However, in every case, the degree of structural recovery is higher than that for the pure cellulose solution.

## REFERENCES

1. A. N. Gonchar, D. D. Grinshpan, S. E. Makarevich, N. G. Tsygankova, and E. V. Sheimo, *Vestn. Belneftekhim. Neftekhim. Kompleks*, No. 1 (6), 6 (2011).
2. D. D. Grinshpan, N. G. Tsygankova, and F. N. Kaputskii, USSR Inventor's Certificate No. 1348396 (1987).
3. H. Boerstoel, H. Maatman, J. B. Westerink, and B. M. Koenders, *Polymer* **42**, 7371 (2001).
4. M. G. Northolt, H. Boerstoel, H. Maatman, R. Huisman, J. Veurink, and H. Elzerman, *Polymer* **42**, 8249 (2001).
5. S. J. Picken, D. J. Sikkema, H. Boerstoel, T. J. Dingemans, and V. Zwaag, *Liq. Cryst.* **38**, 1591 (2011).
6. S. Janjic, M. Kostic, V. Vucinic, S. Dimitrijevic, K. Popovic, M. Ristic, and P. Skundric, *Carbohydr. Polym.* **78**, 240 (2009).
7. S. Z. Rogovina and G. A. Vikhoreva, *Glycoconjug. J.* **23**, 611 (2006).
8. Z. Li, X. P. Zhuang, X. F. Liu, Y. L. Guan, and K. D. Yao, *Polymer* **43**, 1541 (2002).
9. C. M. Shih, Y. T. Shieh, and Y. K. Twu, *Carbohydr. Polym.* **78**, 169 (2009).
10. X. Duan, J. Xu, B. He, J. Li, and Y. Sun, *BioResources* **6**, 4640 (2011).
11. H. Xie, S. Zhang, and S. Li, *Green Chem.* **8**, 630 (2006).
12. O. Kuzmina, T. Heinze, and D. Wawro, *ISRN Polym. Sci.* **2012**, Article ID 251950 (2012).
13. B. Ma, M. Zhang, C. He, and J. Sun, *Carbohydr. Polym.* **88**, 347 (2012).
14. D. R. Biswal and R. P. Singh, Inc. *J. Appl. Polym.* **94**, 1480 (2004).
15. M. Edali, M. N. Esmail, and G. H. Vatistas, *J. Appl. Polym. Sci.* **78**, 1787 (2001).
16. D. D. Grinshpan, A. N. Gonchar, N. G. Tsygankova, S. M. Makarevich, T. A. Savitskaya, and E. V. Shejmo, *J. Eng. Phys. Thermophys.* **84**, 594 (2011).
17. A. M. Ritcey and D. G. Gray, *Biopolymers* **27**, 1363 (1988).
18. V. G. Kulichikhin and L. K. Golova, *Khim. Drev.*, No. 3, 9 (1985).
19. A. Laszkiewicz, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **353**, 127 (2000).
20. L. Schulz, W. Burchard, and R. Donges, *Cellul. Derivat.*, 218 (1998).

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