

UDK 547.99+678.06

**THE PHASE STATE AND RHEOLOGICAL PROPERTIES  
OF CHITOSAN-ACETIC ACID-ETHANOL-WATER SYSTEM**

S.A. USPENSKIY, G.A. VIKHOREVA, A.N. SONINA

(Moscow State Textile University "A.N. Kosygin")

E-mail :hold12@rambler.ru

*The phase state and rheological properties of the chitosan-acetic acid- ethanol-water system were studied over a wide composition range. The possibility of introduction of ethanol up to 40 % in to 6...8 %-th solutions of chitosan with molecular weight  $\sim 1,7 \cdot 10^5$  without their phase separation is shown. The introduction of ethanol leads to an increase of dynamic viscosity of solutions, but a decrease turbidity and provides possibility of increasing the rate of solvent evaporation and formation of films and uniform chitosan covers on fibers.*

**Keywords: chitosan, solutions, viscosity, acetic acid, ethanol, turbidity, activation energy, film.**

**Introduction**

The preparation of chitosan films, pellets, fibers and other products is made by dissolution chitosan. The dilute aqueous solutions of acetic acid commonly are using as the cheapest and most accessible reagent that provides the formation of water-soluble polymer derivative - chitosan acetate. However, the high boiling point of the solvent ( $>100$  °C) and relatively low concentration of the polymer in forming solutions ( $\leq 6\%$ ) causes the low speed of the thermal spinning process.

There are various techniques to increase the speed of the solvent evaporation, e.g. the use of solvent's mixtures with different boiling points, as well as solvent mixtures with precipitator [1]. Despite the fact that it usually provides a "tough" conditions spinning and forming non-equilibrium and defect structure of the polymer products, in some cases the

use of this method is justified. Thus, much attention is paid to the formation of porous structure in obtaining of separation membranes and fibrous sorbents, including bicomponent structure "core-shell".

There are few dates about the influence of alcohol on the rheological properties of aqueous solutions of polymers. It is known that the introduction of alcohol in aqueous solutions of polyvinyl alcohol and methylcellulose improves their dissolution and suppress gelation [2]. The introduction of ethanol in the spinning solutions of cellulose derivatives is widely used for reducing their viscosity and improves the homogeneity [3]. The presence of alcohol in acetic acid chitosan solutions influences on degree protonation of amino groups of polymer [4] that can be important for a number of practical applications, in particular for sorption or crosslinke chitosan. In works [5], [6] introduction methanol in to

chitosan solutions was used for creation softer conditions of polymer acylation and decreasing the viscosity of solutions without any investigation this problem.

The aim of the work is to investigate the influence of the ethanol introduction on structural and rheological properties chitosan's solutions in acetic acid, the rate of curing of solutions and the quality of chitosan membrane affixed on viscose filament to give it a sorption capacity. This article presents the results of a comparative study of properties of dilute and concentrated chitosan solutions in acetic acid in the absence and presence of ethanol. The choice of ethanol is due to a good compatibility with the main solvent, a lower boiling point than water, as well as its relative small toxicity. The used chitosan had  $MM \sim 1,7 \cdot 10^5$ , degree of deacetylation 0.92, degree of crystallinity  $\sim 45\%$ , 100% solubility in 2% acetic acid and  $\leq 0,2\%$  of ash content.

## 2. Experimental Part

The solutions for rheological studies were prepared by conducting the preliminary swelling of chitosan in water, followed by dissolution in acetic acid and diluted alcohol, water-alcohol mixture and water to achieve a given polymer concentration (1-8 wt%) and the content of alcohol (10-40 wt%). Ethanol, water or water-ethanol mixtures are injected into the system in small portions with vigorous stirring to prevent precipitation of the polymer. Non-Newtonian chitosan's solutions are not stable and the viscosity of solutions gradually decreases (most strongly in storage during the first day [7...9]). Therefore, in comparative experiments assessed values of the solution viscosity, measured at a fixed value of shear stress ( $\sigma$ ) or velocity gradient ( $j$ )  $3 \text{ s}^{-1}$ , after conditioning for 24-30 hours. The viscosity of chitosan's solutions essentially depends on acid concentration [10], [11], so to investigate their rheological properties there were used the same molar ratio of acid: chitosan, equal to 2.2, and the same degree of protonation of amine groups. Rheological curves of solution were measured with a Rheotest-2 rotary viscometer. The activation energy  $E_a$  was calculated for polymer solutions in the temperature range  $20...60^\circ\text{C}$  from viscosity values measured at  $\tau = 10 \text{ Pa}$ .

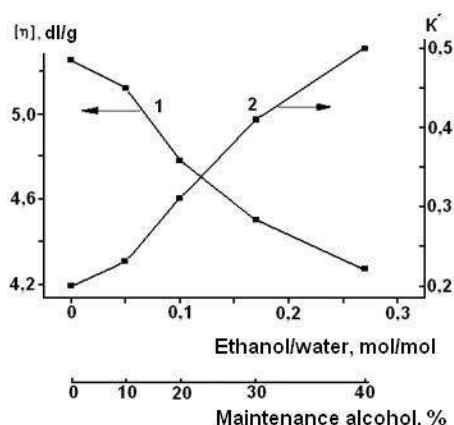
Viscosity of solvents was measured in capillary viscosimeter with a known constant for the calculation of dynamic viscosity.

Characteristic viscosity of chitosan solutions was determined at  $25^\circ\text{C}$  in the viscometer Ubbelode with capillary diameter 0.56 mm. To identify the effect of ethanol on the thermodynamic quality of solvent, and, consequently, the conformation and the degree of macromolecules association, the ionic strength was created by minimal amount of sodium acetate (0.04 mol/l) that subsided polyelectrolyte swelling. The concentration of acetic acid and the initial concentration of chitosan solution are 0,4%. The optical density (D) of 1% solutions was determined on a spectrophotometer UNICO 1200/1201 in the wavelength range ( $\lambda$ ) at  $350...900 \text{ nm}$  with intervals of 40 nm. The calculation of solution's turbidity ( $\tau$ ), number (N) and radius (r) of scattering particles carried in the range  $420...600 \text{ nm}$ , where the difference of optical density of chitosan solutions with and without alcohol is the most significant according to formulas [12]:

$$\begin{aligned} \tau &= 2,3D_{cp} / \ell \\ N &= 1,26 \cdot 10^{17} \tau / \lambda_{cp}^2 \alpha^2 k \\ r &= \lambda_{cp} \alpha / 2 \cdot 3,14n_0 \end{aligned}$$

where  $\ell$  is длина кюветы см,  $\alpha$  and  $k$  – characteristic constants of light scattering [12],  $n_0$  – refractive index of the solvent.

## 3. Results and discussion

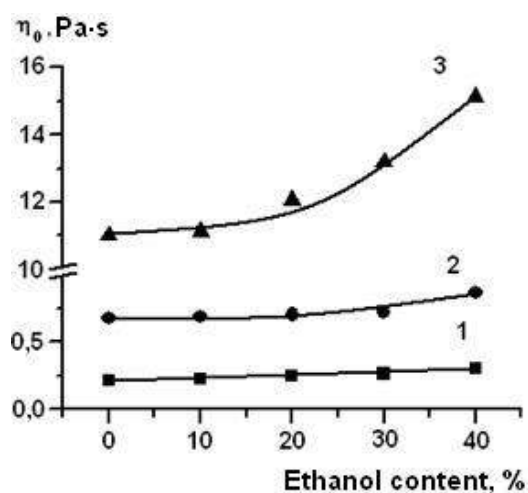


Picture 1

Since ethanol is a precipitator for chitosan, its introduction into solutions of chitosan

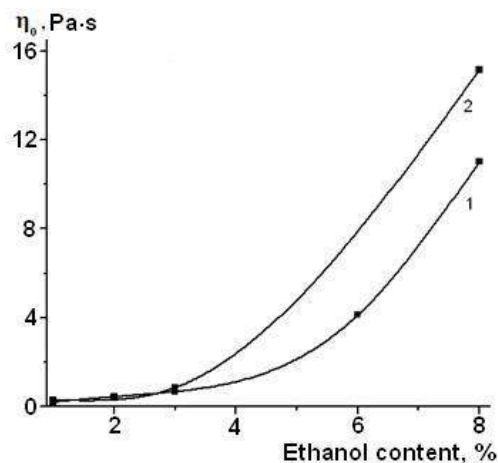
must degrade the thermodynamic quality of the solvent and increase the degree of structuring and dynamic viscosity of concentrated polymer solutions. A monotonic decrease of the intrinsic viscosity and growth of Huggins constant in the studied range the ethanol ratio: water (curves 1 and 2 in Picture 1, respectively) confirm the conclusion about the deterioration of the thermodynamic quality of mixture acetic acid-ethanol solvent.

The dates of Picture 2 and 3 about the dynamic viscosity of 1...8% solutions of chitosan, shows the viscosity increase with the introduction of alcohol, more than have more maintenance of alcohol and chitosan. They



Picture 2

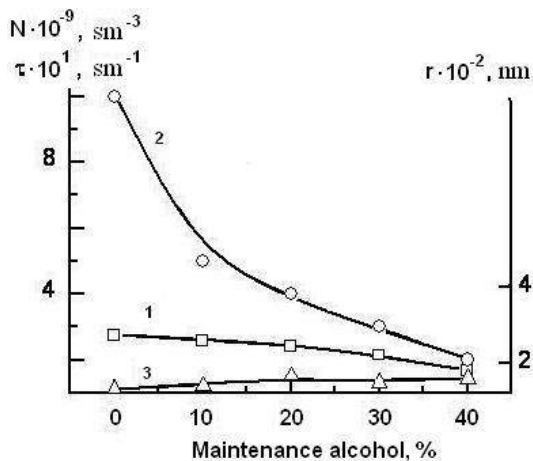
also consistent with the known views on the impact of solvent quality on the properties of the solutions. However, the introduction of ethanol visually observed decrease in turbidity and increase the homogeneity of concentrated (6-8%) solutions chitosan in dilute acetic acid. The decrease of turbidity for 1% solutions is confirmed by calculation (curve 1 in Picture 4). The calculations also showed a significant reduction in the number of scattering particles (curve 2) and some increase in their average sizes (curve 3) with the introduction of ethanol, apparently due to dissolution micro- and nanosized helices.



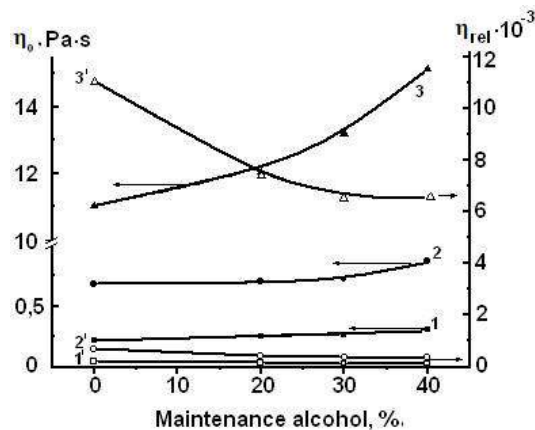
Picture 3

All of this suggests a more complex effect of ethanol on the structural and rheological properties of the chitosan-acetic acid-ethanol-water systems. It was interesting to evaluate the influence of alcohol on the relative viscosity of solutions. According to our measurements the dynamic viscosity of the three-component solvent water-alcohol-acetic acid increases more than twice from 1,0 to 2,4 mPa s with the content of ethanol to 40%. According to [13], the viscosity water-ethanol mixtures with alcohol content of 42% have a maximum value of 2.8 mPa c that indicates a

high degree of structuring of the solvent. As the chitosan solution relative viscosity (Picture 5, curves 1'...3'), reflecting the contribution of the polymer to the bulk viscosity decreases with the introduction of alcohol, thus increasing the viscosity of alcohol solutions of chitosan is due to a large extent the properties of the solvent, structural associates whose in concentrated solutions of polymer formed macroclusters significantly increase the initial viscosity of the system.



Picture 4

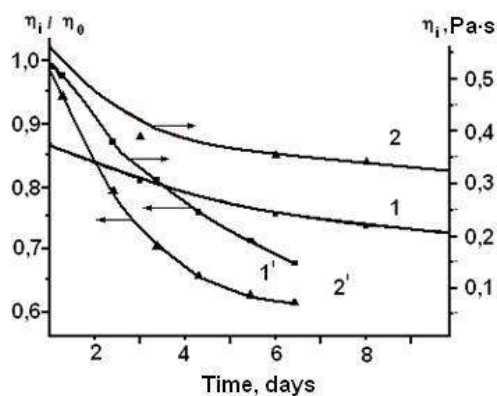


Picture 5

The results of the temperature dependence of solutions viscosity and the calculation of the activation energy of viscous flow ( $E_a$ ), as well as changes in the structuring of the index ( $n$ ) showed similar values of these variables: in 8% solutions containing 40% alcohol and do not contain it,  $E_a = 40$  and  $36$  kJ/mol,  $n = 0,75$  and  $0,80$  (in the range of shear rate  $10 \dots 50$  s<sup>-1</sup>), suggesting that there was no significant difference in the strength of chitosan's associates in solutions with ethanol and without ethanol. Therefore we can assume that the high viscosity of chitosan solutions containing alcohol is due to the increased degree of structuring of the solvent. Thus, the observed increase in viscosity of the spinning solutions of chitosan and reducing turbidity in adding them ethanol is not due to an increase in the size of the macromolecules associates in a thermodynamically poor solvent, but rather dissolution primary associates - liquid micro- and nanocrystals, possibly due to heating of the mixture through energy released during the exothermic process of interaction of ethanol with water.

In favour of such explanation bigger turbidity of 1% chitosan solutions prepared by directly dissolving polymer in an ethanol-containing solvents (20 and 40%) speaks. As well as short-term reversible decrease of the viscosity of the system when adding the next portion of ethanol, visually observed as an increase in speed mixers, significantly exceeds that due to dilution of an equal amount of water.

Instability of viscous properties of chitosan solutions and the fall of viscosity during storage noted above. As shown in [8], the cause is degradation of macromolecules, to warrant the subsequent destruction of the structure of solutions. Reduced viscosity can slow by increasing of the acetic acid concentration, but since the reduction of viscosity spinning of polymer solutions facilitates their processing (transport, filtration), this process can be regarded as a kind of "maturation" solutions. It was of interest to characterize the influence of ethanol on the stability of viscous properties of chitosan solutions. According to our data (Picture 6).



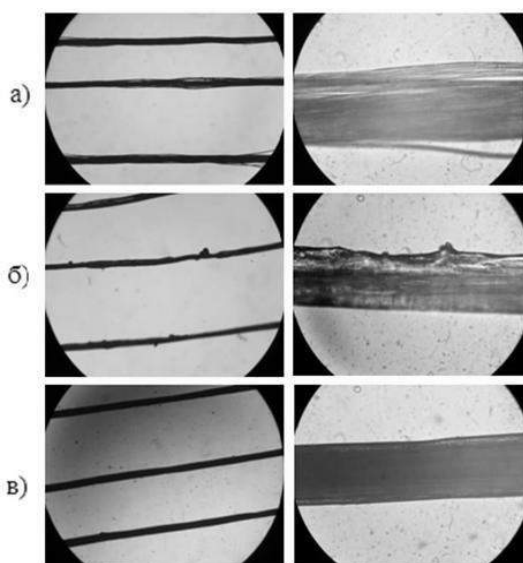
Picture 6

The introduction of alcohol accelerates the process of reducing the viscosity of solutions of chitosan. In this case the viscosity of ethanol-containing solutions remains at a slightly higher level compared with the viscosity of solutions without ethanol. Established reasons

for the lower stability of viscosity of water-ethanol solutions of chitosan and the rate of degradation of the polymer in them requires additional investigation.

Possibility and efficiency of using ethanol containing chitosan's solutions for preparation of products was shown for example in a formation chitosan covers on a viscose thread and creations fibrous chitosancontaining sorbent. Such composite corbent received by stretching an initial viscose thread through a chitosan solution and the calibrated aperture spinneret delete excess of a solution and subsequent evaporation of a solvent.

Threads with the chitosan maintenance  $\geq 10\%$  have the expressed "core-shell" structure. The deformational and strength properties of threads practically do not change up to the chitosan maintenance 20% (relative strength and elongation of the initial and modified threads are 16,8 against 16,5 sN/teks and 17 against 14%, accordingly). The cover put from chitosan's solution with ethanol have more uniformity, it's process evaporation passes with higher speed and has more stability (Picture 7).



Picture 7

Picture 7 – An initial viscose thread (a); a thread with a chitosan cover put from solution without ethanol (b) and a thread with a cover put from ethanolcontaining solution

## CONCLUSIONS

Thus, this study substantiates the possibility of introducing of ethanol into the spinning chitosan's solutions, because it does not lead to phase separation in solution, a significant increase in its initial viscosity and does not affect the viscosity of the 8% solutions with a gradient of shear rate over  $10\text{ s}^{-1}$ , i.e. at the application of even a small mechanical impact, for example, when mixing and transportation solutions. In preliminary experiments showed that the presence of ethanol in solution significantly accelerates the process of curing chitosan films and membranes deposited on viscose filament increases the stability of the process of forming the envelope and received by the uniformity of the filament.

## ACKNOWLEDGEMENTS

This work was supported by the Ministries of Education and Science of the Russian Federation (the contract № 16.740.11.0059)

## BIBLIOGRAPHY

1. Papkov S.P.(1971) Physicochemical Principles of Processing Polymer Solutions, Moscow: Khimiya.
2. Okihito, H. & Masatosi, H. (1973). J. Chem. Soc. Jp. Ind. Chem. Sci. . A147.-R.12.
3. Sedelkin, V.M., Denisov, G.P., Surkov, A.N., Ramazaeva L.F. & Pachina O.V. (2007). Rheological Properties of Molding Solutions for Acetatcellulose Ultrafiltration Membranes. Chemical Fibers, 1, 15-17.
4. Ma O., Lavertu, M., Sun, J., Nguyen, S., Buschmann, M. D., Winnik, F. M. & Hoemann, C. D. (2008). Precise Derivatization of Structurally Distinct Chitosans with Rhodamine B Isothiocyanate. Carbohydrate Polymers, 72, 616–624.
5. Hirano, S., Ohe, Y. & Ono, H. (1979). Selective N-acylation of Chitosan. Carbohydrate Polymers, 47, N2, 315-320.
6. Hirano, S., Nagamura, K., Zhang, M., Kim, S.K. (1999). Chitosan Staple Fibre and Their Chemical Modification with Some Aldehydes. Carbohydrate Polymers, 39, 293-298.
7. Sklyar, A.M., Gamzazade, A.I., Rogovina, L.Z. et al. (1981). The Study of Rheological Properties of Dilute and Moderately Concentrated Solutions of Chitosan. Vysokomolekulyarnye Soedineniya, 23, 6, 1396.
8. Nud'ga, L.A., Petrov, V.A., Bochek, A.M. et al. (1997). Molecular and Supramolecular Transformations in Solutions of Chitosan and Allylchitosan, Polymer Science, 39, 259.
9. Mironov, A.V., Vikhoreva, G.A., Uspenskiy, S.A. & Kildeeva, N.R. (2007). Reasons for Unstable Vis-

cous Properties of Chitosan Solutions in Acetic Acid. *Polymer Science*, 49, Nos. 1–2, 15.

10. *Rinaudo, M., Pavlov, G. & Desbrieres, J.* (1999). Influence of Acetic Acid Concentration on the Solubilization of Chitosan. *Polymers*, 40, 7029.

11. *Vikhoreva, G.A., Rogovina, S.Z., Pchelko, O.M. & Galbraikh, L.S.* (2001). The Phase State and Rheological Properties of Chitosan–Acetic Acid–Water System. *Polymer Science*, 43, Nos. 5–6, 166–170.

12. *Klenin, V.I., Shchyogolev, S.Y. & Lavrushin, V.I.* (1977). Characteristic Features of Light Scattering

of Dispersed Systems. Ed. Dr. S. Ya Frenkel. Saratov: Saratov University.

13. *Afanas'ev V.N., Efremova L.S. & Volkova T.V.* (1988). Physicochemical Properties of Binary Solvents: Aqueous Systems, Ivanovo: Institute Khimii Nevodnykh Rastvorov RAS, part 1.

Recommended by the editorial board. Received 03.06.11.