

Introduction One of the advantages of using chitosan for obtaining various medicinal materials – films, threads, coatings, gels, is its capacity for enzymatic destruction under the action of enzymes of a living organism [1,2,3]. However, it should be taken into consideration that the reactions involving polymers can be controlled in many cases by supermolecular polymer structure and by the density of packing of macromolecular chains [4] which are laid at the stage of obtaining polymeric material. The present work reveals the interaction between the degree of enzymatic destruction of chitosan film coating and the conditions of film formation.

Experimentals A chitosan (CHT) specimen (company «Chimmed», Russia) obtained by alkaline deacetylation of crab chitin was chosen as the object of investigation. To prepare CHT film specimens semi-diluted (2g/dl) solutions were made by dissolving a dry polymer weight at room temperature for 8 – 10 hours. Acetic acid with the concentration of 1- 70 g/dl was used as the solvent. CHT film specimens with the thickness of 0.1 mm were prepared by casting the polymer solution onto glass surface. Viscosimetric studies were carried out according to the standard technique on the Webblode viscosimeter at 25°C. For this purpose the powder of the initial CHT specimen was dissolved in a number of acetate buffers with pH=3.6; 4.0; 4.5; and 4.8. To study the process of enzymatic transformation the chitosan films extracted from acetic acid solutions of different concentration were put on the base moistened by enzymatic preparation solution and were kept at 35° C for a definite period of time. The extent of enzymatic destruction of films was estimated by the difference between the value of initial intrinsic viscosity of CHT solutions in acetate buffer with pH=4.5 obtained from film specimens and that of intrinsic viscosity $[\eta]_{\text{dest}}$ of solutions from film specimens subjected to enzymatic destruction for 1 hour. Food collagenase («Bioprogress», Schelkovo) was used as an enzymatic preparation. The enzymatic preparation concentration on the base was 5% mass of the CHT mass.

Results Discussion At describing the viscosity properties of diluted solution one usually proceeds from the linear dependence of an increment in viscosity on the polymer solution concentration. However, in the case of polar polymers to which CHT belongs there is a possibility of the occurrence of reversible agglomeration process which can take place not only in the area of semi- diluted solutions but even in the area of diluted ones. In this case the contribution to viscosity is made not by separate particles with V_0 volume but by their aggregates whose volume $V(n)$ depends not only on the number of particles constituting it, but also on their density characterized by fraction dimensions D [5]: $V(n) = V_0 \cdot n^3/D$ (1) Due to non-dense particles packing in the aggregate their contribution to viscosity begins to depend on the concentration in a non-linear way: $Dh \sim h_0 c \cdot d$, $d > 1$ (2) Consequently, any deviation of the δ index from one testifies to the fact that this system is structurized. The processing of experimental dependences of specific viscosity of CHT solutions on the concentration in acetate buffer solutions with different pH in double logarithmic coordinates makes it possible to determine the degree index δ in relationship (2) whose corresponding values are given in Table 1. The Table also

demonstrates the values of initial intrinsic viscosity, Huggins constant and the concentration of crossover point C which allow us to judge the quality of the solvent used. The analysis of these data makes it possible to speak about the deterioration of the solvent quality and the decrease in the size of the coils with increasing pH of the solvent. The comparison of the obtained values shows that in all the cases under consideration the values of δ index are higher than 1, even in the area of concentrations up to the crossover point, which unambiguously indicates the fact that aggregation processes in a polymer solution begin in the area of diluted solutions. The given experimental fact is confirmed by rather numerous investigations of the properties of CHT solution in acetic acid [6- 8] and allow us to speak about their being structurized systems. Table 1 - Physico-chemical characteristics of solutions of the CHT specimen used: 1 – solutions obtained from initial CHT powder, 2 – solutions obtained from the film isolated from 1 % acetic acid Type of the used Chitosan material pH of the used acetate buffer [h] η_{sp}/C K' C^* d 1 3.6 3.72 0.36 0.22 1.25 1 4.0 3.65 0.44 0.23 1.28 1 4.5 3.45 0.47 0.24 1.31 2 4.5 2.78 0.32 0.22 1.18 1 4.8 3.09 0.49 0.25 1.32 At extracting CHT film specimens from acetic acid solutions both the supermolecular CHT structure and the extent of its structurization (aggregation) change. This is demonstrated not only by the decrease in the intrinsic viscosity of the film specimen but also by considerable reduction of the δ index (Table 1). However, it is of fundamental importance that the pre-history of film obtaining affects both the extent of δ system structurization and the extent of enzymatic destruction of films. The variation of concentration of acetic acid used for films preparation changes not only the thermodynamic quality of the solvent relative to CHT and the supermolecular solution structure [6] but also the supermolecular structure of the films extracted from the solution. As a result, the CHT solutions in acetate buffer obtained due to films dissolving are characterized by different extent of enzymatic stability (Table 2). However, increasing the extent of films structurization by means of their thermomodification [9] it is possible to increase significantly their stability to enzymatic destruction. Table 2 - Physico-chemical characteristics of chitosan film specimens The concentration of the acetic acid (g/dl) used for films preparation The time of termomodification of films, min The extent of aggregation of diluted CHT solution in acetate buffer with pH =4.5 The degree of enzymatic destruction of films $\Delta\eta$ 1 0 1.18 1.08 5 0 1.13 1.38 5 30 1.17 1.29 5 60 1.22 1.25 10 0 1.14 1.36 10 60 1.20 1.13 20 0 1.17 1.09 50 0 1.10 1.58 50 60 1.21 1.22 70 0 1.09 1.59 70 60 1.22 1.10 As seen from the data in Table 2, the increase of the modification period is accompanied by the regular increase of the δ index and by corresponding decrease of the degree of films enzymatic destruction. Thus, the pre – formation of the film composition – the variation of the concentration of acetic acid used as the solvent as well as conducting the thermo- modification of films, affects the extent of film enzymatic destruction since in the process of preparing and modifying film specimens it is possible to form systems with different structurization degree.