

PHASE TRANSITION OF CHITOSAN CHLORIDE SOLUTIONS AS POTENTIAL MATERIAL FOR APPLICATION IN BIOMEDICAL ENGINEERING

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Introduction

Chitosan is a semi-crystalline amino-polysaccharide obtained through deacetylation of chitin. Due to its physicochemical properties, chitosan has a variety of applications in sewage treatment processes (chelating properties), food industry and biomedicine – in processes of creating smart drug carriers [1].

Chitosan is dissolved in low concentrated solutions of organic and non-organic acids in which it forms salts with dissolvent ions. Chitosan properties change from hydrophobic to hydrophilic and a colloidal system is created in which the polymer chains remain dispersed in a continuous medium – acid solution. Such a system shows a possibility for a sol-gel phase transition. Chitosan hydrogels may form as a result of increasing the concentration of the polymer [2], through the change of pH of the solution or through heating it [1,3,4].

The aim of this work was to create hydrogels sensitive to temperature changes from low-concentration solutions of chitosan and to describe the phase transition by determining the gelation point and activation energy.

Materials and Methods

For the research on chitosan hydrogels three types of chitosan were used. Two high-viscous from the Sigma-Aldrich company (chitosan from shrimps and crabs) and a low-viscous chitosan from the Fluka company. Aqueous solution of hydrochloric acid was used as a dissolvent. β -Glycerophosphate disodium (β -NaGP) was used as a buffer.

The chitosan solution (2.5% w/v) was prepared by dissolving 0.4 g chitosan in 16 ml 0.1M HCl solution. After dissolving, the container with the sample was covered and left for 24 h in room temperature. After that time the sample was left in temperature 5°C for 2 h. Two solutions were made for each kind of chitosan. A previously prepared solution of 2g β -NaGP in 2 ml distilled water was added to one of them, whereas the other solution was left without β -NaGP.

The measurements of rheological properties were conducted in a cone-plate system of a rotational rheometer Anton Paar Physica MR 301. A cone of 50 mm diameter and 1° angle was used. The gelation process was conducted in non-isothermal conditions. Chitosan solutions were put in 5°C temperature in the measuring system of a rheometer. Next the samples were heated with a constant speed of 1°C/min. The phase transition temperature was determined by crossover point of storage modulus G' and loss modulus G'' curves.

Results and Discussion

Based on measurements, the evolution of storage modulus G' and loss modulus G'' as functions of temperature were obtained. From the course of the G' G'' curves, three characteristic regions can be observed.

In first region, the chitosan samples show a typical behaviour for a viscoelastic liquid. There is a predominance of loss modulus over storage modulus. In second region, the values of the storage modulus and the loss modulus rise rapidly. This is a result of the creation of a crosslinked structure (gel). Domination of the storage modulus over the loss modulus was also observed. In the final third region, the gelation process proceeds more slowly. This results from large viscosity values of the medium, slowing down the diffusion of the molecules. The character of the arisen structure changes to glass form.

Comparison of chitosan solutions containing β -NaGP and without this addition reveals that solutions with higher pH value show lower gelation temperature (close to physiological temperature of human). Another basic difference in the gelation phenomenon between the two types of solutions is revealed in the dynamics of changes in second region. A more rapid change for solutions without the addition of β -NaGP compared with the solutions containing the buffer can be observed.

Kinetic model of polymer crystallization [5] allows to determine the activation energy for the gelation process. Comparison of chitosan solutions samples of the same type in two versions (with and without the addition of β -NaGP) indicates that the formation of the structure is more advantageous energetically for solutions with the addition of buffer. The determined value of activation energy also indicates that second region is the key area in the gelation process, absorbing the most input heat energy.

Conclusions

The sol-gel phase transition of chitosans chloride while heated with constant speed of temperature increase is performed in three characteristic areas: (1) the solutions exhibit the behaviours of a viscoelastic liquid, (2) the process of fast crosslinking close to the gelation point – creation of a soft rubber structure, (3) the process of slow gelation at high temperatures – formation of a glass structure.

It was stated that chitosan chloride solutions with β -NaGP until the sol-gel phase transition require far lower energy than analogous systems without β -NaGP.

From the viewpoint of medical use, the systems with the addition of β -NaGP are more desirable. The phase transition temperatures of these systems are close to the human body temperature (~37°C) as opposed to systems without the addition of buffer where the phase transition point drastically exceeds that temperature.

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