

Thermal modification of films based on chitosan for use in manufacturing processes of water purification

T. Solodovnik*, H. Stolyarenko, N. Fomina, S. Kravchenko, Y. Dzhiora

Cherkassy State Technological University, 460, Shevchenko Boulevard, 18006, Cherkassy, Ukraine

* Corresponding author. E-mail: soltav@mail.ru; tel.: +380978727940

Abstract

Films of chitosan were prepared in salt form by method of dry-forming. It is proved that heat treatment films of chitosan reduces solubility. Crosslinking of the polymer occurs through amidation reaction. It was proven effect of heat treatment on the structure and functionality of the films. It was established that during the heat treatment of the films is the process of amidation, which in turn leads to greater streamlining the structure and reduce the solubility of the films.

Аннотация

Пленки хитозана, являющиеся новым видом сырья для производства мембран, получали в виде соли методом сухого формования. Доказано, что тепловая обработка пленки хитозана уменьшает растворимость. Сшивание полимера происходит в результате реакции амидирования. Было показано влияние эффекта термической обработки на структуру и функциональность пленок. Установлено, что в процессе термической обработки пленок возникает процесс амидирования, который в свою очередь приводит к оптимизации структуры и уменьшает растворимость пленок.

Keywords: chitosan, films, mycelium, fungus *Aspergillus Niger*.

Introduction

It is known that aminopolysaccharide chitosan and its derivatives are becoming more widely used in various industries. Chitosan has many beneficial properties. Chitosan extracted from natural polysaccharide chitin. For use of chitosan from chitin deacetylation reaction. The result of this reaction is a substitution of amide groups (NHCO^-) chitin in more active and reactive amino groups (NH_2^-) (Fig.1).

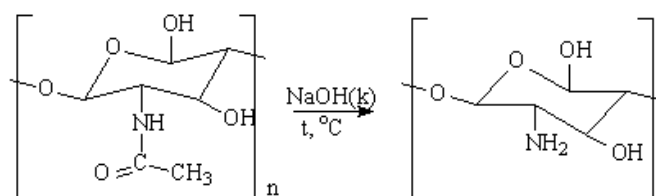


Figure 1 The reaction of deacetylation

Chitosan is a biocompatible, non-toxic and is laid out in an environment characterized by valuable regenerating and healing properties. Chitosan absorbs heavy metal ions, dyes, petrochemicals and oil from water. Chitosan has been successfully used in medicine, food

and chemical industry and biotechnology (Muzzarelli, 1977). Chitosan membranes and films used for drinking water.

Other authors have shown the use of polymeric chitosan films as ion-exchange for alkaline and acidic solutions (Hirano and Tokura, 1982; Singh and Ray, 1998; Begin and Van Calsteren, 1999) The polymeric nature and high chemical activity of chitosan determine prospects of films based on it in water treatment technology and aqueous solutions. The disadvantages of increased use of films and membranes based on chitosan in sorption processes is their lack of stability and solubility in aqueous solutions.

The study of physical - chemical properties of chitosan films to improve their properties and increase stability when used in aqueous solutions of unstable pH is a very pressing issue.

The aim of this work is to study the effects of heat treatment and forming films on their structure and solubility.

Methods

To produce films using chitosan with a degree of deacetylation 87%. Chitosan was obtained from mycelial fungi *Aspergillus niger* biomass – waste of biotechnological production of citric acid by the method (Stolyarenko et al., 2013).

Chitosan films in salt form (S-form) were made with dry molding solutions. Forming solution prepared from 2% chitosan solution in 2% aqueous solution of acetic acid respectively methods (Stolyarenko et al.; 2014). The solution was stirred on a magnetic mixer for 15 minutes.

Chitosan film (S-form) were used for the production of films in the form of polyhydroxide (H-form). For this chitosan film (S-form) was treated with 2% sodium hydroxide for 60 seconds (Samuels, 1981; Arzamastsev et.al., 2008).

Interact with amino groups bound anions solvent (acetic acid) from alkali – NaOH (Fig.2).

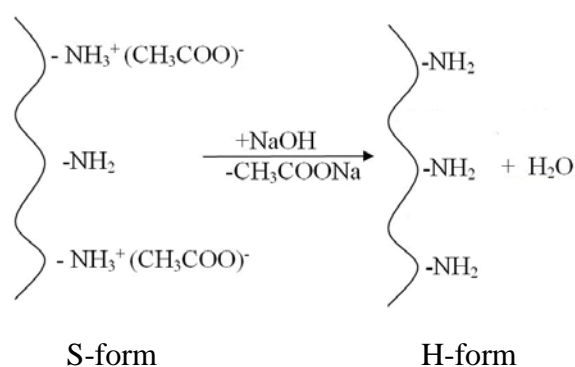


Figure 2 The scheme of transfer films of chitosan (S-form) in the form polihydroxide (H-form).

The content of linked chitosan films acid and amino content was determined by potentiometer titration. (Zotkin et al.; 2004). We used a combined glass electrode. Measurement of pH was carried out with an accuracy of $\pm 0,01$. Electrode checked by standard buffer solution ($pH = 1.1; 4.01; 6.86$ and 9.18). To determine the bound acid sample film weighing about 0.1 g (up to 0.0001) filled with 10 ml of 0.1 M NaOH solution and heated for an hour with constant stirring. After stirring 5 ml of the solution were taken for titration. Titration was performed with 0.1 M HCl solution with constant stirring on a magnetic mixer (temperature $18-20^\circ\text{C}$). It was built in the titration curve coordinates $pH-$

$f(V(\text{HCl}))$). For the titration curve defined volume HCl, which went on titration of excess NaOH. Calculated acid content ($W\%(\text{CH}_3\text{COOH})$) in the film by the formula:

$$W(\text{CH}_3\text{COOH}), \% = \frac{\Delta V(\text{HCl}) \cdot \tilde{n}(\text{HCl}) \cdot K \cdot M(\text{HCl}) \cdot 100}{m},$$

where $\Delta V(\text{HCl})$ – the amount of HCl, which went on titration, l; $c(\text{HCl})$ – molar concentration of HCl mol/l; K – correction factor for the concentration of acid; $M(\text{HCl})$ – molecular weight HCl g/mol; m – film weight, g.

Defined concentration of nitrogen, which describes the presence of amino and amide groups in chitosan films. Film sample weighing approximately 0.1 g (up to 0.0001) was dissolved in 5 ml of 0.1 M HCl solution and stirred for an hour. To the solution was added 5 ml of distilled water and titrated with 0.1 M NaOH solution with constant stirring (temperature 18-20°C). For the titration curve defined volume NaOH, which went on titration and calculated amine nitrogen content $W\%(\text{N})$ by the formula:

$$W(\text{N}), \% = \frac{\Delta V(\text{NaOH}) \cdot \tilde{n}(\text{NaOH}) \cdot 0.014}{m} \cdot 100,$$

where $\Delta V(\text{NaOH})$ – the amount of NaOH, which went on titration; $c(\text{NaOH})$ – molar concentration of HCl mol/l; m – film weight, g; 14 – atomic weight of nitrogen, g/mol.

The degree of substitution at the amino and amide groups was calculated by the formulas:

$$DS_{\text{NH}_2} = \frac{W(\text{N}) \cdot 203}{1400 + 42 \cdot W(\text{N})} \quad \text{and} \quad DS_{\text{NHCO}} = \Delta DS_{\text{NH}_2} + 0.13$$

The degree of conversion of amino amide as calculated by the formula:

$$DC_{\text{NH}_2} = \frac{\Delta DS_{\text{NH}_2}}{0.87},$$

where 0.87 – degree deacetylation of chitosan.

The process of curing the films were performed in the temperature range from 20 to 75°C for 10 to 72 hours. The film of chitosan was heated in an oven at 115°C for 1 to 3 hours. The kinetics swelling investigated the gravimetrically on an analytical balance. To create the proper environment using buffers with pH : 1.1; 5.5; 6.86.

The degree of swelling of the films (α) was calculated using the formula:

$$\alpha = \frac{m - m_0}{m_0} \cdot 100\%,$$

where m_0 – weight chitosan film to swelling, g; m – weight chitosan film after swelling, g.

Kinetic curves were constructed in the coordinates: the degree of swelling - a process of swelling. For kinetic curves determined equilibrium value of the degree of swelling (α_{eq}).

The films of chitosan in S-form and H-form was analyzed using IR spectroscopy (Specord IR-75). The samples were cut into small pieces before grinding with KBr powder in

the ratio of approximately 2:100 of sample to KBr. The IR spectra were run in the wave number ranges of 400-4000 cm^{-1} with 32 scan at 4 cm^{-1} resolution. Explanation spectra were performed using the program MicroCAL Origin v.6.10.

Results and Discussion

Established that an increase in temperature and increase the curing time leads to a reduction solvent (CH_3COOH) in films of chitosan (Table 1). Virtually unchanged degree of substitution for amide and amino groups in structure of chitosan.

Table 1 Terms curing of films and composition films of chitosan before heat treatment*

Terms curing of films		Composition films of chitosan				
$T, ^\circ\text{C}$	τ , hours	$W\%(\text{CH}_3\text{COOH}), \%$	$W\%(\text{N}), \%$	DS_{NH_2}	DS_{NHCO}^{**}	DC_{NH_2}
20	72	36.1	7.3	0.87	0	0
50	20	25.0	7.8	0.87	0	0
75	10	18.9	7.8	0.85	0.02	0.02

* Heat treatment was performed at 115 $^\circ\text{C}$ for 3 hours; ** Increase DS_{NHCO} from baseline of chitosan

As can be seen from Table 2, at high temperatures (115 $^\circ\text{C}$) in films of chitosan observed reduction solvent of acid and increasing the number of amide groups in the structure of chitosan.

Table 2 Terms curing movies and films of chitosan to heat treatment

Terms curing of films		Composition films of chitosan				
$T, ^\circ\text{C}$	τ , hours	$W\%(\text{CH}_3\text{COOH}), \%$	$W\%(\text{N}), \%$	DS_{NH_2}	DS_{NHCO}^{**}	DC_{NH_2}
20	72	18.0	5.08	0.64	0.23	0.26
50	20	14.8	3.97	0.51	0.36	0.41
75	10	10.95	4.3	0.55	0.32	0.37

* Heat treatment was performed at 115 $^\circ\text{C}$ for 3 hours; ** Increase DS_{NHCO} from baseline of chitosan

Under the influence of temperature on the chitosan film is strengthening polymer in the amidation reaction (Fig.3).

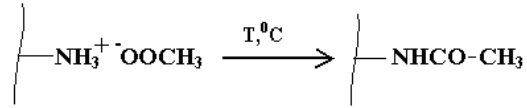


Figure 3. Scheme amidation reaction of films of chitosan

It is proved that when converting films of chitosan S- H-form appears intense absorption band at 1635 cm^{-1} in the IR spectrum, which is characteristic of amino groups (Figure 4, Figure 6). Under the influence of temperature in the infrared spectra of chitosan films (S-form) a decrease in the intensity of the absorption bands Amide I ($1633, 1630 \text{ cm}^{-1}$) and there is an intense absorption band Amide II (1550 cm^{-1}). For films of chitosan in H-form (Fig.7) observed accumulation of amide groups ($1550 \text{ cm}^{-1}, 1495 \text{ cm}^{-1}$). This confirms amidation reaction that occurs during the thermal impact on the films of chitosan. In the stretching vibration of hydroxyl and amino groups ($2980\text{-}2350 \text{ cm}^{-1}$) by the action of the temperature distribution is the intensity of the absorption maximum in the offset area smaller wavelengths.

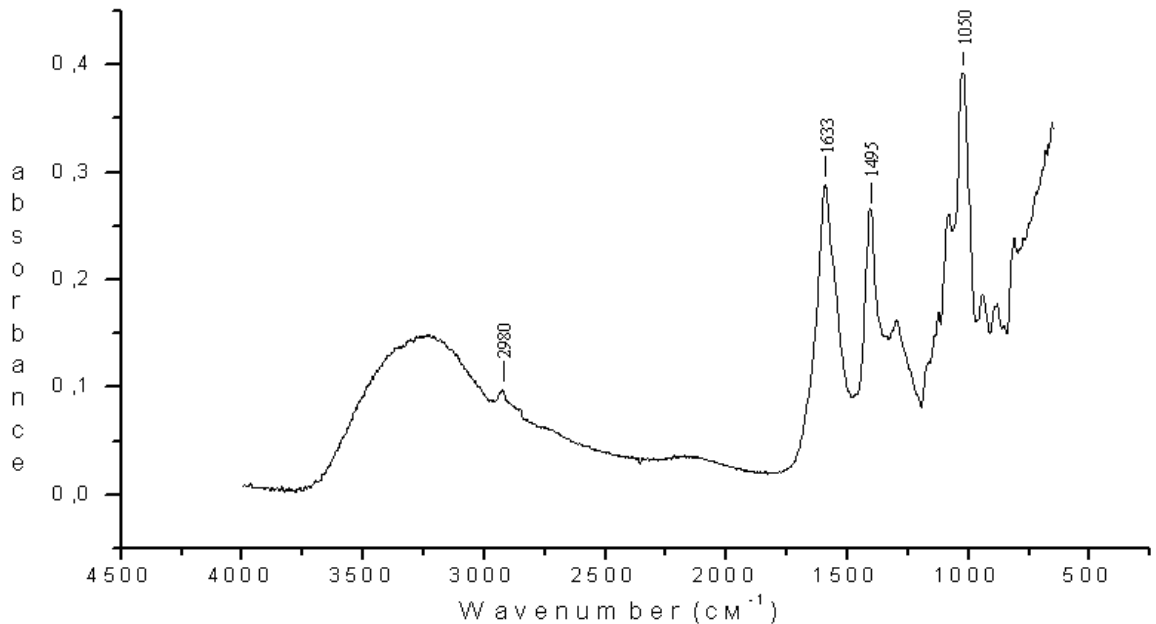


Figure 4 IR spectrum of chitosan film in the S-form before heat treatment.

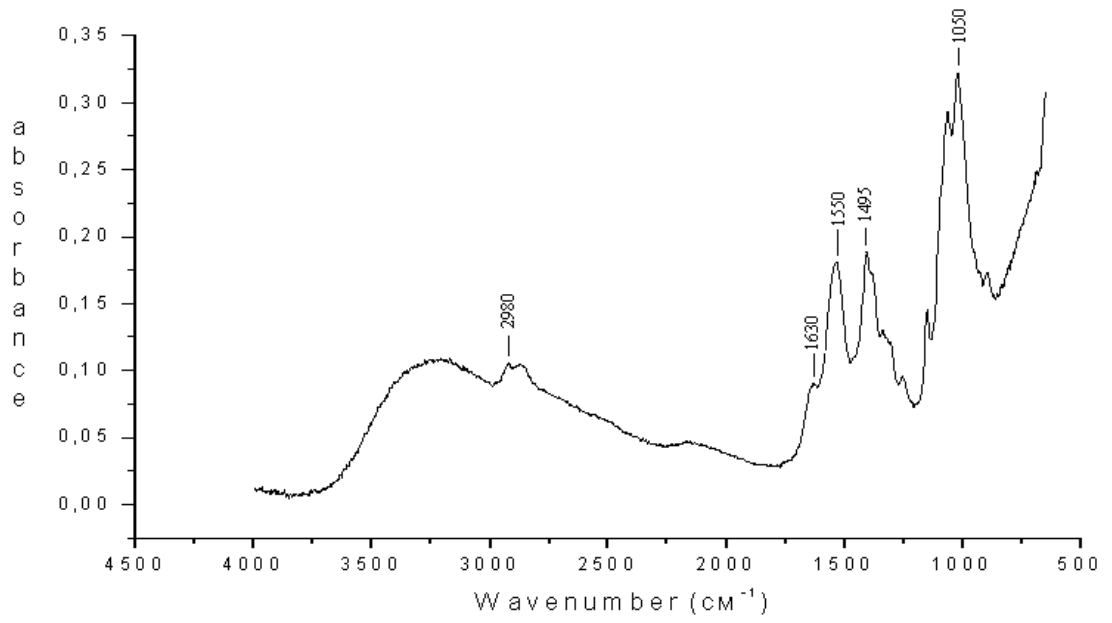


Figure 5 IR spectrum of chitosan film in the S-form after heat treatment

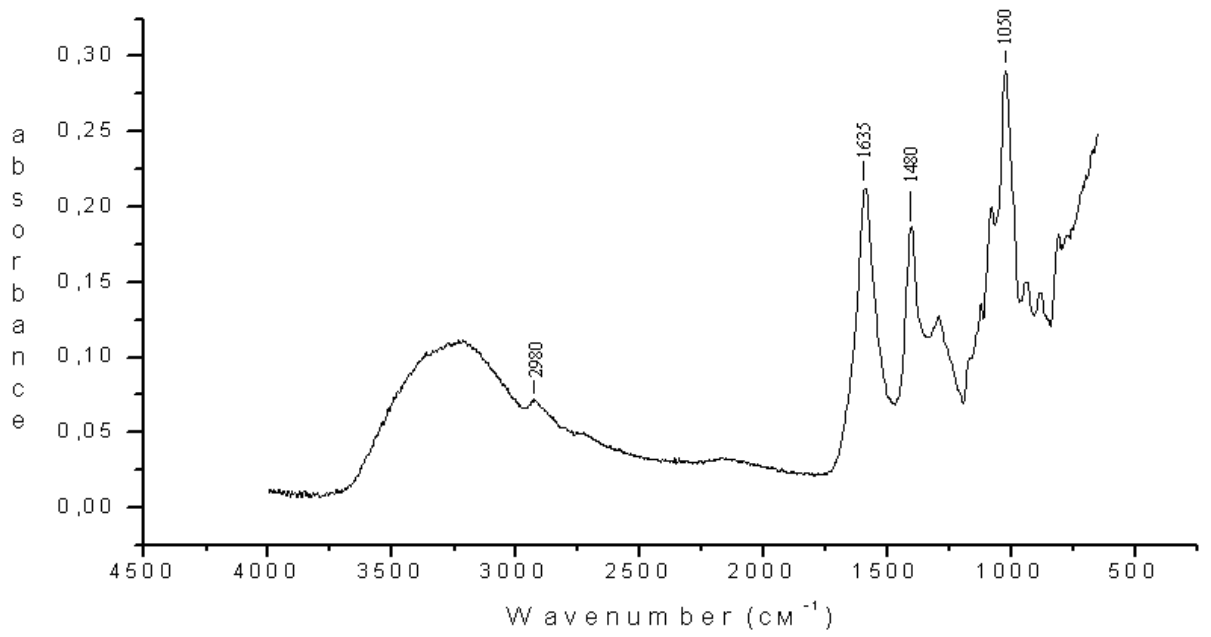


Figure 6 IR spectrum of chitosan film in the H-form before heat treatment

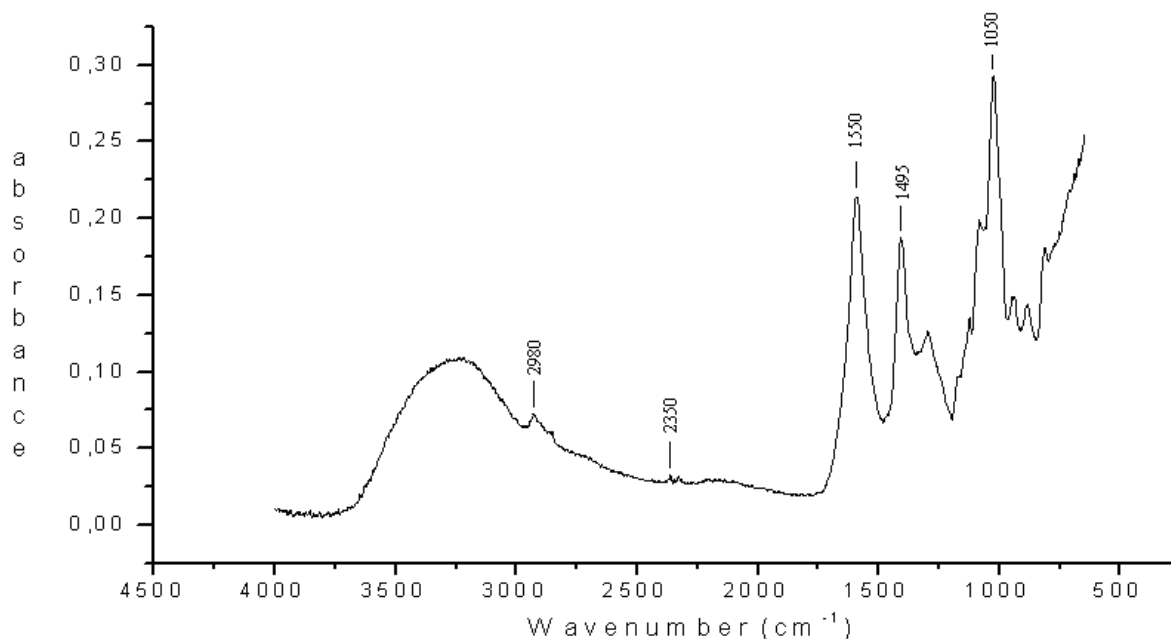


Figure 7 IR spectrum of chitosan film in the H-form after heat treatment

Table 3 presents the results of research degree of swelling of chitosan films before and after exposure to temperature. Established that under the influence of temperature decreases the degree of swelling of chitosan films in the S- form and H- form.

It is proved that under the influence of temperature in the macromolecules of chitosan, a decrease in the number of amino groups and reduce the ability of ionized molecules participate in conformational transformations.

Table 3 Effect of heat treatment and pH of the solutions to the equilibrium degree of swelling of chitosan films in S- and H-form

pH	Equilibrium degree of swelling α_{eq}			
	S-form*	S-form-T**	H-form*	H-form-T**
1.1	-	-	-	-
5.5	375	280	200	175
6.86	250	170	150	95

* - chitosan film before heat treatment; ** - chitosan film after heat treatment at 95°C for 1 hour

The process amidation and organization of the structure, which reduces the solubility of chitosan films. The results are in good agreement with data obtained by other authors (Kim, C.H. et.al., 2004; Pielichowski, K. and Njuguna, J., 2005; Rivero S. et.al., 2012)

Conclusions

Was established that the increase in temperature and duration of curing films of chitosan leads to reduction of acid solvent (CH₃COOH) in freshly formed films. The Amidation reaction does not occur.

It is proved that heat treatment films of chitosan reduces solubility. This can be explained by substitution of amino groups (NH₂-) on amide (NHCO-). There is a formation of chains structure of chitin and chitosan. Crosslinking of the polymer occurs through amidation reaction.

IR spectra of films of chitin in the C- and H-form show an increase in the number of amide groups in the process of heat treatment and suggest streamlining the structure of chitosan, which reduces the solubility.

Discussed in the work modifying of films of chitosan demonstrate feasibility of their application for films with improved properties. Films of chitosan after thermal modification can be used in different sectors of the economy, and especially in the manufacturing processes of water purification.

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