

*Angela Murzagildina¹, Roza Mudarisova², Elena Kulish¹, Sergei Kolesov²
and Gennady Zaikov³*

CHITOSAN FILMS DOPED WITH IODINE VAPOURS

¹The Bashkir State University, Ufa, Bashkortostan

²The Institute of Organic Chemistry of the Ufa Scientific Centre,
Russian Academy of Science, Ufa, Bashkortostan

³Emanuel Institute of Biochemical Physics, Russian Academy of Sciences,
4 Kosygina str., 119991 Moscow, Russia; chembio@sky.chph.ras.ru

Received: February 01, 2012 / Revised: April 02, 2012 / Accepted: August 23, 2012

© Murzagildina A., Mudarisova R., Kulish E., Kolesov S., Zaikov G., 2013

Abstract. Through the process of modification of chitosan films obtained from solutions in acetic acid, the possibility of obtaining iodine polymer films with controlled release of iodine has been shown.

Keywords: chitosan, polymer films, iodine, modification.

1. Introduction

Peculiarities of chemical and spatial structure of chitosan determine its capability for forming specific complexes with various compounds [1]. Among the pharmacological molecules special attention is to be paid to iodine, the simplest biocide preparation of the local action, for which not a single fact of any known microorganisms habituation has been revealed [2]. With the aim of prolongation of iodine action and decrease of its toxicity it makes sense to introduce iodine into the polymer matrix. The obtaining of iodine polymer films on the basis of chitosan – the polymer which itself has immunostimulating and bacteriostatic effect – can be promising for use in medicinal practice as protective coatings for suppurative, burning and surgical wounds.

2. Experimental

The object of investigation was the food chitosan (ChT) (the company “Bioprogress”, Schelkovo) obtained by alkaline deacetylation of crab chitin (the deacetylation degree is ~ 83 %, the molecular mass is 87 kDa). ChT films were produced by the method of casting the polymer solution onto the glass surface. The mass concentration of polymers in the initial solution was 2 g/dl. 1 % Acetic acid was used as the solvent. The thickness of films was 0.1 mm. The modification of the obtained chitosan films was

carried out in two ways: 1) by the transition to the basic form through holding the produced film in 0.1 N solution of NaOH during 30 min with succeeding washing in distilled water and 2) by thermal modification through heating films during 30 min at the temperature of 393 K. The saturation of chitosan films with iodine vapours (doping) was carried out at 294 K. The study of the kinetics of iodine release from the doped films was conducted in water medium simulating the wet wound surface. For this purpose the specimens of doped films ChT-iodine were held in water for a certain period of time, then dried up to constant weight and weighed. The kinetics of release of iodine into water medium was determined by the loss of mass. In order to take UV spectra of thin films the ChT solution was applied to a quartz bed, dried in the air and analyzed on the spectrophotometer “Specord M-40”. IR spectra of the films (with the thickness of 0.1 mm) were recorded on the spectrophotometer “Specord M-80” in the region of 500–4000 cm⁻¹.

3. Results and Discussion

The IR spectrum of the chitosan film obtained in the salt form is of diffuse character, which testifies to its polymeric nature and gives general information on the polymer molecule. In the spectrum (Fig. 1, curve 1) one can observe a wide absorption band in the region of 3700–3100 cm⁻¹ which belongs to valent vibrations of OH- and NH-bonds (non-distinct structure). Its position and width are indicative of the existence of intermolecular hydrogen bond involving these functional groups. A broadened band in the region of 2960–2920 cm⁻¹, to which valent vibrations of both methylene and methyl groups belong is also observed. The band in the region of 1593 cm⁻¹ with

the bend at 1673 cm^{-1} corresponds to deformation vibrations of the aminogroup. The band of C=O bond of the acetyl substituent may correspond to the bend. In the region of $1500\text{--}1200\text{ cm}^{-1}$ the bands with the maximums at 1462 cm^{-1} of the deformation vibration of CH_2 or CH_3 groups and at 1377 cm^{-1} of the deformation vibration of OH bond were registered. The spectrum region of $900\text{--}1200\text{ cm}^{-1}$ is characterized by the intensive band, in which one can distinguish three peaks with the frequencies 1153 , 1074 and 1033 cm^{-1} , which are likely to belong to valent vibrations of C–O, C–N and C–C bonds of the molecule skeleton. The IR-spectrum of the chitosan film subjected to doping with iodine vapours is of another kind (Fig. 1, curve 2). Absorption bands in the region of $3700\text{--}2900\text{ cm}^{-1}$ belonging to valent vibrations of OH-group, CH- and NH- bonds disappear. The band corresponding to deformation vibrations of the aminogroup is shifted by 80 cm^{-1} to the region of greater wave lengths. In the region of $1400\text{--}1300\text{ cm}^{-1}$ the bands corresponding to deformation vibrations of CH_2 -, CH_3 - and OH-groups are not registered as well. The results obtained make it possible to suggest the progress of the interaction of amino- and hydroxyl groups.

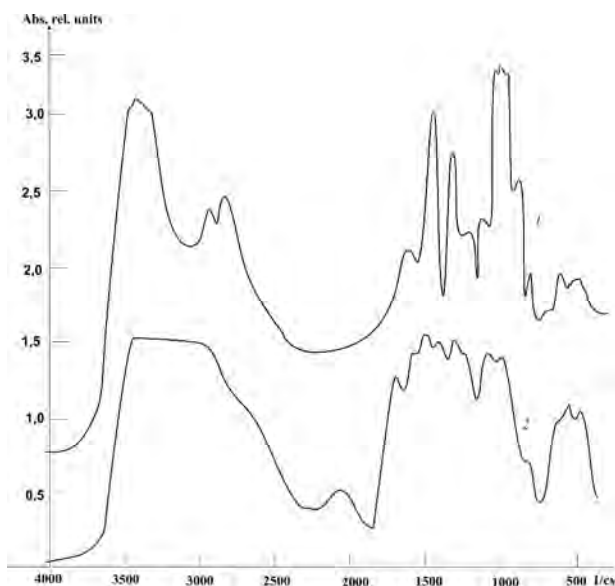


Fig. 1. IR spectrum of a chitosan film in the non-doped (1) and doped (2) with iodine vapours salt form

The changes occurring at doping of thin chitosan films obtained in the salt form with iodine vapours are also supported by UV-spectroscopy data (Fig. 2). ChT standing in iodine vapours even for 10–15 s results in the appearance of the absorption band with $\lambda_{\text{max}} = 290\text{--}300\text{ nm}$, which can be assigned to the absorption of I_3^- ions. The increase of the doping time results in the strengthening of the absorption band I_3^- and in the appearance of a new wide absorption band of high

intensity with poorly expressed maximum in the region of $400\text{--}500\text{ nm}$, which can be assigned to polyiodides absorption [3]. At further increase in the doping time one can observe the decrease in the intensity of the absorption band of $290\text{--}300\text{ nm}$ and the increase in the intensity of the absorption band in the region of $400\text{--}500\text{ nm}$.

After the beginning of iodine vapour doping of a chitosan film in the basic form the absorption bands at wave lengths of 290 and 360 nm belonging to I_3^- ions appear in UV spectrum of the film (Fig. 3). At further saturation of the film with iodine vapours for 30 min active accumulation of I_3^- ions is observed, which is demonstrated by the increase in the intensity of the corresponding bands. Besides, I_3^- ions are formed in the film, which is indicated by the broadening of the peak at 380 nm and its hypsochromic shift by 10 nm . In 90 min one can observe still greater broadening of triiodide ions bands and their shift to the region of greater wave lengths by 40 nm (300 and 420 nm respectively), which points to the lengthening of the iodide chain and to the formation of I_3^- and I_7^- ions. Within 5 h after the beginning of doping the intensity of bands belonging to I_3^- and I_5^- ions decreases as there takes place the formation of polyiodide chain. The absorption band previously registered in the region of 370 nm also widens and the absorption maximum is shifted to the region of 420 nm , which testifies to the polyiodides accumulation.

On the contrary, in the thermally treated iodine-containing film polyiodides are absent (Fig. 4). Within 5 min after the doping beginning in UV spectrum one can register an absorption band in the region of 290 nm and a weakly expressed one – in the region of 360 nm . The intensity of both bands remains practically constant up to the doping time equal to 200 min . A sharp increase in intensity is observed after 300 min of treatment with iodine vapours. The absorption maximums are shifted to the region of larger wave lengths by $5\text{--}10\text{ nm}$, which indicates that triiodide-ions combine with ChT to form a complex but the broadening of bands in the regions of $370\text{--}420\text{ nm}$ does not occur.

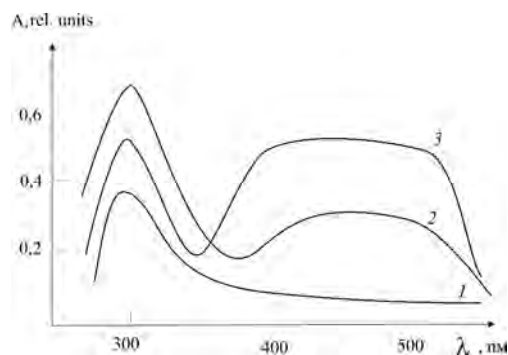


Fig. 2. Electronic spectrum of a thin chitosan film in the salt form doped with iodine vapours during 15 s (1), 30 min (2) and 2 h (3)

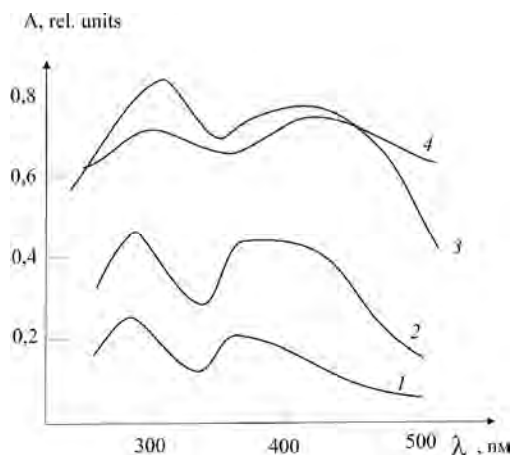


Fig. 3. Electronic spectrum of a thin chitosan film in the basic form doped with iodine vapours during 5 min (1), 30 min (2), 90 min (3) and 5 h (4)

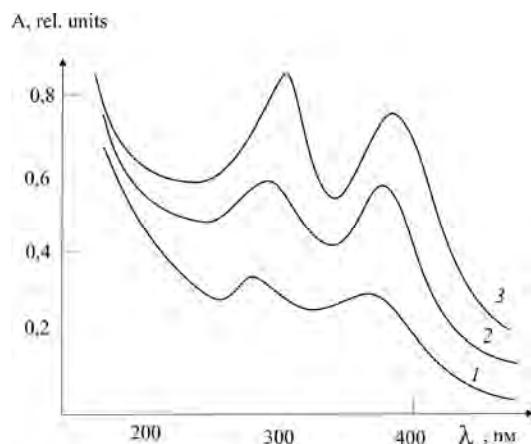


Fig. 4. Electronic spectrum of a thermotreated thin chitosan film doped with iodine vapours during 5 min (1), 3.5 h (2) and 4.5 h (3)

Thus, modification of chitosan films is accompanied first of all by regular changes in structural and physical condition of film specimens. For example, chitosan films obtained in a salt form are known to be readily soluble in water, which promotes accelerated mechanical disintegration of a polymer film on the wound surface. The transfer of ChT from the salt form to the basic one results in the loss of film solubility in water, in the increase of the density of macromolecules packing and in the increase of the degree of its crystallinity [4]. On the contrary, the thermal modification of salt films makes it possible to obtain water-insoluble films with less crystalline but more morphologically uniform structure [5]. Secondly, there takes place the change in the interaction of films with iodine vapours. Thus, the amount of iodine absorbed by the chitosan matrix increases regularly at transition from thermomodified films to the salt and then the basic ones (190, 205 and 230 mas %,

respectively). Thirdly, the corresponding regularities of iodine release from films take place.

At placing iodine-containing films into water there occurs their swelling, which contributes to iodine release from the polymer matrix. In this case kinetic regularities of iodine release from films are changing in accordance with the variation of the crystallinity degree of ChT in films. As seen from Fig. 5, the rate and degree of iodine release is maximal in the case of the films subjected to preliminary thermal treatment and is minimal for the films in the basic form. As this takes place, the increase of the time of films modification both in the case of films obtained in the basic form and in the case of the thermomodified ones is accompanied by the regular decrease of the rate and extent of iodine release.

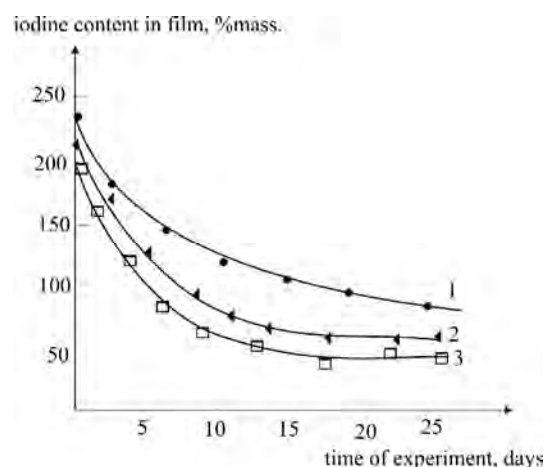


Fig. 5. The kinetics of iodine release from chitosan films in basic (1), salt (2) and subjected to preliminary thermomodification (3) forms

The prolonged standing of films in the air (during 1 year) results in the fact that the position of absorption bands in the complex spectrum is retained, only their intensity somewhat decreases. This confirms greater stability of polyiodide ions in the composition of the complex.

4. Conclusions

Conducting of the process of chitosan films doping with iodine vapours makes it possible to obtain iodine-containing chitosan films for potential use in medicinal practice as film coatings. The process of chitosan films modification consisting in the transition of the produced film to the basic form or in thermal heating of the film allows us to change the structural and physical condition of the film and correspondingly to regulate both the degree of interaction of the polymer with iodine and the release of a medicinal preparation from the films.

Acknowledgements

The work has been carried out due to the financial support of the RFFR and Republic of Bashkortostan (grant r_povolzhye №11-03-97016)

References

- [1] Muzarelli R.: Chitin. Pergamon Press, Oxford 1977.
- [2] Abrosimov V.: Biologicheski Aktivnye Veschestva v Rastvorah: Struktura, Termodinamika, Reakcionnaya Sposobnost. Nauka, Moskva 2001.
- [3] Kalninysh K. and Lyubimova G.: Phys. Khim., 1983, **57**, 2995.

[4] Nikolaev A., Prokopov A. and Shulgina E.: Zh. Prikl. Khim., 1985, **LVIII**, 1870.

[5] Ageev E., Vikhoreva G., Zotkin M. et al.: Vysokomolec. Soed., 2004, **46**, 2035.

ХІТОЗАНОВІ ПЛІВКИ, ПРОМОТОВАНІ ПАРАМИ ЙОДУ

Анотація. Показано можливість отримання йодованих полімерних плівок з контрольованим вивільненням йоду в процесі модифікації хітозанових плівок з розчину оцтової кислоти.

Ключові слова: хітозан, полімерні плівки, йод, модифікація.