

THE EFFECT OF IONIC CROSSLINKING ON THERMAL PROPERTIES OF HYDROGEL CHITOSAN MEMBRANES

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Abstract

Ionically crosslinked one-component chitosan (Ch), two-component chitosan/sodium alginate (Ch/NaAlg) and chitosan/pentasodium tripolyphosphate (Ch/TPP) membranes as well as three-component chitosan/sodium alginate/pentasodium tripolyphosphate (Ch/NaAlg/TPP) membranes were prepared. Formation of ionic interactions between Ch and NaAlg and/or TPP was confirmed by FTIR analysis. An effect of a crosslinking process on thermal properties of hydrogel membranes was examined using TG/DTG/DTA and DSC methods. Changes in the number of thermal degradation steps of the studied hydrogel membranes were observed. Considering the temperature at which thermal degradation starts as a criterion of the thermal stability, it was concluded that the thermal stability increases according to the series: Ch/NaAlg \approx Ch/NaAlg/TPP \approx Ch/TPP < NaAlg < Ch < TPP.

Key words: *hydrogel, chitosan, crosslinking, thermal stability, TG/DTG, DSC.*

1. Introduction

According to the most commonly used definition hydrogels are three-dimensional networks of hydrophilic polymers able to absorb a large amount of water and biological fluids. Recently, the attention of researchers is mainly focused on hydrogel materials based on natural biodegradable polymers, especially on such cationic polyelectrolyte as chitosan (Ch) [1].

Chitosan is a deacetylated derivative of chitin. It is a copolymer of β -(1 \rightarrow 4)-linked 2-acetamido-2-deoxy- β -D-glucopyranose and 2-amino-2-deoxy- β -D-glucopyranose (**Figure 1.a**) [2]. To avoid chitosan dissolution in acidic media its modification through crosslinking is widely used. Among others, hydrogels based on chitosan and with ionic bonds as the predominant crosslinking interactions constitute an abundant group [1].

The aim of presented work was synthesis of ionically crosslinked chitosan membranes. High molecular anionic polyelectrolyte - sodium alginate (NaAlg) (**Figure 1.b**) and low molecular ionic compound - pentasodium tripolyphosphate (TPP) (**Figure 1.c**) were used as crosslinking agents.

Changes in chemical structure of chitosan hydrogel membranes after their ionic crosslinking were analysed by FTIR spectroscopy. The influence of crosslinking process on thermal stability of chitosan membranes was studied using thermogravimetric and differential scanning calorimetry methods.

2. Materials and methods

2.1. Materials

Commercially available chitosan from crab shells of medium (MMW-Ch) and high (HMW-Ch) molecular weight, sodium alginate (NaAlg) and pentasodium tripolyphosphate (TPP) were purchased from Sigma Aldrich (Germany). Acetic acid (HAc), sodium

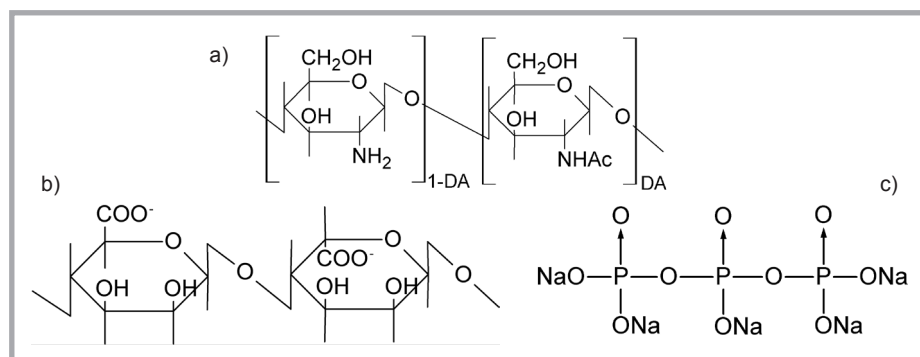


Figure 1. Chemical structure of chitosan (DA-degree of acetylation) - a, sodium alginate (NaAlg) - b and pentasodium tripolyphosphate (TPP) - c.

acetate (NaAc) and hydrochloric acid (HCl) were analytical grade and were purchased from POCh (Poland). Potassium bromide (KBr) for spectroscopy was purchased from Merck (Germany).

2.2. Polymer characterization

Degree of deacetylation, DDA (= 1 - DA), of chitosan was determined by potentiometric titration method [3]. The viscosity average molecular weight of chitosan and sodium alginate, \overline{M}_v , was determined by viscometry [4, 5]. The details of above measurements have been presented elsewhere [6]. Degree of deacetylation was equal to $75.72 \pm 3.82\%$ and $79.53 \pm 1.49\%$ for MMW-Ch and HWM-Ch, respectively. \overline{M}_v was equal to 730 kDa for MMW-Ch, 980 kDa for HWM-Ch and 100 kDa for sodium alginate.

2.3. Membrane preparation

One-component chitosan membranes (Ch) and two-component chitosan/sodium alginate (Ch/NaAlg) membranes were prepared by casting solution and solvent evaporation technique. To obtain *pure chitosan membranes* 1 wt.% chitosan solution, prepared by dissolving MMW-Ch or HMW-Ch powder in 2 wt.% HAc, was cast as film on clean glass plate, evaporated to dryness at 37°C and further dried under vacuum at 60 °C. To obtain *chitosan/sodium alginate polyelectrolyte complex* (PEC) 1 wt.% chitosan solution in 2 wt.% acetic acid and 1 wt.% sodium alginate solution were mixed in the 3:1 volume ratio ($\text{pH}_{\text{solution mixture}} = 3.5$). Ch/NaAlg membranes were prepared analogously as chitosan films.

Two-component *chitosan/pentasodium tripolyphosphate* (Ch/TPP) membranes were prepared by immersing of pure chitosan membranes in aqueous 1.3% (w/v) tripolyphosphate solution for 60 min. Applied crosslinking conditions were as follows: $T_{\text{crosslink}} = 4 \text{ }^\circ\text{C}$, $\text{pH} = 9.0$ (initial pH) and 5.5 (initial solution acidified with HCl).

Three-component *chitosan/sodium alginate/pentasodium tripolyphosphate* (Ch/NaAlg/TPP) membranes were prepared by immersing of two-component Ch/NaAlg membranes in aqueous 1.3% (w/v) tripolyphosphate solution for 60 min. Applied crosslinking conditions were as follows: $T_{\text{crosslink}} = 4 \text{ }^\circ\text{C}$, $\text{pH} = 5.5$ (initial solution acidified with HCl). The obtained two- and three-component membranes before drying were additionally thoroughly washed with deionised water.

2.4. FTIR spectroscopy

FTIR spectra of chitosan, sodium alginate, pentasodium tripolyphosphate and ionically crosslinked two- and three-component chitosan (ICCh) samples in KBr disc form were recorded on Perkin-Elmer 2000 FTIR spectrometer from 400 to 4000 cm^{-1} with a resolution 4 cm^{-1} and at 100 scans. Ch, NaAlg, TPP and ICCh polymers were thoroughly powdered and powders dried under vacuum at 60°C for 24 hours before milling with anhydrous KBr.

2.5. Thermal analysis

Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis were carried out with SDT 2960 Simultaneous TGA-DTA Thermal Analyzer System (TA

Instruments, USA). All measurements were performed with a 5 mg samples (Ch membrane, NaAlg, TPP and ICCh) in aluminium pans under dynamic nitrogen atmosphere in the temperature range from room temperature to 500 °C at the scanning rate of 10 °C/min and gas flow of 100 mL/min.

Differential scanning calorimetry (DSC) analyse were performed with Polymer Laboratories Ltd. (Epsom, United Kingdom) differential scanning calorimeter equipped with a liquid nitrogen cooling accessory. The temperature scale of the apparatus was calibrated using water. Thoroughly dried chitosan membrane, sodium alginate, pentasodium tripolyphosphate and ionically crosslinked chitosan membrane samples (about 15 mg) were weighed in an aluminum pan designated for volatile samples and sealed. Samples were heated from room temperature to 400°C at the heating rate of 10 °C/min under constant purging of nitrogen at 4 mL/min. An empty cup was used as a reference.

2.6. X-ray diffraction studies

Wide angle X-ray diffraction patterns of NaAlg and TPP powders and Ch, ICCh membranes were measured by an X-ray diffractometer (X-Pert PRO Systems, Philips, The Netherlands).

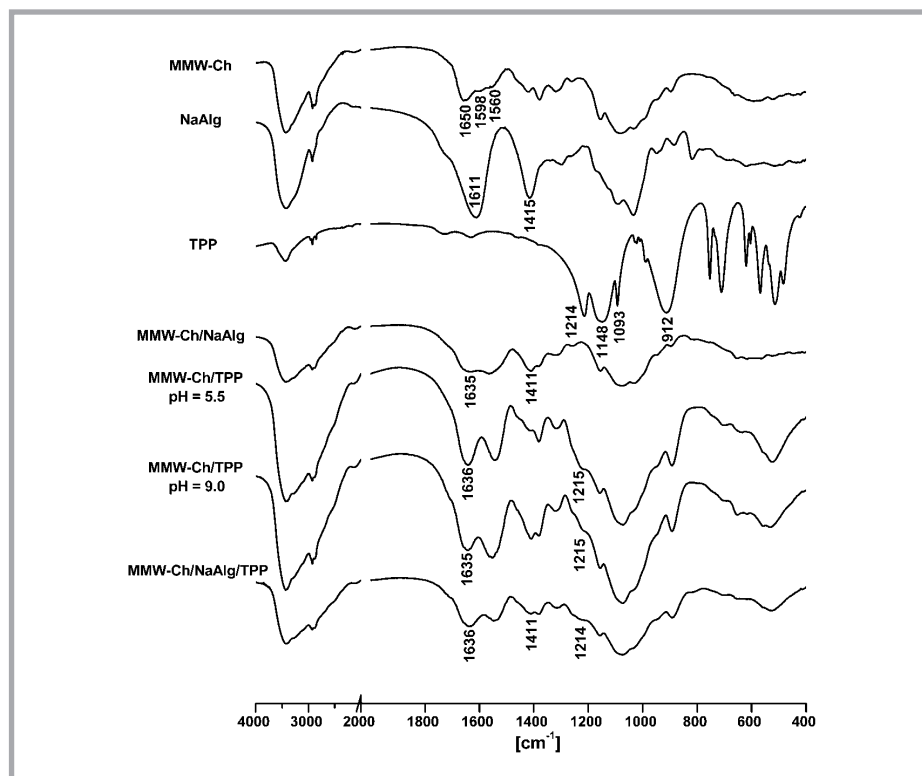


Figure 3. FTIR spectra of chitosan, sodium alginate, pentasodium tripolyphosphate and ionically crosslinked chitosan membranes.

Measurements were performed by exposing samples to CuK α radiation ($\lambda = 1.54056 \text{ \AA}$) and scanning from $2\Theta = 5^\circ$ to 40° at a step size of 0.02° .

3. Results and Discussion

FTIR spectra of pentasodium tripolyphosphate (TPP), individual polymers: chitosan (Ch), sodium alginate (NaAlg) and ionically crosslinked two- and three-component chitosan (ICCh) are shown in **Figure 2**. All spectra, except for TPP, exhibit a strong and broad antisymmetric band at about 3430 cm^{-1} that results from overlapping of the O-H and N-H stretching vibrations of functional groups engaged in hydrogen bonds [7]. As we reported previously [8], the spectrum of Ch exhibits characteristic absorption bands at: 1650 cm^{-1} (C=O stretching in amide group, amide I vibration), 1598 cm^{-1} (N-H bending in nonacetylated 2-aminoglucose primary amine) and 1560 cm^{-1} (N-H bending in amide group, amide II vibration). Absorption bands at 1153 cm^{-1} (antisymmetric stretching of the C-O-C bridge), 1083 cm^{-1} and 1031 cm^{-1} (skeletal vibrations involving the CO stretching) are characteristic of chitosan saccharide structure [9]. In the FTIR spectrum of NaAlg two strong absorption peaks at 1611 and 1415 cm^{-1} are seen. They can be assigned to the antisymmetric and symmetric stretching vibrations of the carboxylate group, respectively [7]. In TPP spectrum following characteristic bands can be observed: 1214 cm^{-1} (P=O stretching), 1148 cm^{-1} (symmetric and antisymmetric stretching vibrations in PO_2 group), 1093 cm^{-1} (symmetric and antisymmetric stretching vibrations in PO_3 group), 912 cm^{-1} (antisymmetric stretching of the P-O-P bridge) [10].

After crosslinking process in the spectra of all ICCh samples there appears a new band at 1635 cm^{-1} . This band can be assigned to antisymmetric deformation N-H vibrations in NH_3^+ ion [7, 8]. Moreover, some additional changes in the spectra of chitosan after its ionic crosslinking can be observed. In the spectrum of two-component Ch/TPP membrane a new band at 1215 cm^{-1} appears that corresponds to P=O stretching vibrations in phosphate ions [10]. Moreover, Ch/TPP membranes crosslinked in different pH conditions differ in intensity of 1215 cm^{-1} band. This clearly indicates on variation in Ch/TPP crosslinking density. In the spectrum of Ch/NaAlg an absorption band at 1411 cm^{-1} can be observed that corresponds to C-O antisymmetric vibrations in COO^- ions [6, 7]. In the spectrum of three-component Ch/NaAlg/TPP membrane absorption bands at 1411 and 1214 cm^{-1} , observed earlier for two-component Ch/NaAlg and Ch/TPP membranes, respectively, can be seen.

FTIR results indicate that NH_3^+ groups of chitosan form ionic crosslinks with COO^- groups of NaAlg and/or tripolyphosphate ions. The chemical structures of ionically crosslinked chitosan membranes were presented elsewhere [8].

Figure 3 exhibit DTG and DSC curves for sodium alginate, pentasodium tripolyphosphate as well as one-, two- and three-component chitosan membranes.

For all polymer systems the first stage of thermal decomposition starts below 100°C and corresponds to the loss of water sorbed by polymer. The next stages correspond to the thermal decomposition of polyelectrolytes or complexes and vaporization of decomposition products. Results obtained for Ch membrane, NaAlg and TPP stay in good agreement with literature data [11, 12].

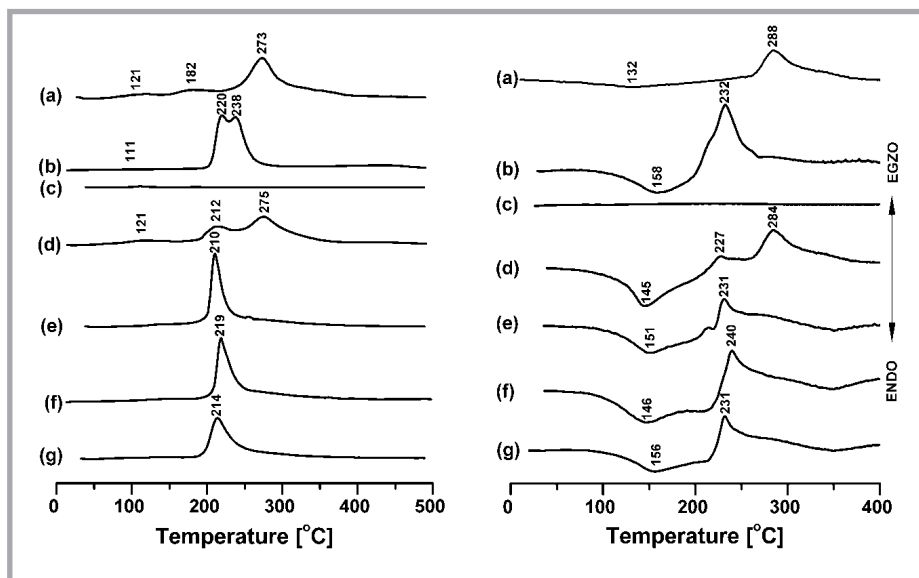


Figure 3. DTG (left) and DSC (right) thermograms of: (a) Ch membrane, (b) NaAlg, (c) TPP, (d) MMW-Ch/NaAlg, (e) MMW-Ch/TPP (pH = 5.5), (f) MMW-Ch/TPP (pH = 9.0), (g) MMW-Ch/NaAlg/TPP.

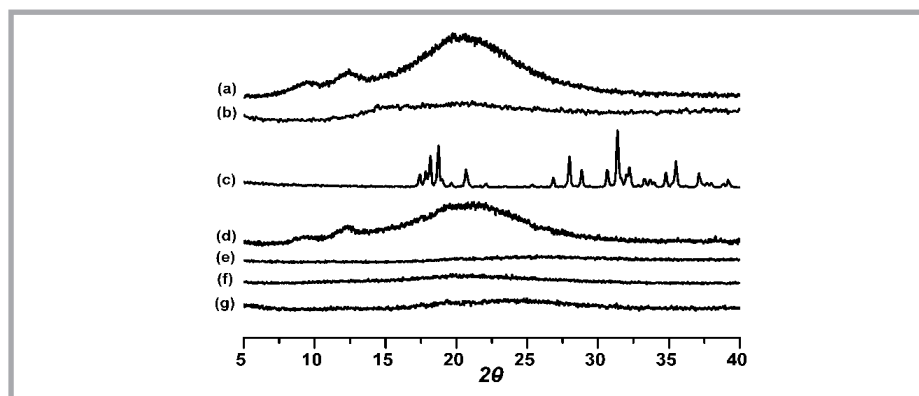


Figure 5. X-ray diffractograms of: (a) Ch membrane, (b) NaAlg, (c) TPP, (d) MMW-Ch/NaAlg, (e) MMW-Ch/TPP (pH = 5.5), (f) MMW-Ch/TPP (pH = 9.0), (g) MMW-Ch/NaAlg/TPP.

There were observed some changes in the number of thermal degradation steps and temperature of maximum degradation of the studied chitosan membranes after their crosslinking. In the DTG curves of Ch/NaAlg two new peaks with a maximum at 212 °C and 275 °C are observed. These peaks, as we have discussed earlier [6], can be assigned to the formation of ionic pairs between Ch and NaAlg. DTG curves for Ch/TPP (pH = 5.5) and Ch/TPP (pH = 9.0) are characterized by a single peak at 210 °C or 219 °C, respectively. Similar

results were noted by others for chitosan membranes modified with poly(vinyl phosphonic acid) [13] and they confirm the interactions between chitosan and TPP ions. Only one thermal decomposition stage can be also observed on DTG curves for Ch/NaAlg/TPP membranes. Analogous results indicating the change of number of thermal degradation steps after ionic crosslinking of chitosan membrane were observed in DSC thermograms.

Considering the temperature at which thermal degradation starts as a criterion of the thermal stability, the thermal stability increases according to the series: Ch/NaAlg \approx Ch/NaAlg/TPP \approx Ch/TPP < NaAlg < Ch < TPP.

As it was indicated by Denuziere [14], lowering of chitosan membranes thermal stability after their crosslinking processes can be related with changes in their molecular structure.

It can be seen from X-ray diffraction studies, that after crosslinking hydrogel membranes are more amorphous (**Figure 5**). The changes in supramolecular structure of chitosan membranes result both from ionic crosslinks formation as well as from breaking of intermolecular chitosan's hydrogen bonds.

4. Conclusions

Physical crosslinking process strongly affected the thermal stability of chitosan membranes as well as their supramolecular structure. There was not observed a visible effect of crosslinking density on thermal stability of two-component Ch/TPP membranes. Molecular weight of chitosan only slightly influenced the thermal properties of chitosan, chitosan/sodium alginate, chitosan/pentasodium tripolyphosphate and chitosan/sodium alginate/pentasodium tripolyphosphate membranes.

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6. References

1. **Dumitriu S.**; (2001) *Polysaccharides as Biomaterials*. In: Dumitriu S (ed), *Polymeric Biomaterials*, CRC Press, Boca Raton, pp. 1-62.
2. **Struszczyk M. H.**; (2002) *Chitin and chitosan. Part I. Properties and production*. *Polymer (Warsaw)* 47, pp. 316-325.
3. **Muzzarelli R. A. A., Rocchetti R., Stanic V., Weckx M.**; (1997) *Methods for the determination of the degree of acetylation of chitin and chitosan*. In: Muzzarelli R. A. A., Peter M. G. (eds), *Chitin Handbook*, Atec Edizioni, Grottammare, pp. 109-119.
4. **Ilina A. V., Varlamov V. P.**; (2004) *Hydrolysis of chitosan in lactic acid*. *Appl Biochem Microbiol* 40, pp. 300-303.
5. **Martinsen A., Skjåk-Bræk G., Smidsrød O., Zanetti F., Paoletti S.**; (1991) *Comparison of different methods for determination of molecular weight and molecular weight distribution of*

- alginates. *Carbohydr Polym* 15, pp. 171-193.
6. **Ostrowska-Czubenko J., Gierszewska-Drużyńska M.;** (2009) Effect of ionic crosslinking on the water state in hydrogel chitosan membranes. *Carbohydr Polym* 77, pp. 590-598.
 7. **Rao C. N. R.;** (1963) *Chemical Application of Infrared Spectroscopy*. Academic Press, New York, London.
 8. **Pieróg M., Gierszewska-Drużyńska M., Ostrowska-Czubenko J.;** (2009) Effect of ionic crosslinking agents on swelling behavior of chitosan hydrogel membranes. In: Jaworska M. M. (ed), *Progress on Chemistry and Application of Chitin and its Derivatives*, Polish Chitin Society, Łódź 2009,
 9. **Pawlak A., Mucha M.;** (2003) Thermogravimetric and FTIR studies of chitosan blends. *Thermochim Acta* 396, pp. 153-166.
 10. **Corbridge D. E. C., Lowe E. J.;** (1954) The infra-red spectra of some inorganic phosphorus compounds. *J Chem Soc*, pp. 493-502.
 11. **Neto C. G. T., Giacometti J. A., Job A. E., Ferreira F. C., Fonseca J. L. C., Pereira M. R.;** (2005) Thermal analysis of chitosan based networks. *Carbohydr Polym* 62, pp. 97-103.
 12. **Soares J. P., Santos J. E., Chierice G. O., Cavalheiro E. T. G.;** (2004) Thermal behaviour of alginic acid and its sodium salt. *Eletica Quim* 29, pp. 57-64.
 13. **Göktepe F., Ünügür Çelik S., Bozkurt A.;** (2008) Preparation and the proton conductivity of chitosan/poly(vinyl phosphonic acid) complex polymer electrolytes. *J Non-Cryst Solids* 354, pp. 3637-3642.
 14. **Denuziere A., Ferrier D., Domard A.;** (1996) Chitosan-chondroitin sulfate and chitosan-hyaluronate polyelectrolyte complexes. *Physico-chemical aspects*. *Carbohydr Polym* 29, pp. 317-323.