THERMAL DEGRADATION OF DOUBLE CROSSLINKED HYDROGEL CHITOSAN MEMBRANES

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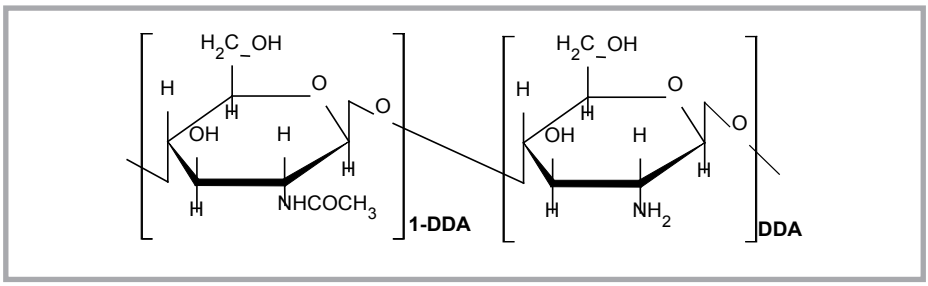
Abstract
The thermal degradation behaviour of uncrosslinked and crosslinked chitosan membranes were studied by means of dynamic thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) over the temperature range 25-500°C in nitrogen atmosphere. Modified chitosan membranes were prepared using a crosslinking method based on covalent crosslinking of chitosan with glutaraldehyde and subsequent ionic crosslinking with sodium citrate, sulfuric acid, sulfosuccinic acid and tripolyphosphate, respectively. Chemical structure of modified chitosan membranes before and after their thermal degradation was characterized by FTIR spectroscopy. Both TGA and DSC experiments as well as spectral results (FTIR spectra of thermal degradation residues) indicated some differences in the mechanism of thermal degradation of uncrosslinked and crosslinked chitosan membranes.

Key words: *chitosan membrane, thermal degradation, thermogravimetry, DSC, FTIR.*

1. Introduction

Chitosan (Ch), the fully or partially deacetylated form of chitin, consists of two residues: N-acetylglucosamine (2-acetamido-2-deoxy-β-D-glucopyranose) and glucosamine (2-amino-2-deoxy-β-D-glucopyranose) (***Scheme 1***) [1, 2]. This polymer due to its interesting properties, such as biocompatibility, biodegradability, non-toxicity, high hydrophilicity, excellent chemical-resistant properties and good film-forming character has found different applications, especially in medicine and pharmacy and in various industrial areas [1]. Chitosan is also one of the most promising polymers for the preparation of membranes for various uses [3]. However, chitosan membranes highly swell in water (especially in acidic solutions) and have a low mechanical stability in the swollen state. Thus their application is limited. In order to overcome these problems chitosan is modified by different methods, including blending, multilayer casting, addition of inorganic reinforcements and crosslinking.



Scheme 1. Chemical structure of chitosan (DDA - degree of deacetylation)

Application of hydrogel membranes, including chitosan membranes, generally depends on their mechanical properties, but in many areas of their uses the thermal characteristics must be also considered. Recently, we have reported the synthesis and thermal characteristics of modified (Ch) membranes obtained by crosslinking of chitosan with low- and high-molecular ionic substances: pentasodium tripolyphosphate and sodium alginate [4]. In the present study chitosan membranes were prepared using a crosslinking method based on covalent crosslinking of chitosan (Ch) with glutaraldehyde (GA) and subsequent ionic crosslinking with such ionic crosslinkers as sodium citrate (CIT), sulfuric acid (SA), sulfosuccinic acid (SSA) and pentasodium tripolyphosphate (TPP). The thermal degradation of single and double crosslinked chitosan membranes (Ch/GA, Ch/GA/SA, Ch/GA/SSA, Ch/GA/CIT, Ch/GA/TPP) was studied over the temperature range 25 - 500 ºC in nitrogen atmosphere by thermogravimetry (TGA) and differential scanning calorimetry (DSC).

2. Materials and methods

2.1. Materials

Commercially available chitosan from crab shells in the form of powder was purchased from Aldrich (Germany). Crosslinking agents (GA, SA, SSA, CIT, TPP) of analytical grade were purchased from POCh (Poland) or Aldrich (Germany). Acetic acid, sodium hydroxide and hydrochloric acid were analytical grade and were purchased from POCh (Po-

land). Potassium bromide (KBr) for spectroscopy was purchased from Merck (Germany). The average molecular weight of chitosan, determined by viscometry **[5]**, was equal to 720 ± 16 kDa. The average deacetylation degree of chitosan (DDA), determined by potentiometric titration method [5], was equal to 77.0 ± 2.3%.

2.2. Membrane preparation

Pure chitosan (Ch) membrane was prepared by casting and solvent evaporation technique, as described previously [5]. Two-component chitosan/glutaraldehyde (Ch/GA) membrane was prepared in a similar way. First, 1% (w/v) chitosan solution in 2% (w/v) acetic acid and 0.25% (w/v) glutaraldehyde solution in water were mixed and stirred at room temperature for at least 6 hrs to obtain a homogeneous solution. Then, the obtained homogeneous mixture was cast as film on a clean glass plate and evaporated to dryness at 37 °C. The content of glutaraldehyde in casting solution was 2.5 wt.%. Finally, the prepared Ch and Ch/GA membranes were washed repeatedly with deionized water, immersed in 2 M sodium hydroxide solution for 5 min, again washed with deionized water and dried at air. Three-component chitosan membranes: Ch/GA/SA, Ch/GA/SSA, Ch/GA/CIT and Ch/GA/TPP were prepared by immersing Ch/GA membrane in appropriate crosslinking agent solution (0.5 M SA, 0.5% (w/v) SSA, 5.0% (w/v) CIT (T = 4 °C, pH = 5.0) or 1.3% (w/v) TPP (T = 4 °C, pH = 5.5)) for 1 hr. Then membranes were thoroughly washed with deionized water, dried at air and under vacuum at 60 °C for 24 hrs.

2.3. Thermal analysis

Thermogravimetric analysis (TG) was performed using SDT 2960 Simultaneous TGA-DTA Thermal Analyzer System (TA Instruments, USA). All measurements were performed with polymer samples (about 5 mg) 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. The solid residues after thermal degradation were cooled to room temperature and left to spectral analysis. For each degradation step the temperature at which the degradation starts (T_{onset}), temperature at maximum process rate (T_{max}), temperature at which the degradation is finished (T_{endset}) and percentage weight loss (W%) were calculated from DTG curves.

Differential scanning calorimetry (DSC) analysis was performed with Polymer Laboratories Ltd. differential scanning calorimeter (Epsom, United Kingdom), equipped with a liquid nitrogen cooling accessory. Samples (about 15 mg) 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 aluminium cup was used as a reference.

2.4. FTIR spectroscopy

FTIR spectra of unmodified and modified chitosan samples (before and after thermal degradation) in KBr disc form were recorded on Perkin-Elmer 2000 FTIR spectrometer from 4000 to 400 cm^{-1} with a resolution 4 cm^{-1} and at 100 scans. Polymer membranes before milling with anhydrous KBr were thoroughly powdered and powders were dried under vacuum at 60 ºC for 24 hrs.

3. Results and discussion

3.1. FTIR analysis of uncrosslinked and crosslinked chitosan membranes

FTIR spectra of membranes are presented in ***Figure 1.A***. Both single as well as double crosslinked membranes show FTIR spectra different from that of pure chitosan polymer membrane. There can be observed some changes mainly in the 3500-3150 cm^{-1} (not presented in this figure) and 1800-1600 cm^{-1} regions. After chitosan crosslinking with GA the peak at 1656 cm^{-1} (C=O stretching in amide group, amide I vibration) shifts to 1648 cm^{-1} and instead of the band at 1598 cm^{-1} (N-H bending in nonacetylated 2-aminoglucose primary amine) a broad band with two maxima at 1595 cm^{-1} and 1566 cm^{-1} appears [6 - 8]. The band at 1648 cm^{-1} is most probably composed of amide I band of chitosan and the C=N stretching band of Schiff's base [8]. The broad complex band with two submaxima at 1595 and 1566 cm^{-1} seems to be composed of two peaks, observed in FTIR spectrum of chitosan at 1598 cm^{-1} and 1560 cm^{-1} (N-H bending vibrations), respectively. The lack of the band at ~1715 cm^{-1} indicates that there are not free aldehyde groups in Ch/GA membrane.

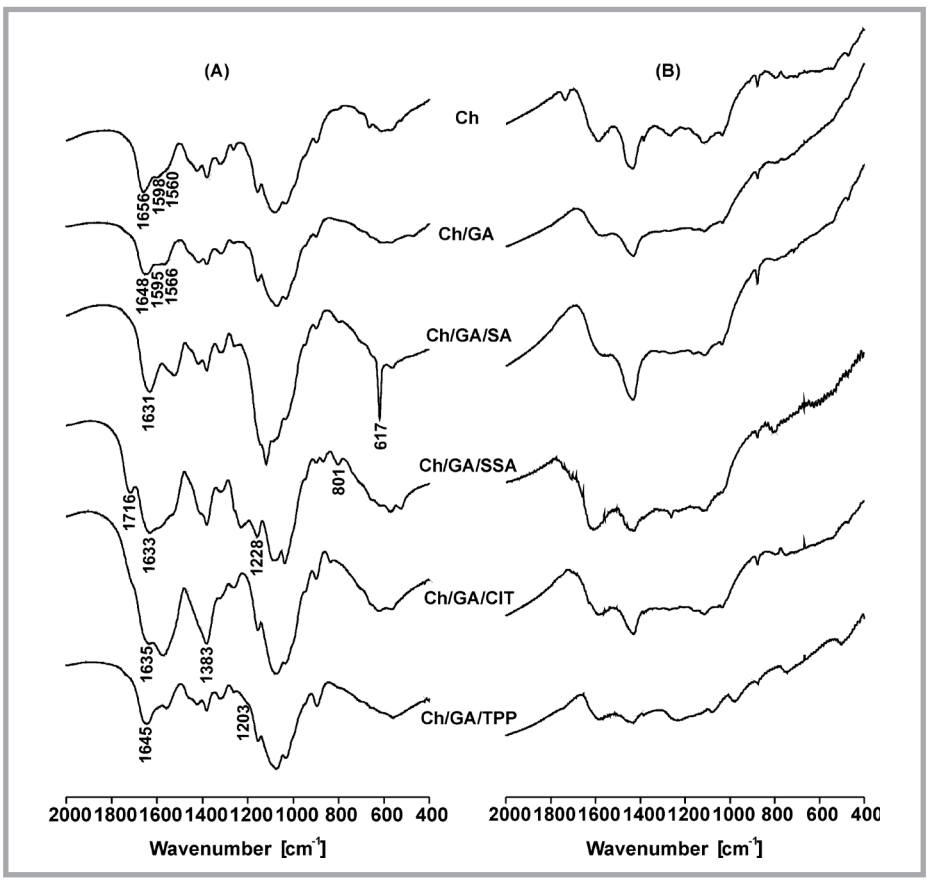
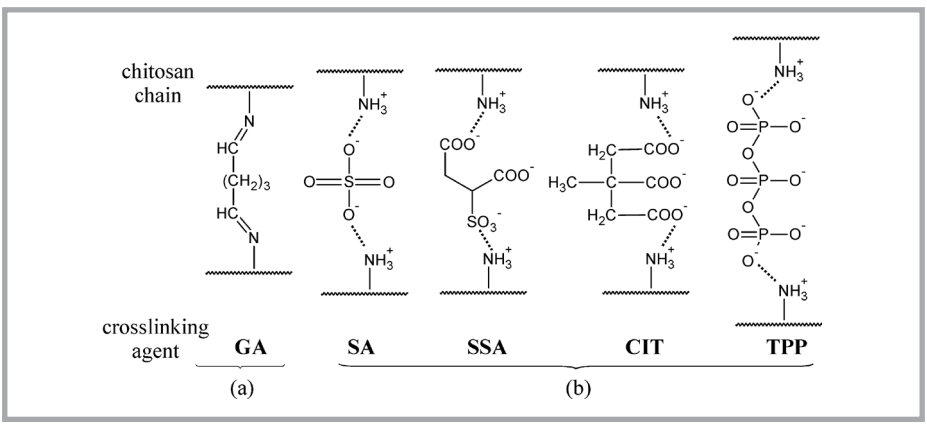


Figure 1. *FTIR spectra of chitosan membranes before (A) and after thermal degradation (B).*

After crosslinking of Ch/GA membrane with ionic crosslinking agent the peak at 1648 cm^{-1} shifts to lower frequency (i.e. to 1631 cm^{-1} for Ch/GA/SA, 1633 cm^{-1} for Ch/GA/SSA, 1635 cm^{-1} for Ch/GA/CIT and 1645 cm^{-1} for Ch/GA/TPP). In the spectra of double crosslinked chitosan membranes the band at about 1640 cm^{-1} derives mainly from the antisymmetric N–H deformation vibrations in protonated amines, but the initial amide-I, amide-II and imine bands are possibly overlapped by these vibrations. Absorption band at about 1635 cm^{-1} due to $–NH_3^+$ ion vibrations was observed earlier by us in the FTIR spectra of two-component chitosan/sodium alginate and chitosan/pentasodium tripolyphosphate membranes [4, 5]. Protonated amines show an antisymmetric and symmetric N-H deformation vibrations in the 1625-1560 cm^{-1} and 1550-1505 cm^{-1} range, respectively [8], but in our case the second band is obscured by other strong absorption bands appearing in the same region. In the FTIR spectra of double crosslinked membranes they can be seen some additional absorption bands corresponding to crosslinking agents: at 617 cm^{-1} for Ch/GA/SA, at 1228 cm^{-1} and 801 cm^{-1} for Ch/GA/SSA, at 1383 cm^{-1} for Ch/GA/CIT and at 1203 cm^{-1} for Ch/GA/TPP.

The spectral changes characterized above indicate the formation of covalent or/and ionic crosslinks between chitosan and GA and/or SA, SSA, CIT, TPP, as schematically presented in ***Scheme 2***.

Figure 1.B shows FTIR spectra of the thermal degradation residues remaining at 500 ºC. There were observed some spectral changes indicating the degradation of the polymers as a consequence of their heating. The decrease of the intensities of the absorption bands characteristic for chitosan, namely at 3430 cm^{-1} (O-H stretching vibration in hydroxyl group, not shown in ***Figure 1***) and 2910 cm^{-1} (CH_2 stretching vibration in pyranose ring, not shown in ***Figure 1***), at about 1650 cm^{-1} (C=O stretching vibration in amide group), 1380 cm^{-1} (C-H stretching vibration in amide group), 1153 cm^{-1} (antisymmetric -C-O-C- stretching vibration in glycosidic linkage), 1083 cm^{-1} and 1031 cm^{-1} (skeletal vibrations involving C-O stretching) can be attributed to collapse of the chitosan structure comprising



Scheme 2. *Structure of (a) chemical crosslinks between Ch and GA and (b) ionic crosslinks between NH_3^+ groups of Ch and SA, SSA, CIT, TPP ions.*

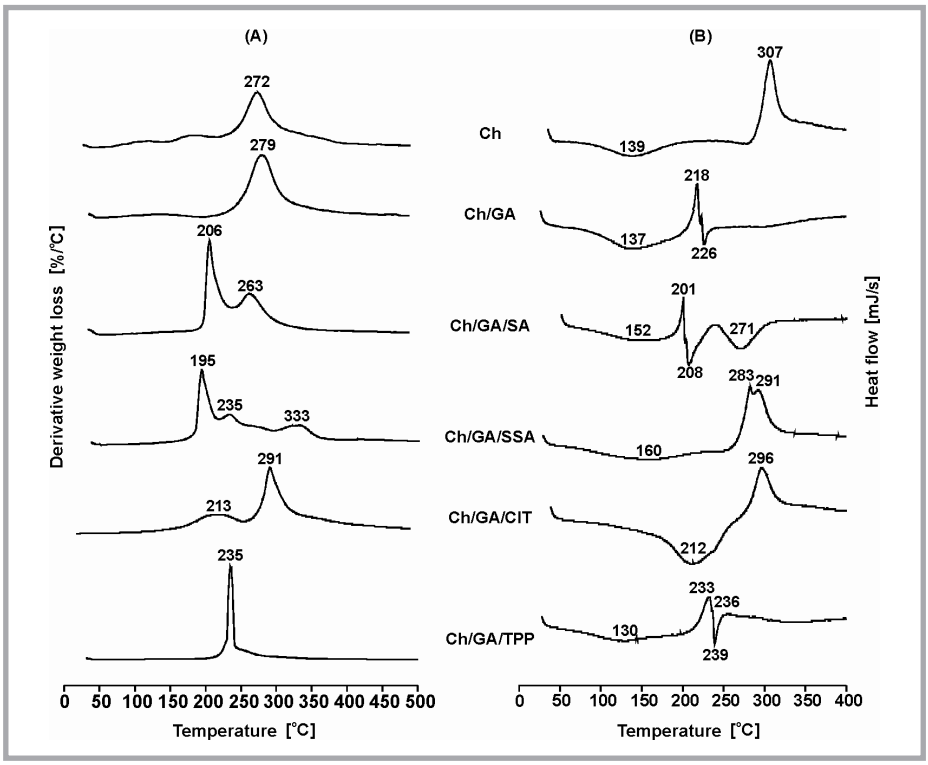


Figure 2. *DTG (A) and DSC curves (B) of various chitosan membranes.*

dehydration, deacetylation and depolymerization processes [9 - 11]. It is difficult to conclude on the amine, imine, protonated amine and amide bands behaviour in the 1700 – 1500 cm^{-1} range, because after degradation new bands appear in the same absorption region, that are characteristic for unsaturated structures formed during the thermal degradation of chitosan [8, 9]. FTIR spectra of crosslinked membranes after their thermal degradation seem to be more complex then FTIR spectrum of degraded chitosan, suggesting some differences both in the chemical composition of residual polymer samples as well as in the mechanism of thermal degradation of uncrosslinked and crosslinked polymers. Results of TG/DTG/DSC analysis presented below point to the same conclusion.

All membrane samples after thermal degradation were brownish and insoluble in acetic acid solution. It resulted from the chemical reactions involved in thermal degradation being characterized above.

3.2.Thermal analysis of uncrosslinked and crosslinked chitosan membranes

Figure 2.A shows the results of thermogravimetric analysis of uncrosslinked and crosslinked chitosan membranes.

TG curves (not shown in ***Figure 2.A***) and DTG curves indicate, that the first thermal event occurs at temperature range 25 - 150 °C and is accompanied by the weight loss ranging from 1% to 4 %. This stage can be assigned to the loss of the residual water present in the samples. The following peaks on the DTG curves correspond to thermal decomposition of pure chitosan or modified chitosan, vaporization and elimination of volatile products. Thermal degradation of chitosan structure is a complex reaction. Different decomposition products were observed by thermogravimetric analysis coupled with FTIR spectroscopy and mass spectrometry [9 - 15]. According to literature data pyrolysis of chitosan starts by a random spliting of the glycosidic bonds, followed by a further decomposition to acetic, butyric and lower fatty acids [7, 9 - 13]. It can be supposed that in the observed steps of thermal degradation of crosslinked membranes small molecular degradation products both of chitosan as well crosslinking agents are liberated.

Considering the temperature at which thermal degradation starts as a criterion of the thermal stability of membrane, the thermal stability decreases according to the series: Ch > Ch/GA > Ch/GA/TPP > Ch/GA/SA > Ch/GA/SSA > Ch/GA/CIT. Thus, the type of crosslinking ionic agent determines the thermal stability of chitosan membrane.

Figure 2.B shows DSC thermograms of uncrosslinked and crosslinked chitosan membranes. There can be observed some changes in the number of exothermic/endothermic peaks and their positions. The thermograms of both uncrosslinked as well crosslinked membranes show a broad endothermic peak around 100 °C that is related to the evaporation of residual water and/or acetic acid from membrane. Pure chitosan membrane shows also one exothermic peak at 307 °C that can be attributed to the decomposition of chitosan. In the case of Ch/GA the exothermic decomposition peak shifts to 218 °C. It indicates that the addition of glutaraldehyde reduces the thermal stability of chitosan membrane. This result is in accordance with finding of Yang et al. [15]. As ***Figure 2.B*** shows, DSC thermograms of double crosslinked chitosan membranes in the temperature range from 180 to 500 °C are complex, but all DSC peaks appear at temperature lower than exothermic transition of chitosan.

4. Conclusions

TGA and DSC experiments showed that thermal degradation of uncrosslinked chitosan membrane in nitrogen atmosphere was a two-step reaction, but thermal degradation of crosslinked membranes proceeded in several stages. This result suggests some differences in the mechanism of thermal degradation of uncrosslinked and crosslinked chitosan membranes. FTIR spectra of the thermal degradation residues confirmed some differences in the mechanism of degradation of pure chitosan membrane and covalently and ionically crosslinked chitosan membranes. Considering the temperature at which thermal degradation starts as a criterion of the thermal stability, it can be concluded that the thermal stability decreases according to the series: Ch > Ch/GA > Ch/GA/TPP > Ch/GA/SA > Ch/GA/SSA > Ch/GA/CIT. Thus crosslinking lowers the thermal stability of chitosan membrane.

5. References

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