Surface Characteristics of Ionically Crosslinked Chitosan Membranes

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ABSTRACT: In this study, homogenous dense chitosan membranes were prepared by solution-casting procedure. Then the membranes were ionically crosslinked by sulfuric acid. The surfaces of chitosan membranes before and after crosslinking were characterized by using FTIR-ATR, X-ray photoelectron spectroscopy (XPS), and atomic-force microscopy (AFM) techniques. The XPS data suggest that the surface composition of crosslinked membrane does not change significantly with respect to uncrosslinked membrane and the most important evidence is a certain amount of sulfur, coming from the crosslinker. The result from FTIR-ATR data shows the effectiveness of the crosslinking procedure by the shift in amide I and amide II bands. The investigation of membrane surfaces by AFM indicates that the crosslinking procedure modifies the surface morphology of chitosan. After crosslinking, the surface topography becomes more homogenous and relatively flat. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3884–3888, 2007

Key words: chitosan membrane; ionic crosslinking; FTIR-ATR; XPS; AFM

INTRODUCTION

Chitosan is a copolymer of β-(1→4)-linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose.[1] This polysaccharide polymer has reactive hydroxyl and amino groups for various chemical modifications.[2] In recent years, chitosan is receiving attention as a pervaporation membrane material as the active skin layer due to its high affinity to water, good membrane forming properties, easy modification, and good chemical stability.[3–5] The pervaporation performance for alcohol dehydration[3–6] and dimethyl carbonate (DMC) separation[7] have been investigated using chitosan and modified chitosan membranes. In those applications, membrane modifications have been reported including crosslinking,[6–8] blending,[9] multilayer casting,[10] and chemical modification.[11,12] Among these, crosslinking is one of the most effective approach for improving membrane stability and increasing separation characteristics by controlling the permselectivity.[3,7] Various crosslinkers[3,5–7,13] are used to interconnect the polymer chains leading to the formation of a rigid and compact structure and strong mechanical properties. Currently, chitosan membranes have been prepared by reversible ionic crosslinking, which is a simple and mild procedure.[2,6–8] In this case, the crosslinking procedure can be applied by simply dipping pieces of membranes into the crosslinker solution.[14] A charged ionic crosslinker is needed to prepare the chitosan network.[2] The multivalent counter-ions of the ionic crosslinker form bridges between polymeric chains of chitosan. As chitosan is a polycation, anions or anionic molecules are generally required to form ionic interactions between the negative charges of the crosslinker and positively charged groups of chitosan.[2] The chitosan is ionically crosslinked on the top of the ultrafiltration membranes to form an active skin layer for pervaporation process.[3] Lee et al.[6] prepared the composite membranes by surface crosslinking of chitosan with sulfate anions coming from sulfuric acid. They showed that ionic crosslinking leads to membranes with higher separation factor and less permeation flux for water–alcohol mixtures than that of uncrosslinked chitosan membrane. Won et al.[7] also used sulfuric acid for the ionic crosslinking of chitosan membranes for separation of DMC/methanol/water mixtures by pervaporation. For DMC/water mixtures they observed that the crosslinking restrains membrane swelling thus reducing the diffusivity of the permeant. The permeability decreases in crosslinked mem-

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branes which are less hydrophilic. All those studies have revealed that the presence of crosslinked chitosan thin layers is very important to achieve the desired pervaporation characteristics. However, these thin films have not been characterized yet.

In this study, we prepared chitosan membranes crosslinked with sulfuric acid to perform the surface characterization studies. The obtained data were evaluated to discuss the effect of ionic crosslinking on the membrane surfaces. FTIR-ATR analysis was used to examine the structural changes after ionic crosslinking. X-ray photoelectron spectroscopy (XPS) analysis was performed to determine the surface atomic composition on uncrosslinked and crosslinked membranes. Atomic-force microscopy (AFM) measurements were used to evaluate the effect of crosslinking procedure on the surface roughness and the homogeneity of the chitosan membranes. The results obtained from these analyses provide detailed information on the structural characteristics of ionically crosslinked chitosan thin layers.

MATERIALS AND METHODS

Preparation of crosslinked chitosan membranes

Chitosan membranes were prepared by solution casting method, followed by crosslinking with sulfuric acid. Chitosan flakes (1.0 g, >85% deacetylation, Cat. No: C- 3646, Sigma, Germany) were first dissolved in acetic acid solution (1% (v/v), 100 mL, Merck, Germany), poured into glass Petri dishes and air dried. After the membranes were detached from the glass surface without NaOH treatment, they were submerged into a crosslinking solution comprising 0.02 *M* sulfuric acid (Merck, Germany) in 50% (v/v) aqueous acetone solution for 1 h at room temperature. The crosslinked chitosan membranes were washed with deionized water and air dried.

Surface characterization studies

FTIR-ATR spectroscopy

Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra for the chitosan (without crosslink) and crosslinked chitosan membranes were obtained by using a Perkin-Elmer Spectrum One IR spectrometer (USA). The spectra of samples were taken at 400–4000 cm^{-1} wavelength and analyzed with the standard software package, Perkin-Elmer, Spectrum One.

X-ray photoelectron spectroscopy

XPS analysis was performed by using a PHI 5600 Multi Technique Spectrometer equipped with dual Al/Mg anode, hemispherical analyzer, and electrostatic lens system (Omni Focus III). The electron take-off angle was typically 45°, corresponding to a sampling depth of about 6 nm. The analyzer was operated in fixed analyzer transmission (FAT) mode by using the Al $K\alpha_{1,2}$ radiation with pass energies of 187.5 eV for survey scans and 11.75 eV for the detailed scans. The pressure in the main vacuum chamber during the analysis was kept below 3×10^{-8} mbar. The binding energy (BE) of 285.0 eV of the main C1s component (assigned to C—C and C—H bondings) was used as a reference to calibrate the energy position of the various peaks.[15]

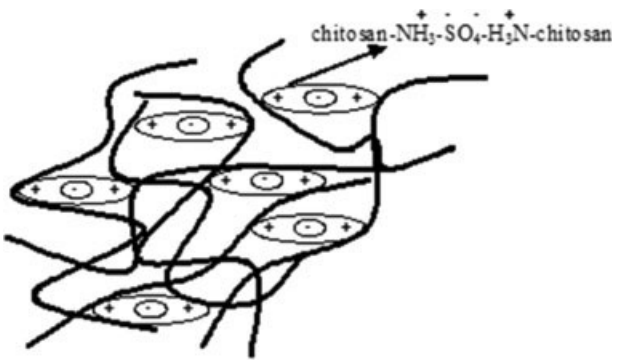

Figure 1 Structure of chitosan hydrogels prepared by ionic crosslinking with sulfuric acid. ____: chitosan chain; +, positive charge of chitosan (NH_3^+); −, negative charge of sulfuric acid (SO_4^{-2}); ⊕⊖⊕, ionic interaction.

Atomic-force microscope

The surface roughness and morphology at micro- and nanometer scale were measured with a Multimode/Nanoscope IIIA Atomic Force Microscope (AFM) (VEECO, USA) in tapping mode in air with a standard silicon tip. The relative room humidity was 30% and the room temperature was 23°C. Data were acquired on square frames having edges of 5 μm, 1 μm, and 500 nm. Images were recorded using both height and phase-shift channels with 512 × 512 measurement points (pixels). Measurements were made twice or thrice on different zones of each sample. Surface roughness values were determined in three random areas per sample, scanning across areas 1 × 1 μm^2. Roughness parameters R_a; average roughness that is the average deviation from the mean surface plane and R_{ms}; root mean square that is the standard deviation of the height values on the surface were calculated using Nanoscope III software.

RESULTS AND DISCUSSION

Crosslinked chitosan membranes

Homogeneous and dense chitosan membranes were prepared by solvent casting method. Sulfuric acid was chosen as the crosslinking agent as it is known

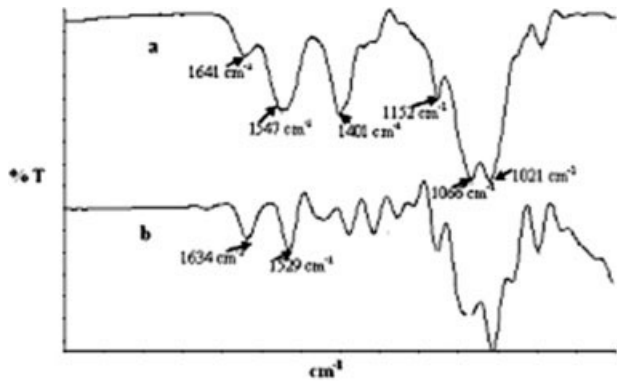

Figure 2 FTIR-ATR spectra for (a) uncrosslinked and (b) crosslinked chitosan membranes.

as one of the most effective crosslinking agents for chitosan membranes used in pervaporation studies.[7,8] Chitosan was protonated to form a solution of ammonium salt when it was dissolved in dilute acetic acid solution (p*Ka* for chitosan is 6.3–7.0). The protonated amine groups on the different chitosan chains and negatively charged oxygen atoms on the sulfate ions have Coulombic interactions. As a result, sulfate ions crosslink the chitosan main chains ionically as shown in Figure 1.

The crosslinking time for the chitosan membranes used in this study was determined as 1 h. Won et al.[7] dipped the chitosan membranes for 5 min for the crosslinking procedure. Lee et al.[6] examined the effect of crosslinking time on ionically surface crosslinked chitosan membranes and they have concluded that by increasing the crosslinking time, a membrane shows an optimum separation factor with low permeation flux. In their FTIR-ATR results it is shown that the crosslinking takes place in 1 h time. Nam and Lee determined the optimum crosslinking time

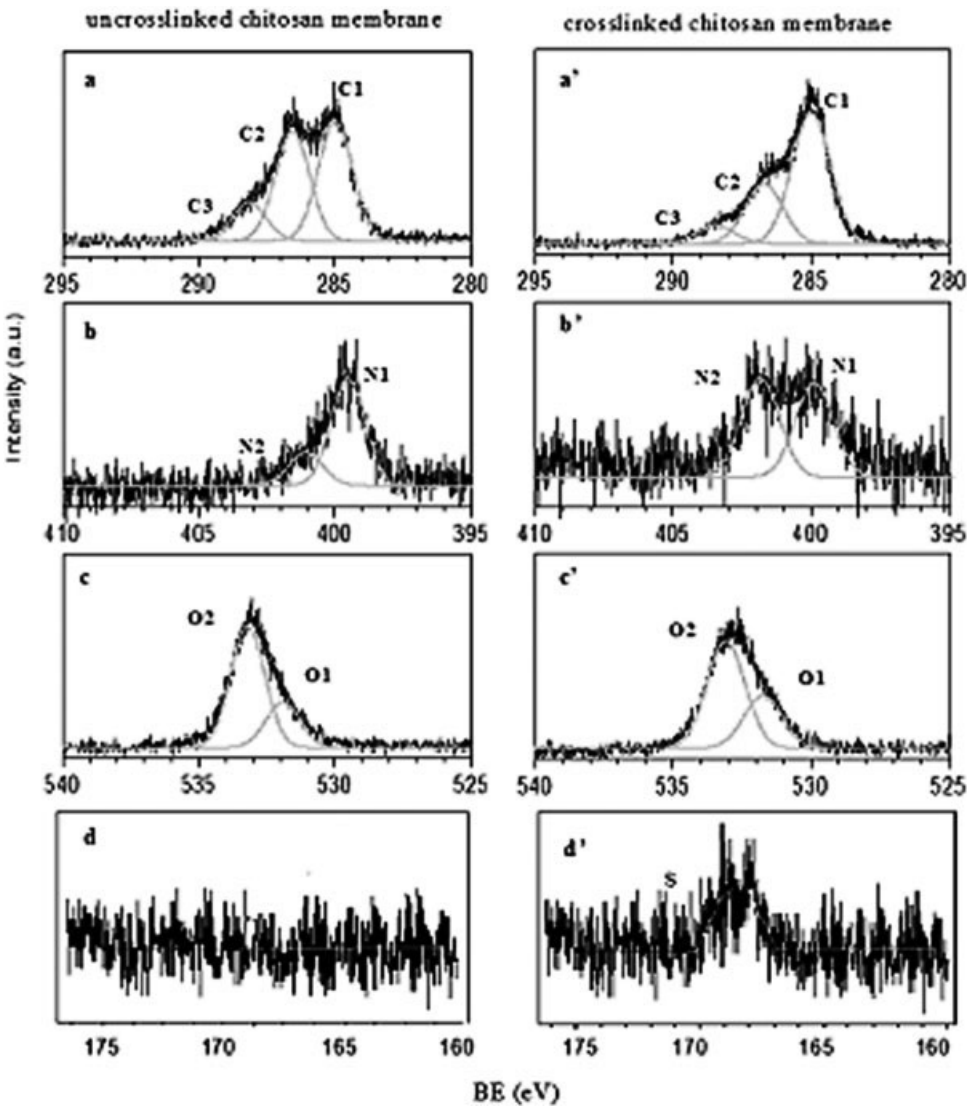

Figure 3 High resolution XPS spectra for uncrosslinked and crosslinked chitosan membranes; (a–a′) C1s; (b–b′) N1s; (c–c′) O1s peaks and (d–d′) S2p peaks.

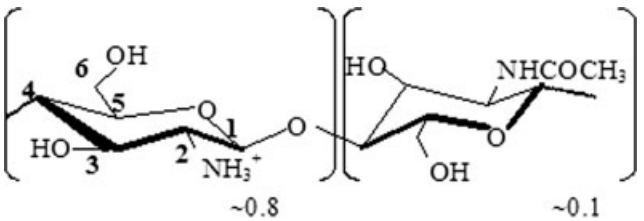

Figure 4 Schematic presentation of the chemical structure of partially deacetylated (>85% deacetylation) chitosan.

as 80 min for the separation of ethylene glycol–water mixture. It can be suggested that the crosslinking time may vary according to the application and separation procedure and the dimensions of the membrane also. In this study it was only aimed to gain insight in the surface characterization of ionically crosslinked chitosan membranes. So the crosslinking time was decided to be taken as 1 h regardless the application. The effect of the crosslinking process has been studied in detail by means of FTIR-ATR spectroscopy for relatively thick layers (1–2 μm) and XPS for the shallowest layers at the membrane surface.

Surface characterization of the membranes

FTIR-ATR results

Figure 2(a,b) show the FTIR-ATR spectra for the uncrosslinked and crosslinked chitosan membranes. The spectral region between 800 and 2400 cm^{-1} is reported for the uncrosslinked and crosslinked samples, respectively. However, the region of 1200–1800 cm^{-1} is the information rich-region. Indeed, the broad intense band at 1000–1200 cm^{-1} was attributed to cellulose-ether type absorption, 6-membered ring, and bridge C—O—C vibrations. Faint absorption around 1550 cm^{-1} due to NH_2 deformations (amide I) and absorption around 1640 cm^{-1} for C=O bond (amide II) shift to 1528 cm^{-1} for amide I and 1630 cm^{-1} for amide II band after the crosslinking process [Fig. 2(b)], in agreement with previous reports on crosslinking effects in chitosan membranes.[6]

XPS results

The structure of partially deacetylated chitosan is quite complex since the actual structural unit arrangement of chitosan with long repeating units and the nature of random copolymer units are not fully described.[16,17] Figure 3 reports the XPS spectra for C 1s, N 1s, O 1s, and S 2p photoelectron regions for the uncrosslinked chitosan membranes.

According to the peak fitting procedure, carbon 1s peak could be analyzed in terms of three components: the C1 component, centred at 285.0 ± 0.2 eV of BE is assigned to C—C and C—H moieties; the C2 component, centred at 286.6 ± 0.2 eV of BE, is due to C—O—C, C—OH linkages, i.e., C atoms in position 3, 4, 5, and 6 in Figure 4, and C—N bonds (C atom in position 2), and the C3 component, centred at 288.3 ± 0.2 eV, is assigned both to C=O groups, due to residual chitin-like rings, and [—O—C—O—] moieties of the rings, i.e., C atoms in position 1 in Figure 4.[18] After crosslinking, there is a relative decrease of C2 components at ~ 286.7 eV and C3 components at ~ 288 eV with respect to the C1 component at ~ 285 eV. The results from C1s spectrum suggest that the ionic crossslinking affects C atoms in position 2 (Fig. 4) and the interactions occur through the protonated amine groups ($C—NH_3^+$) as described in Figure 1.

The nitrogen 1s peak for uncrosslinked membranes exhibits two components; component N1, at 399.6 ± 0.2 eV, is mostly due to neutral amine groups from chitosan units with an additional small contribution, not distinguishable in the spectrum, from amide groups in residual chitin-like rings. The component N2, at 401.1 ± 0.2 eV can be assigned to protonated amine groups.[19] After the crosslinking step, the component N1 shifts to 399.9 ± 0.2 eV and the component N2 shifts to 401.8 ± 0.2 eV. Additionally, the crosslinking process is known to involve a massive formation of quaternary ammonium groups in the strongly acidic environment here employed. Accordingly, about 50% of the N 1s peak is due to the ammonium component, and the remaining 50% to unaffected amine groups.

Finally, the oxygen 1s peak is formed by two components whose BE remain practically unchanged before and after crosslinking. In particular, O1 is found at 531.8 ± 0.2 eV, assigned to C=O moieties, and O2 is found at 533.2 ± 0.2 eV of BE, including contribution of C—O—C (at 532.9 eV) and O—H groups (at 533.5 eV).[18]

Table I reports the surface atomic composition as obtained from XPS analysis for the uncrosslinked

TABLE I
Average Surface Atomic Composition[a] and Corresponding Atomic Ratios for Chitosan Membranes

Membranes	O1s (at %)	C1s (at %)	N1s (at %)	S2p (at %)	O/N	C/N
Uncrosslinked chitosan	27.2	67.0	5.8	–	4.7	11.6
Crosslinked chitosan	29.6	63.0	5.4	2.0	5.5	11.7

[a] Typical error = ±1%.

and crosslinked chitosan membranes. The surface composition of crosslinked chitosan does not change significantly with respect to uncrosslinked chitosan membranes and the certain amount of sulfur coming from the crosslinker is an evidence for the crosslinking. The ensemble of these observations allows assessing the occurrence of the crosslinking, also if this seems related to a certain degree of modification of the structure of the rings.

AFM analysis

Figure 5 shows the AFM height and phase images of uncrosslinked and crosslinked chitosan membranes. Table II reports the quantitative data on roughness in terms of root mean squared (R_{ms}) and averaged (R_a) roughness.

Figure 5(a,b) show that the crosslinking procedure strongly modifies the surface morphology of chitosan. In fact, the uncrosslinked chitosan exhibits a quite dense coverage by features of about 24 ± 2 nm of height and typical diameters of 20–30 nm. After crosslinking, the surface topography becomes more homogeneous [see phase contrast image in Fig. 5(b)] and relatively flat (Table II), with smooth features of regular average diameter, about 15–20 nm. This effect could be explained in terms of the formation of bundles of chitosan fibers, due to the crosslinking process, while the highly heterogeneous topography before crosslinking could be due to uneven termination of free fibers. The change of nanotopograhy could affect the surface wettability and surface reactions e.g. capillary reaction, etc.

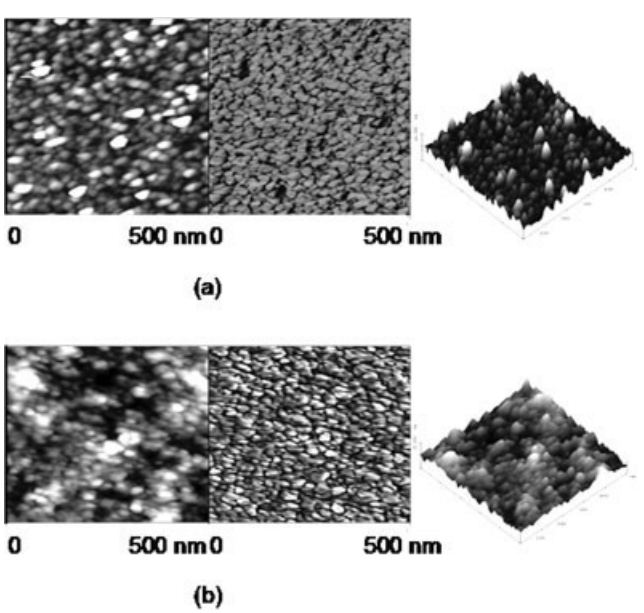

Figure 5 AFM images of chitosan membranes; height and phase images on the left-hand side, 3D image on the right-hand side, scale: 500 nm (a) uncrosslinked and (b) crosslinked chitosan membranes.

TABLE II
R_{ms} and R_a Values on 1 × 1 μm² Scanning Area for Various Chitosan Membranes

Membranes	R_{ms} (nm)	R_a (nm)
Uncrosslinked chitosan	5.11 ± 1.10	3.41 ± 0.69
Crosslinked chitosan	2.16 ± 0.16	1.71 ± 0.13

CONCLUSIONS

The chitosan membranes prepared by using solvent casting method were ionically crosslinked by means of Coulombic interactions between sulfate ions and NH_3^+ cations of chitosan chains. The objective of this study was to investigate the effects of this ionic crosslinking procedure on the surface properties and composition of chitosan membranes. The effectiveness of crosslinking method was evaluated by using FTIR-ATR and XPS techniques. The results obtained from these studies showed that the surface composition was not significantly affected by the procedure except the contribution of sulfur after crosslinking, coming from sulfuric acid. The surface topography however, became more homogenous after the crosslinking of the membranes.

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