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Comparing homogeneous and heterogeneous routes for ionic crosslinking of chitosan membranes

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ABSTRACT

H_2SO_4 — ionically crosslinked chitosan membranes were prepared via homogeneous and heterogeneous routes. The control variable in homogeneous crosslinking was the SO_4^{2-}/NH_3^+ molar ratio (1:4 e 1:6) while for heterogeneous crosslinking it was the immersion time of pure chitosan membrane in H_2SO_4 0.5 M aqueous solution (5 and 30 min). FTIR-ATR suggested lower crosslinking degree for homogeneous crosslinking, corroborated by XRD analysis that indicated the maintenance of the crystalline structure for such membranes. Thermal analysis showed very similar degradation processes for homogeneous and pure chitosan but quite different for heterogeneous: not only in terms of degradation temperature but also in amount and signal of heat involved. Swelling index results were very dependent on pH of medium. Particularly in acidic medium, homogeneous crosslinked membranes, presented a higher swelling capacity than the heterogeneous ones. Mechanical properties revealed that both methodologies render membranes with lower tensile strength and elongation but with Young modulus about four times higher, due to the interactions of SO_4^{2-} groups of H_2SO_4 with NH_3^+ of chitosan. Finally, AFM images showed dramatic changes on surface topology, with reduction of roughness for heterogeneous and an increase for the homogeneous one.

1. Introduction

Chitosan is a polyaminosaccharide, produced by partial N-deacetylation of chitin. It is a biodegradable, non-toxic, semi-synthetic polymer with excellent biocompatibility [1,2]. It can be defined as a copolymer of 2-amino-2-deoxy-D-glucopyranose and 2-acetoamido-2-deoxy-D-glucopyranose whose units are linked by β(1 → 4) bonds [3,4]. Chitosan exhibits unique physicochemical properties and it is highly suitable to innumerable applications in a wide range of fields such as food and nutrition, biotechnology, material science, drugs and pharmaceuticals, agriculture, environmental protection, and gene therapy, among others [5]. As a copolymer soluble in acidic medium, chitosan can be obtained under the form of fibers, films, membranes, powder, particles, beads and solution, which enhances its usefulness.

Chitosan has free amino and hydroxyl groups on its backbone, which can undergo chemical modifications in order to turn chitosan more bacteriostatic, and to improve its chemical and mechanical resistance [6]. Among this, crosslinking is one of the most effective approaches for improving membrane stability [7]. There are two main ways to crosslink these membranes: by covalent bonds, using agents such as glutaraldehyde or ethylene glycol, or through ionic bonds, using, e.g., sulfuric acid or tripolyphosphate [8]. The use of sulfuric acid as crosslinking agent has been proved to increase the separation factor in pervaporation experiments of ethanol/water and methanol/methyl t-butyl ether [9–11]. Most of the work done on ionic crosslinking of chitosan membranes using sulfuric acid used the heterogeneous route, where the membrane is immersed in a sulfuric acid solution for a period of time and then removed and dried [1,12,13]. The homogeneous route is very little described in literature in comparison with the heterogeneous one. The main difficulty is to achieve a low degree of crosslinking without induce the solution gelification (which could hinder the casting process). As far as we know, most of the homogeneous route described in literature use glutaraldehyde as crosslinking agent [14] but no studies were found using sulfuric acid.

In this work, we investigated the influence of the crosslinking routes (homogeneous and heterogeneous) on the final properties of sulfuric acid-crosslinked chitosan membranes. The purpose was to obtain membranes with low degrees of crosslinking, in order to confer chemical resistance in acid medium but still maintain a relatively high number of NH_2 groups available for interactions related to sorption applications.

2. Experimental

2.1. Materials

Chitosan used in this work was purchased from Polymar LTD (Brazil). It had a deacetylation degree of 88%, determined by CHN elemental analysis and conductometric titration as described elsewhere [15], intrinsic viscosity [η] = 0.360 g L^{-1}, and average viscometric

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molar mass, $M_v = 1.6 \times 10^5$ g·mol^{-1} (determined using Mark–Houwink–Sakurada equation) [16,17]. Acetic acid (P. A., Cromato Produtos Químicos LTD, Brazil), Sodium hydroxide (P. A. Vetec LTD, Brazil) and sulfuric acid (P. A. Vetec LTD, Brazil) were all analytical grade reagents and used as received.

2.2. General procedure for membrane preparation

2.2.1. Homogeneous route

Chitosan was dissolved in a 2.0% v/v aqueous acetic acid solution for 24 h under mechanical stirring in order to form a 2.0% w/v solution. The resulting solution was filtered twice, first using a nylon filter and then using a Millipore® Millex filter, with 0.40 μm of pore diameter. A 0.5 M sulfuric acid solution was added to 25 mL of chitosan solution so that SO_4^{2-}/NH_3^+ molar ratios of 1:6 and 1:4 were obtained. The mixtures were kept under mechanical stirring for 1 h. Afterwards the solutions were cast onto a glass plate and left at room temperature for 2 days for solvent evaporation. The membranes were then neutralized trough immersion in a 5.0% (w/v) sodium hydroxide solution for 2 h. Following, they were repeatedly washed with distilled water and fixed on a support to dry at room temperature. These membranes were denominated CS16 and CS14.

2.2.2. Heterogeneous route

Heterogeneous crosslinked membranes were prepared using pure chitosan membranes obtained as described above, without the addition of sulfuric acid solution. After the neutralization and washing processes, the membranes were immersed in sulfuric acid solution 0.5 M for 5 and 30 min. Then the membranes were exhaustively washed with distilled water and fixed on a support to dry at room temperature. These membranes were denominated CS5 and CS30.

2.3. Physico-chemical characterization

Infrared spectra were obtained using a Spectrum65 FTIR coupled to a universal ATR sampling accessory from Perkin Elmer, operating in the range of 400–4000 cm^{-1}, 32 scans and resolution of 4 cm^{-1}.

Morphologies of chitosan membranes were studied with an X-ray diffractometer Shimadzu model XRD-7000, radiation of CuK α (λ = 1.5406 Å), angle variation 2θ from 5° to 40°, with scanning speed of 2°min^{-1} and step of 0.02°.

The surface roughness and topology at nanometer scale of the membranes were measured, at room temperature, using a Shimadzu SPM-9700 atomic force microscope (Kyoto, Japan) in dynamic mode with a resonance frequency of 320 kHz and scan rate of 1.0 Hz. The scan areas were 5.0 μm × 5.0 μm and 10.0 μm × 10.0 μm.

Swelling index was gravimetrically determined. The dry membrane (W_d) was initially weighted and promptly immersed in distilled water at room temperature. The membranes were removed from water, wiped off, weighted, and returned to water at different time intervals: five minutes for the first 30 min, 1 h until complete 12 h, and them 24 h and 48 h. The experiments were done in triplicate. The water sorption capacity or swelling index, W(%) was calculated according to Eq. 1:

$$W(\%) = [(Ww - W_d)/W_d] * 100 \quad (1)$$

where W_w is the membrane wet weight and W_d is the membrane dry weight.

The swelling index was also determined in acidic medium using a H_2SO_4 0.01 mol/L aqueous solution.

2.4. Thermo characterization

A Shimadzu TGA-50 thermogravimetric analyzer was used to study the thermal stability of the membranes. Samples with 6 mg were submitted to a heating rate of 10 °C/min in nitrogen atmosphere, using alumina crucible and range of temperature from 25 °C to 600 °C.

DSC analysis were obtained using a Shimadzu DSC 50, temperature range from 25 °C up to 450 °C, in nitrogen atmosphere (flow of 20 mL/min) and heating rate of 10 °C/min.

2.5. Mechanical characterization

Ultimate tensile strength, modulus and elongation percentage of the membranes were measured in a universal test dynamometer, Dyna View model AME-5kN (Oswaldo Filizola LTDA, Brazil), according to ASTM D638. The test samples were cut into strips (100 mm × 10 mm). The crosshead speed was 10 mm/min. All samples were tested at room temperature and the data were instantaneously recorded. At least 10 samples of each membrane were measured and the presented results are the average values.

3. Results and discussion

3.1. FTIR spectroscopy

The first difference observed when comparing all membranes is related to their physical aspects. While pure and heterogeneous crosslinked membranes were transparent, the homogeneous ones were opaque. However, despite their different appearances, all crosslinked membranes behaved similarly when immersed in acetic acid solution for over 24 h, maintaining their integrity and therefore confirming the crosslinking process.

Fig. 1 shows the FTIR-ATR spectra of pure and crosslinked membranes while Table 1 summarizes the main absorption peaks for pure chitosan. Regarding the heterogeneous crosslinked membranes, the first spectral changes observed are in the 3600–2500 cm^{-1} region, where the O–H and N–H$_2$ absorption bands became less distinct, and a new absorption band appeared at 3220 cm^{-1} and broadened as the reaction time increased. Besides, C–H stretching vibration peak shifted to lower wavenumbers (from 2875 to 2963 cm^{-1}). The new band at 3220 cm^{-1} is assigned to the stretching vibration of N^+–H [1] indicating that the NH_2 groups in chitosan were protonated by the presence of sulfuric acid forming NH_3^+ groups. Crosslinking process occurs when an SO_4^{-2} anion interacts with two NH_3^+ groups by ionic attraction. The shift at the C–H stretching vibration peak is an indication that there was an additional interaction between sulfuric acid and chitosan membrane. At lower wavenumbers, between 1750 and 1500 cm^{-1}, it is

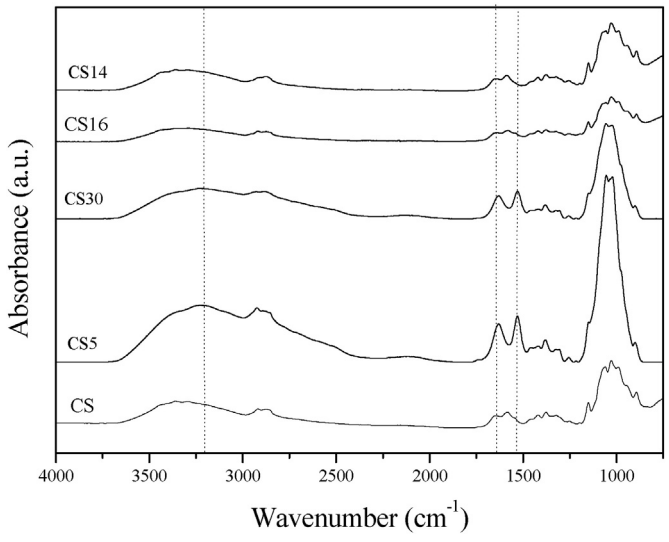

Fig. 1. FTIR-ATR spectra of chitosan (CS), heterogeneous (CS5 and CS30) and homogenous (CS14 and CS16) crosslinked chitosan membranes.