

Synthesis and Characterization of ETS-10/Chitosan Nanocomposite Membranes for Pervaporation

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ABSTRACT

Chitosan (CS) and microporous titanosilicate ETS-10/CS mixed matrix membranes (MMMs) were prepared. The pervaporation performance was tested on the of water-ethanol mixtures in the range 85-96 wt. % ethanol. The permeate flux increased from 0.45 to 0.55 kg m⁻² h⁻¹ at 50 °C for the ETS-10/CS MMM with respect to the pure CS membranes. Characterization by SEM and TEM, XRD, DSC and TGA allowed inferring an intimate contact between the dispersed ETS-10 and the continuous chitosan phase. The 5 wt. % loading of titanosilicate scarcely decreased the hydrophilic character of the mixed matrix membrane but increased the molecular sieving effect on the transport and separation properties, thus affecting the membrane behavior on pervaporation.

Keywords: Mixed matrix membranes; Pervaporation dehydration; Water-ethanol separation; Chitosan, Microporous titanosilicate; ETS-10

1. Introduction

Separation processes have always been of special importance in the chemical industry. However, conventional separations entail relatively high energetic and economic costs, especially in specific cases as, for example, high purification processes where the removal of a small amount of water is needed. Therefore, the necessity of continuous improvements and increasing competitiveness has boosted the research in new and alternative separation techniques, which can replace or complement the traditional existing ones [1, 2]. In this context, membrane separation processes have been relevant for the past twenty years, due to their low energy consumption, easy operation and low maintenance. In particular, pervaporation has been postulated as an alternative potential technology to offset the traditional bulky and less environmentally friendly methods. Transport through a dense-polymeric membrane usually takes place through the solution-diffusion mechanism in three steps: (i) the selective component is adsorbed in the membrane, (ii) which is diffused through the membrane and (iii), the component is desorbed from the other side in vapour phase, due to the low pressure kept at the permeate side, usually achieved by a vacuum pump. However, current commercial polymer membranes have limited resistance to high temperature, are usually inadequate to high flow rates or sensitive to clogging by dust.

The membrane is the key element since the separation phenomenon occurs in it, so the material used in the membrane preparation determines the separation performance [3]. For instance, hydrophilic membranes are more selective to water so this can be separated from a mixture with organic compounds. Depending on the material, membranes can be classified as inorganic [4], polymeric [5] and, more recently, mixed matrix membranes (MMMs), where the combination of organic and inorganic materials has been proved an attractive way of merging and enhancing the

properties of both phases, for pervaporation. Inorganic have good catalytic and separation behaviour, and present good chemical and temperature resistance. On the other hand, polymeric membranes are easily processed at low costs. This work focuses on the last type, since combining organic polymers and inorganic materials has been proved an attractive way of merging and enhancing the properties of both components. Chitosan (CS) is the deacetylated derivative from chitin, an abundant natural polymer, cheap and obtained from renewable sources, *i.e.* the shell of crustaceans. Chitosan, poly[$\beta(1\rightarrow4)$ -2-amino-2-deoxy- D-glucopyranose], is a linear polysaccharide obtained by deacetylation of chitin, poly[$\beta(1\rightarrow4)$ -2-acetamido-2-deoxy- D-glucopyranose]. The chemical formula is shown in Figure 1. Chitosan is biodegradable, biocompatible, and non-toxic. Its hydrophilic character makes it very interesting for water elimination from a mixture with other compounds [6]. Chitosan has long been studied as membrane material for dehydration by pervaporation process [7, 8] due to its high affinity towards water, good film forming properties and the presence of functional groups that can be easily modified. Its mechanical stability has nevertheless been tried to improve by coating on a porous polysulfone support [9], crosslinking [10] and physical mixing with zeolite particles [11, 12]. The structure of the microporous titanosilicate ETS-10 is made of orthogonal TiO_6 octahedra and SiO_4 tetrahedra linked by oxygen atoms shared in the corners. Ti atoms in a six-coordinated state have two negative charges that are balanced by Na^+ and K^+ [13]. The high cation exchange capacity is what makes ETS-10 very interesting in adsorption [14], catalysis and membrane separation processes [15]. ETS-10 can be synthesized in difference sizes including nanosized [16], which may be homogeneously dispersed in a polymer providing this with its intrinsic characteristics. This work studies the preparation of CS and ETS-10/CS mixed matrix membranes and its behavior in the dehydration of ethanol

by pervaporation. MMMs with different thermal, mechanical and transport properties could have potential in the improvement of the conversion of an esterification process using a membrane reactor [17, 18].

1. Experimental

2.1. ETS-10 synthesis

The nanosized ETS-10 crystals were prepared according to a hydrothermal synthesis method previously reported [16] using TiO₂-anatase (powder, 99.8 wt. %, Aldrich) and sodium silicate solution (27 wt. % SiO₂, 8 wt. % Na₂O, Merck) as Ti and Si source, respectively. 35.06 g of parent gel with molar composition 5.6 SiO₂: 1 TiO₂: 4.6 Na₂O: 1.9 K₂O: 137 H₂O was poured into a Teflon-lined autoclave and submitted to hydrothermal synthesis at 230 °C for 24 h, after which time, the autoclave was removed from the oven and quenched under cold tap water to room temperature, and the solid washed and centrifuged at least 3 times, and dried at 100 °C overnight to recover about 2.8 g of final product.

2.2. Membrane preparation

CS (coarse ground flakes and powder, Sigma-Aldrich), with molecular weight from 310,000 to >375,000 based on the viscosity range of 800-2000 mPaS was used as purchased. Chitosan 1 wt. % solutions were prepared by dissolving the polymer in 2 wt. % acetic acid (glacial, Panreac) aqueous solutions and stirred at 80 °C for 24 h under reflux conditions. The CS solution thus obtained was filtered in order to remove insoluble impurities. A volume of 10 mL was then degassed in ultrasonic bath for about 15 min before casting on a polystyrene Petri dish per membrane, which was evaporated

at room temperature for 2-3 days. CS membranes were then removed from the Petri dish. A 15 cm² membrane area was cut from the film for pervaporation tests and treated at 120 °C for 12 h under vacuum before pervaporation performance, in order to provide mechanical resistance to the membrane and completely remove the solvent from the membrane matrix [19].

For the ETS-10/CS MMM with 5 wt. % ETS-10 loading, 0.01 g of ETS-10 particles were first dispersed in distilled water (proportion 1:100 wt.) in an ultrasound bath for 10 min at room temperature. Then, 10 mL of CS solution, prepared as has been indicated above, were added and degassed in the ultrasound bath for other 15 min until a homogenous white dispersion was obtained and cast as described above. MMMs with higher ETS-10 loadings (10 – 20 wt. %) were prepared in the same way.

Thicknesses were measured using a Micrometer (Mitutoyo Corp. with an accuracy of 0.001 mm).

2.3. Characterization of the membranes

The ETS-10 crystals and MMMs were measured by X-ray diffraction analyses (Rigaku/Max System diffractometer, Cu K α radiation with $\lambda = 1.5418 \text{ \AA}$ and graphite monochromator). The morphology and cross section of ETS-10/CS membranes were observed using scanning electron microscopy (HITACHI S2300) of gold-sputtered samples at 10 kV. Transmission electron microscopy images of resin-embedded membrane samples were taken in a JEOL-2000 FXII equipment at 200 kV, allowing a closer look at the interaction between ETS-10 nanoparticles and the chitosan polymer. Thermogravimetric analyses (TGA) were performed by a TGA/SDTA851e system (Mettler Toledo) in air at a heating rate of 10 °C/min. The glass transition temperature

were measured in a DSC822e (Mettler Toledo), on the second heating cycle at 100-300 °C at 50 °C/min, after a previous cycle at 100-200°C at 10°C/min to remove the thermal history of the membrane material. The density of the membrane films was determined from the electronically measured weight of the circular film and the calculated volume. The static water contact angle measurements were performed in a Dataphysics instrument using SCA20 software. To compare the wettability of hybrid membranes to the pure chitosan, contact angle between samples surface and water was measured in air using the sessile drop method. Films were preserved in humid atmosphere for 48 – 72 h prior to measurement. At least four measurements were performed for each membrane in order to account for reproducibility. Swelling experiments in water and water/ethanol mixtures were conducted for membrane samples with 0, 5, 10 and 20 wt. % ETS-10 content. These were carried out on 0.5 x 2 cm² membrane strips at room temperature. Then the pieces of membrane were immersed in distilled water or water/ethanol mixture for 24 h to reach sorption equilibrium. The membrane wet weight was obtain by blotting it in tissue paper to remove free water and weighed rapidly. The swelling coefficient is calculated using the following relationship,

$$S.D. = \frac{w_{wet} - w_{dry}}{w_{dry}} \times 100 \quad (1)$$

where w_{dry} is the dry weight of the membrane (g) and w_{wet} , the weight of the swollen membrane (g).

The porosity of the membrane can be calculated from the volume occupied by water and the volume of the membrane, by taking into account the water density at 25

°C (0.997 g/cm³) and the density of the membrane in the dry state (Table 1), as in Magalad et al. [20].

The free volume is thus calculated as,

$$V_f = \left(\frac{W_{wet} - W_{dry}}{\rho_{water}} \right) + \frac{W_{dry}}{\rho_m} \quad (2)$$

where ρ_m is the density of the membrane in the dry state (Table 1).

The porosity, thus is calculated as

$$Porosity(\%) = \frac{(W_{wet} - W_{dry})}{\rho_{water} V_f} \quad (3)$$

2.4. Pervaporation plant

Figure 2 shows a scheme of the pervaporation plant used for the experiments. Briefly, the liquid mixture (3-5 mL/min) was pumped with a Variable Flow Peristaltic Pump (Fischer Scientific) from the feed tank to the membrane module (Stainless Steel Filter Holder, Albet Labscience), which was placed inside a forced convection oven (UFE 400, Memmert) in order to control the operation temperature. The pervaporation took place in the membrane producing two effluents: the liquid retentate that was recirculated to the feed tank and the permeate vapor, which was collected in a trap cooled down with liquid nitrogen to be recovered for analysis. All the elements and connections downstream were kept at low pressure (2 mbar) by a vacuum pump (RV3 Rotary Vane Pump, Edwards). Permeate was weighed and the ethanol concentration

analyzed by a gas chromatograph (GC 7820A, Agilent Technologies) equipped with a flame ionization detector (FID) and using helium as carrier gas.

Pervaporation is described by the flux ($\text{kg m}^{-2}\cdot\text{h}^{-1}$), J , of the permeating component, water, of the binary mixture comprising water and ethanol, and can be computed as: $J = W/(A \cdot t)$, where W (kg) is the weight of permeate collected in the cold trap, A (m^2), the effective area of the membrane, and t (h), the permeation time interval. The water/ethanol separation factor is defined as follows,

$$\alpha = \frac{y_{\text{water}} / y_{\text{ethanol}}}{x_{\text{water}} / x_{\text{ethanol}}} \quad (4)$$

where y and x are the weight fractions in the permeate and the feed, respectively.

3. Results and Discussion

3.1 Membrane characterization

The morphology of ETS-10 particles (Figure 3) was the typical square truncated bi-pyramid, with an average crystal size of about 320 nm and 410 nm in the edge of the base and the height of each truncated pyramid, respectively, as reported elsewhere [16, 21].

The thickness is in the same order for pure polymer and MMMs, approximately 43 μm in Figure 4(a) and 53 μm in Figure 4(b), respectively, in agreement with the routine measurements with the micrometer, which gave values around 40-60 μm ,

for the dried membranes prepared. The dispersion of the 5 wt. % ETS-10 within the polymer in a MMM is shown in the cross-sectional SEM micrographs of Figures 4(b,c). The filler distribution is seemingly homogeneous, without apparent segregation and no agglomeration of the particles are presented. In the TEM image of Figure 4(d) the close contact between ETS-10 particles and the rubbery CS matrix may be inferred by the observed plasticity of the polymer around the particles. This is attributed to the affinity between the filler and the polymer. Besides, this also agrees with the dispersability of the crystalline particles in the polymer matrix observed by SEM.

TGA, DSC and XRD were used to determine the degree of integration of the ETS-10 in the chitosan matrix. For this purpose, MMMs with higher loadings than 5 wt. % were prepared.

The X-ray diffraction patterns of ETS-10, CS and ETS-10/CS MMMs are shown in Figure 5. The characteristic peaks of chitosan and ETS-10 titanosilicate can be clearly distinguished in the XRD of the MMMs with 5, 10 and 20 wt. % loadings. The chitosan membranes prepared in this work seem to contain both crystal forms of the chitosan polymer: form I at $2\theta = 11.2$ and 18.0° , form II at 20.9 and 23.8° . The intensities of these chitosan reflections decrease with increasing ETS-10 loading, which some authors have attributed to the enhanced interaction between chitosan and the inorganic crystalline particles while the interaction among chitosan chains themselves is decreased [11, 22, 23].

Thermal properties of pure chitosan and ETS-10/CS MMMs were measured by DSC and TGA (Figure 6). There were no significant changes on the glass transition temperature of chitosan with increasing ETS-10 loading (222 ± 3 °C for the pristine chitosan membrane and 230 ± 3 °C for the MMM with 5 wt. % of ETS-10), as observed

by DSC analyses repeated 4-6 times. These results indicate the increased rigidification of the chitosan matrix upon addition of the inorganic crystalline particles [24]. However, the difficulty to discern the T_g agrees with literature reporting that chitosan is not prone to reveal thermal transitions upon crosslinking [25].

Thermogravimetric analyses of pure CS membranes (Figure 6) show an initial weight loss below 180 °C related to water molecules, in agreement with their hydrophilicity. Above this temperature, the decomposition of chitosan starts with a second peak of decomposition, which could be attributed to degradation of the chitosan chain and a third peak of weight loss consequence of the complete oxidation of residual organic groups [26, 27]. In the ETS-10/CS MMMs, similar to bare polymer, there are three peaks of weight loss. It is noticeable the delay in the third peak where the maximum temperature increases with the ETS-10 loading. This could be related to the interaction between the two components (inorganic material and polymer) in the membrane [11]. The remaining weight loss allows the verification of the nominal wt. % loading of inorganic filler present in the corresponding MMM, thus, according to Figure 6, the residual contents of 5.2, 11.4 and 17.9 wt. % agree with the nominal 5, 10 and 20 wt. % ETS-10 loadings, respectively.

Figure 7 shows the effect of ETS-10 loading in the degree of swelling of the ETS-10/CS MMMs. Water uptake was conducted for membranes at room temperature. After the heat treatment, chitosan-based membranes could not dissolve in water, but the hydrophilic –OH and –NH₂ groups could still form H-bonds with water molecules. This resulted in a degree of swelling of 189% for the uncrosslinked, pure chitosan membrane. This agrees with the high swelling values reported in literature [10]. MMMs have been reported to possess a reduced swelling behavior compared with pure polymer membranes, upon particle introduction [28]. As expected, the introduction of ETS-10

particles had an effect of crosslinking in the rubbery chitosan polymer chains, up to 10 wt. % loading, with a minimum swelling of 115 % after 60 min in water. However, the degree of swelling at higher ETS-10 loadings increased again. A similar effect was observed when chitosan membranes were chemically cross-linked with trimesoyl chloride (TMC) [10], organosilanes [29] or inorganic fillers [12]; in those cases, it was attributed to the insertion of the cross-linker increasing the fractional free volume among the polymer chains available for water transport. In this work, this is reflected in the decrease of the density of the membrane upon ETS-10 introduction (Table 1), since the volume occupied by water, or free volume, V_f , followed the same trend as the swelling degree. This may be attributed to the hydrophilicity that the ETS-10 nanoparticles impart to the MMMs, which accounts for the different behavior of ETS-10/CS MMMs compared with other MMM reported for water-ethanol pervaporative separation [28]. In this work, the water contact angle of the pure CS and 5 wt. % ETS-10/CS MMMs scarcely decreases, as will be further discussed later. The porosity values followed the reverse trend, in agreement with literature [20], except for pure CS membranes, which are reported as 30.2 wt. % and were very difficult to measure in this work, due to the huge swelling capacity of uncrosslinked chitosan.

3.2. Membrane pervaporation performance

In the pervaporation experiments, after an initial stabilization period, the membranes showed a constant performance. This period is called “conditioning time” and the values may vary greatly in the first hours of pervaporation operation [30]. This may be attributed to the high swelling capacity of the chitosan polymer [31]. The discussion presented below regarding the influence of concentration on the

pervaporation performance of CS and CS/ETS-10 MMMs is based on the results obtained in the steady state condition.

The pervaporation flux and water/ethanol separation factor for pure chitosan (CS) and 5 wt. % ETS-10/CS MMMs at 50 °C with a feed water/ethanol 15/85 wt. % are collected in Table 2. To assure reproducibility, error bands correspond to the standard deviation of three experiments carried out in the same conditions with different membranes. The CS membrane gave lower fluxes but higher water/ethanol separation factors than the MMMs. In CS membranes, a water/ethanol separation factor of 47 was attained, against the water/ethanol separation factor of 30 for the MMM. The flux was 1.5 times higher in MMMs ($0.55 \text{ kg m}^{-2} \text{ h}^{-1}$) than in the pure polymer membranes ($0.45 \text{ kg m}^{-2} \text{ h}^{-1}$), whereas the separation factor is decreased, in agreement with pervaporation experiments conducted on pure ETS-10 tubular membranes, where a water/ethanol separation factor of around 6 at 60 °C was reported [15]. The introduction of inorganic fillers in the chitosan matrix is usually reported to decrease the hydrophilicity of the membrane, revealed by an increased water contact angle. However, in this work the water contact angle only varied from $69 \pm 15^\circ$ for pure CS membranes, value that agrees with literature [29], to $67 \pm 15^\circ$, for ETS-10/CS MMMs with 5 wt. % loading, which is almost negligible. This is attributed to the hydrophilic character of the ETS-10 particles, which confirms that the addition of ETS-10 crystals had an actual influence in the membrane performance, decreasing the separation factor by compensation changes on the hydrophilic character of the membrane, but increasing the flux due to ETS-10 molecular sieving and adsorption properties.

The influence of the concentration of ethanol in the feed at 50 °C is presented in Figure 8. For CS and MMMs, the total and water fluxes decrease as the ethanol in the feed increased, whereas the water/ethanol separation factor showed the reverse effect.

The decrease of the water flux can be attributed to the decrease in adsorbed water molecules with increasing water concentration and the slight increase of ethanol concentration in the retentate. Error bands correspond to the standard deviation of at least two, usually three, experiments with different membranes in order to assure reproducibility. Permeation fluxes are higher than others reported for chitosan –based mixed matrix membranes (Table 2). Separation factors are in the same order of magnitude, considering the different working conditions reported by the authors (higher water content in the feed, higher temperature), which gives an idea of the potential of ETS-10/CS MMMs for pervaporation.

4. Conclusions

ETS-10/CS MMMs were prepared by introducing small amounts of the inorganic filler in the polymer matrix, with good adhesion and improved hydrophilic and molecular sieving properties that were validated on the separation performance in water/ethanol separation by pervaporation. There was a good adhesion between ETS-10 nanoparticles and chitosan and the pervaporation performance was enhanced from 0.45 to 0.55 kg m⁻² h⁻¹ at 50°C by the increasing amount of filler loading up to only 5 wt. %, ETS-10 in the MMM, which did not significantly decrease the hydrophilic character of the MMMs.

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Table 2. Pervaporation flux and water/ethanol separation factor in the dehydration of water/ethanol mixture using CS-based MMMs.

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Figure 1. Molecular formula of chitosan.

Figure 2. Scheme of the pervaporation setup: (1) feed tank; (2) pump; (3) membrane module; (4) retentate recovery; (5) temperature control; (6) feed pressure control; (7), 3-way valves; (8) cold traps, and (9) vacuum pump.

Figure 3. TEM image of ETS-10 nanoparticles.

Figure 4. SEM images of the cross section of a CS membrane (a), the cross-section of a ETS-10/CS MMM, with a 5 wt% ETS-10 loading (b), the top surface of ETS-10/CS MMM (c) and a TEM image of the detailed interaction between ETS-10 and CS matrix (d).

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