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Synthesis and characterization of novel nanocomposite Chitosan membranes for Ethanol dehydration

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ABSTRACT

Polyacrylonitril (PAN)-supported chitosan (CS) nanocomposite membranes were prepared by cross-linking the CS with 3-aminopropyl-triethoxysilane (APTEOS) via sol-gel method. Pervaporative performances of the CS-SiO$_2$/PAN membrane for dehydration of aqueous alcohol solutions were investigated. From SEM cross-sectional images of the membrane, the spongy pores and the finger-like pores were found in cortex and intermediate layer. The PAN microporous substrate and the top layer were about 100 and 7.4 μm thick, respectively. The separation factor and permeation flux of the synthesized CS/PAN and CS-SiO$_2$/PAN membranes indicated that introducing 5% of nanosilica to skin layer of the composite membrane improved its pervaporative properties. At 30°C, a separation factor of 20.03 and 34.25 were achieved for CS/PAN and CS-SiO$_2$/PAN membranes, respectively.

Keywords: *Chitosan; 3-Aminopropyl-triethoxysilane; Nanosilica; Nanocomposite membrane; Pervaporation.*

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INTRODUCTION

Incorporation of inorganic nanoparticles into polymeric membranes leads to the improvement of mechanical and thermal properties of the membranes. Nanocomposite membranes usually have better pervaporation (PV) performance than polymeric membranes. PV dehydration process shows great achievements on separation of organic solvent–water azeotropic mixtures, which are hard being separated by conventional distillation processes. In most cases, water-selective membranes are utilized and the dehydration is performed through a solution-diffusion mechanism. Hydrophilic membranes, such as poly (vinyl alcohol) and chitosan (CS) based membranes, are good candidates owing to their water-permselectivity and high permeation fluxes [1-5]. CS is one of the promising membrane materials and has been widely studied [6, 7]. It can be used as membrane material for ultra filtration, reverse osmosis, PV [6] and other kinds of applications.

In PV separation of water–ethanol mixtures, CS is regarded as the most effective water-permselective material since CS membranes have high separation factors [8]. CS, the second most biopolymer in nature, is the deacetylated form of chitin, which has been considered as one of the most promising materials due to its biodegradability, biocompatibility and non-toxicity [9-11]. CS is also a multifunctional polymer containing large numbers of reactive amine groups together with hydroxyl groups which make it a hydrophilic material and capable of reacting with groups such as epoxy group [12]. These hydrophilic groups are considered to play an important role in preferential water sorption and diffusion through the CS membrane [13]. CS has been proven to have good film forming properties, chemical resistance and high water permselectivity. It can be used for homogenous membranes or the skin layer of composite membranes [6, 8]. PAN is one of the most important polymers widely used as the substrate of membrane. It showed good mechanical strength as a film with a good thermal stability [14].

In the present work, a novel nanocomposite membrane was prepared by using PAN microporous membrane as sublayer, chitosan coating as top layer, and the PV properties for separating aqueous solvents through this membrane were investigated. In order to enhance the PV properties of chitosan membrane, silica nano particles were incorporated within membrane matrix.

EXPERIMENTAL

Materials

CS (medium molecular weight) was purchased from Chemopol Nellore, India. Acetic acid (99.9%), hydrochloric acid (HCL) and N, N-dimethylformide (DMF) and ethanol were supplied by Merck. APTEOS, a precursor for silica nanocomposite, and PAN was purchased from Shanghai Yaohua Chemical Plant (China) and Polyacryl Iran Corp., respectively.

Fabrication of PAN support

A dope of PAN in dimethylformamide (DMF) was casted and then immersed and kept for 2 days in water coagulation bath without evaporation of solvents. After precipitation, the microporous support was washed with deionized water.

Nanocomposite mixed matrix membrane preparation

Homogeneous dense CS membranes were also prepared by solution casting technique. Firstly, CS was dissolved in an acetic acid aqueous solution to form a solution of 1.0 wt% CS. The solution was stirred for 10h at room temperature and filtered to remove undissolved matter. Then, a certain amount of APTEOS as well as concentrated HCL as a catalyst were added to initiate the cross-linking reaction. A bubble-free solution was coated onto the microporous PAN support. The solvent captured in this thin layer was evaporated at room temperature to obtain a dense nonporous membrane layer on the PAN support. The thickness of ultra-thin CS selective layer was measured using SEM images.

Membrane structurally characterization

The morphology of the fabricated membranes was examined using scanning electron microscopy (SEM). The samples were coated with gold and observed with a Philips XL30 (Philips, The Netherlands) scanning electron microscope.

PV experiments

PV experiments were carried out on a laboratory scale apparatus. In PV, the feed solution of 90 wt. % ethanol and the rest water was in direct contact with the membrane and was kept at 30℃. The membrane was housed in a PV cell that consisted of two detachable stainless steel parts. A porous steel plate was imbedded in one of the parts to support the membrane, and the two parts were set in proper alignment. Rubber O-rings were used to provide a pressure tight seal between the membrane and the permeation cell. The effective area of permeation was 21 cm^2. The feed mixture with a predetermined composition was circulated

from a thermostated feed tank to the permeation cell using a feed pump, and the retentate from the permeation cell was recycled to the feed tank. Vacuum was applied to the permeate side of the membrane, and the permeate vapor was condensed and collected in a Pyrex glass cold trap immersed in liquid nitrogen. In all the experiments, the feed was kept at atmospheric pressure, whereas the permeate pressure was maintained at 2–3 mbar, which was monitored by a Pirani vacuum gauge (MKS Instruments). The permeation rate was determined gravimetrically by weighing the permeate sample collected over a given period of time using an analytical balance, and the permeate composition was analyzed using a Hewlett-Packard gas chromatography equipped with a thermal conductivity detector. The feed circulation rate was kept substantially high as compared to the permeation rate so as to minimize the effect of concentration polarization. All the experimental data were collected after steady state of PV had been reached. The time required to reach the steady state was depending on the permeation flux through the membrane. The membrane was tested for the separations of the mentioned water/ethanol mixture. The permeate concentration and the permeation flux were used to characterize the membrane performance. In this permeation of binary mixtures, separation factor was also used to characterize the permselectivity of the membrane. In PV, the flux '*J*'of a given species, say faster permeating component '*i*'of a binary liquid mixture comprising of *i* (water) and *j* (ethanol) is given by:

$$J_i = \frac{W_i}{At} \qquad (1)$$

Where W_i represents the mass of water in permeate (kg), *A* the membrane area (m^2) and *t* the evaluation time (h). The membrane selectivity is the ratio of permeability coefficients of water and ethanol and can be calculated from their respective concentrations in feed and permeate as given below:

$$\alpha = \frac{y(1-x)}{x(1-y)} \qquad (2)$$

Where *x* and *y*, represented the feed and permeate concentrations of the faster permeating component '*i*', which is water in the present case.

Quite often, PV separation index (PSI) is used to describe the overall performance of a membrane for a selected feed mixture. This can be calculated from the product of water flux, *J* and selectivity, *α*:

$$PSI = J \times \alpha \qquad (3)$$

RESULTS AND DISCUSSION

In preparing the membranes, APTEOS was first hydrolyzed in presence of an acid catalyst (HCl), leading to the formation of silanol groups. Then, the hydroxyl groups in one silanol formed siloxane bonds with those in another silanol or with the amine groups in CS through a dehydration or de-alcoholysis reaction during the membrane drying. Also, the hydroxyl groups and amine groups in the silanol can form hydrogen bonds with the dissociative hydroxyl groups or amine groups in the CS amorphous region, and these hydrogen and siloxane bonds are the cross-linking spots in the hybrid membranes.

Cross-sectional scanning electron micrographs of PAN-supported CS-nanoSiO$_2$ membrane are shown in Figure 1. As shown in Figure 1a, the thickness of microporous PAN substrate was about 100 μm and the thickness of the skin layer (selective layer) of the membrane was about 7.4 μm.

The formation of CS layer on top surface as well as the porous structure of PAN support could clearly be observed in Figure 1b. As seen, the spongy pores and the finger-like pores were found in support layer. Also, Figure 1c and d show a good stickiness between PAN and CS layers.
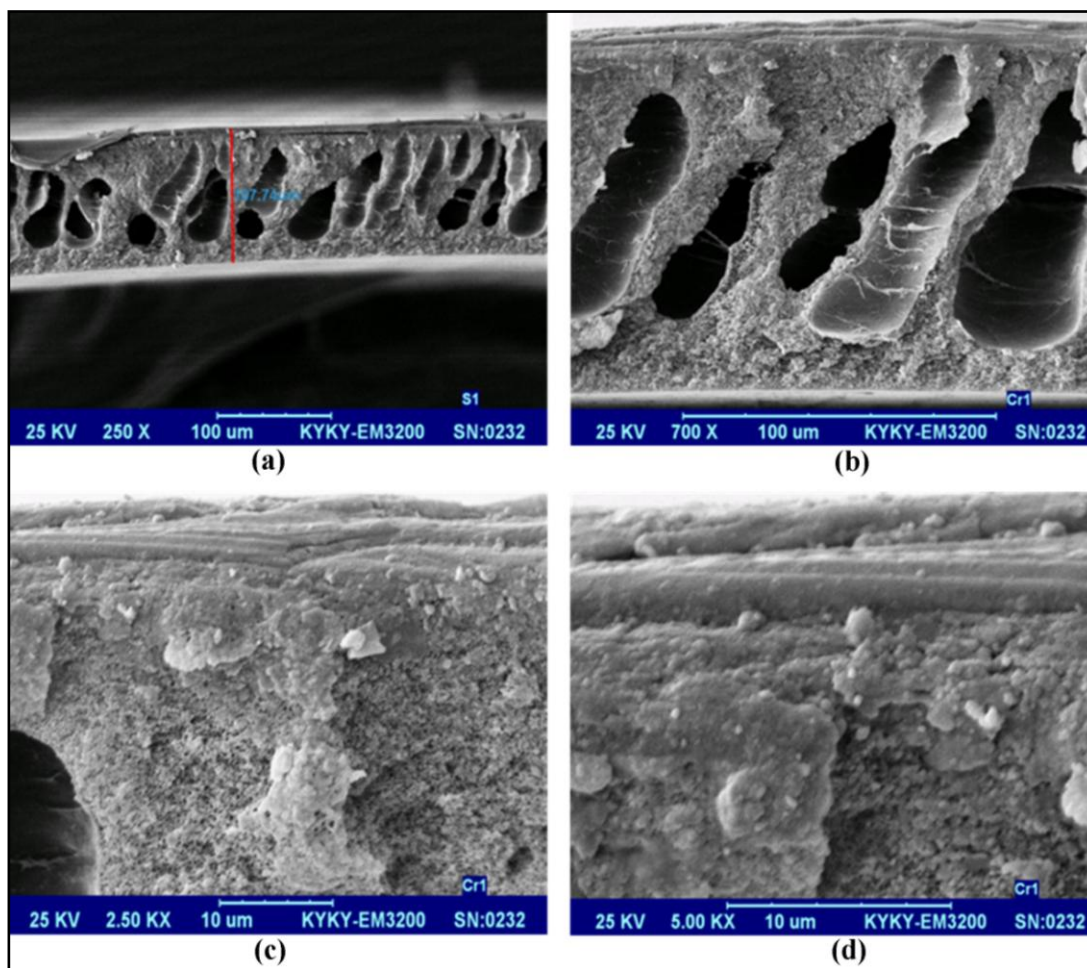
Fig. 1. Cross-sectional SEM images of PAN-supported CS-nanoSiO$_2$ membranes, a) 250 X, b) 700 X, c) 2500 X, d) 5000 X

The formation of CS layer on top surface as well as the porous structure of PAN support could clearly be observed in Figure 1b. As seen, the spongy pores and the finger-like pores were found in support layer. Also, Figures 1c and d show a good stickiness between PAN and CS layers.

The chemical structure of microporous support layer and nano particles makes great influence on pervaporative performance of the composite membrane. PAN is one of the most important polymers widely used as the substrate of membrane. It showed good mechanical strength as a film with good thermal stability. The permeation flux and separation factor of CS/PAN and CS-SiO$_2$/PAN membranes at a temperature of 30℃ was calculated according to Eq. (1) and (2). Table 1 summarizes the flux permeation and separation factor values of the CS/PAN and CS-SiO$_2$/PAN

membranes. As seen, it could be concluded that the incorporation of silica nano particles into the polymeric matrix enhanced both the flux and separation factor of the composite membranes. Due to presence of 5wt% nano-SiO$_2$, the separation factor significantly increased from 20.03 to 34.25.

Table 1. Permeation flux and separation factor of CS/PAN and CS–SiO$_2$/PAN membranes at 30 °C (EtOH in Feed = 90 wt %)

Membrane	Permeation Flux, J (g/m^2·h)	Separation Factor, α	Separation Index, PSI (J·α)
CS/PAN	152.38	20.03	3653.8
CS-SiO$_2$/PAN	180.12	34.25	6169.11

CONCLUSIONS

Novel composite CS/PAN and CS-nanoSiO$_2$/PAN membranes were synthesized to study the effect of incorporation of nano-SiO$_2$ on the permeation flux and separation factor of the composite membrane in PV separation of an ethanol/water mixture. It was concluded that the nanocomposite membrane had better pervaporative performance than the polymeric composite membrane. The results of ethanol dehydration experiments indicated an increase in separation factor. Due to presence of nano particles, the CS-nanoSiO$_2$/PAN membrane had better separation factor of 34.25 and flux of 180.12 g/m^2·h than CS/PAN membrane with separation factor and flux of 20.03 and 152.38g/m^2·h, respectively.

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