Journal of Molecular Liquids 246 (2017) 7–16

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Molecular simulation and experimental investigation of temperature effect on chitosan-nanosilica supported mixed matrix membranes for dehydration of ethanol via pervaporation

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ARTICLE INFO

Article history:
Received 18 April 2017
Received in revised form 7 August 2017
Accepted 13 September 2017
Available online 15 September 2017

Keywords:
Pervaporation
Chitosan
SiO_2
Molecular dynamic simulation
Monte Carlo method

ABSTRACT

In this study, novel chitosan/silica mixed matrix membranes were prepared by 10 wt% loading of TEOS and APTEOS into chitosan matrix and simultaneously results were simulated by molecular simulation methods to investigate the reliability of the experiment results. The fabricated membranes were structurally characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), and operationally evaluated by ethanol dehydration permeation tests. SEM analysis showed a uniform distribution of silica nanoparticles in the polymer matrix. FTIR analysis indicated that, compared to the neat membrane, the presence of APTEOS and TEOS initiators caused formation of stronger bonds of hydroxyl (OH) and amino (NH) groups. The XRD test was also done by molecular simulation to investigate the crystallinity of the simulated membranes. Results revealed that membrane containing APTEOS was more amorphous than membrane containing TEOS. Also, the glass transition temperatures the membranes containing APTEOS and TEOS was calculated to be 162 and 160.8 °C, respectively. Permeation test results indicated that for both membranes the permeation flux increased and separation factor decreased with temperature. The maximum flux and best separation factor for CS/APTEOS and CS/TEOS were obtained at 70 °C and 30 °C, respectively. Chitosan/TEOS membrane showed the best separation factor of 450 in 30 °C, while for Chitosan/APTEOS membrane this value was less than 400. CS/APTEOS membrane showed better pervaporation separation index (PSI); however, the results showed that separation index of both membranes, which was initially more than 320 in 30 °C, decreased with temperature and reached to less than 130 in 70 °C. Also, the simulation results were in good agreement with experiment results.

1. Introduction

Pervaporation (PV) is defined as one of the industrial processes with a wide range of applications include solvent dehydration, solvent recovery, azeotropic separation, etc. [1–4]. PV is a membrane-based separation process which benefits from lower required energy and environment pollution, smaller operating space, and more simplicity of the process compared to traditional ones such as distillation and evaporation. In the dehydration operation, hydrophilic membranes are good candidates owing to their high water-permselectivity [5]. Chitosan (CS) is a linear polysaccharide which often derived from marine crustacean shells and contains both amino and hydroxyl groups which enhance its hydrophilicity. Furthermore, it is so flexible, biodegradable, and non-toxic and has good chemical resistance. Some properties of chitosan are tabulated in Table 1. Regarding these features, CS is a perfect nominee for dehydration of ethanol using PV method.

Beside various beneficence of chitosan, it is highly swollen in aqueous solutions and swollen polymers show weak separation performance in long-time operations [5]. Recently different methods have been used to solve this problem and improve both physical and chemical properties of chitosan membranes include crosslinking [7], preparation of composite membranes, manufacturing of mixed matrix membranes (MMMs) [8,9]. An overview of the resources related to polymeric membranes is presented in Table 2.

Previous studies showed that silica can enhance permeability, compatibility, and stability of biomaterials like chitosan by combination of stability effects of inorganics and high flux of polymers [7,14]. Silica also decreased the degree of swelling of poly(vinyl alcohol) [15] and chitosan [5] membranes in aqueous-organic separation processes.

One of the main problems of MMM production is the agglomeration of nanoparticles through polymeric matrix. Furthermore, sedimentation of fillers due to differences in density of matrix and fillers [16,17] and

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http://dx.doi.org/10.1016/j.molliq.2017.09.045
0167-7322/

Table 1
The chemical properties of chitosan [6].

Chemical properties
- Linear aminopolysaccharide with too much nitrogen content
- Rigid D-glucosamine structure; high hydrophilicity, crystallinity
- Enable to form hydrogen bonds intermolecularly; high viscosity
- Consisting of great reactive groups for cross-linking and chemical activation
- Insoluble in water and organic solvents; soluble in dilute aqueous acidic solutions
- Forms salts with organic and inorganic acids
- Film-forming ability; adhesivity materials for isolation of biomolecules

rigidification effect [18] are other important problems of MMMs which causes deformation and weak spatial distribution of membrane structure and formation of defects on the surface of membranes [19]. Formation of a homogenous solution of polymer with introduction of inorganics extracted from nanosilica-containing precursors could effectively solve the described problems and form a defect less membrane [20]. Additionally, incorporation of silica nanoparticles, like APTEOS and TEOS, reinforce the structure of polymer using cross-linking of polymers and also can curb the thermal motion of polymer chains and therefore decrease the plasticization effect through membranes [21]. Previous works showed that incorporation of APTEOS or TEOS can effectively enhance the permselectivity and permeation flux of membranes. APTEOS and TEOS are a powerful cross-linking agent and experimental studies revealed strong interaction between these materials and various polymers. Studies confirmed the formation of hydrogen bonding between residual hydroxyls on the APTEOS or TEOS and polymers, and therefore causes enhancement of mechanical properties [22–26].

Incorporation of nanosilica particles through polymers increases the free volume of polymers by disruption of chain packing and, as a result, enhances the permeability and selectivity of membranes [27]. Studies demonstrated that the permeability of membranes directly improve with the degree of conversion of silica through polymer, the silanes concentration, and the size of nanosized silica particles formed through membranes [28]. It could be deduced that incorporation of silica nanofillers could effectively improve the thermal and mechanical resistivity of produced membranes [29].

Beside of some spectacular properties of chitosan which made it suitable for different separation performance, swelling and low separation performance of chitosan membrane is two main problems for this polymer [3,30]. Literature review about incorporation of silica-containing nanoparticles into polymers showed modification of produced membranes with silica nanoparticles could have brilliant effect on the separation performance of produced membranes and attentions go toward using TEOS and AOTEOS as filler of chitosan-based membranes [9,22].

Furthermore, previous studies showed that operational properties such as feed temperature have important effect on performance of polymeric membranes [31,32]. The variation in feed temperature causes variation in crystallinity of polymer chains, diffusion rate of molecules, and solubility of molecules through membrane. Therefore both flux and selectivity of prepared membranes are depended to feed temperature, as described by Arrhenius correlation [33].

Beside different studies about the application of silica in chitosan, no attempts were reported for developing and investigation of temperature effect on tetraethoxysilane (TEOS)-chitosan and 3-aminopropyltriethoxysilane (APTEOS)-chitosan hybrid membranes by pervaporation method.

Additionally, in order to ensure about accuracy of results, molecular simulation could give an overview about trend of experimental results. In the last two decades, molecular simulation has been applied to predict the behavior of systems such as membranes in water and gas separation industries in molecular and atom scales, [34,35]. Nowadays, molecular simulation have been used for prediction of flux of different liquid molecules through the polymeric membranes and different features of these systems such as adsorption and diffusion mechanism, free volume and wide-angle XRD (WAXD) have been widely investigated [36,37].

In this study, the initiator of tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTEOS) were used as a source of silica (SiO_2) particles, and 10 wt% of the material was employed which was considered the optimum mode of these materials. Also, hydrochloric acid was used as a catalyst and the sol-gel method was used for synthesis of silica nanoparticles to improve the performance of polymeric membranes. In order to evaluate the performance of MMMs in different temperatures, the permeation flux experiments were carried out in different temperatures and consequently structural analyses have been presented to identify the physical and chemical properties of the membranes and. As we know and it can be seen, molecular simulation study on the Chitosan membranes has not been broadly undertaken yet and there is no molecular simulation investigation on these types of membrane for pervaporation processes. MD and Monte Carlo (MC) simulation were also applied to investigate and simulate the transport properties of prepared membranes.

2. Experimental

2.1. Materials

CS (medium molecular weight), tetraethoxysilane (TEOS), and 3-aminopropyltriethoxysilane (APTES) were purchased from Sigma-Aldrich. Polyacrylonitrile (PAN) copolymer (94% acrylonitrile and 6% methyl acrylate with an average molecular weight of 80,000 (g/mol)) was supplied by Polyacryl Co. (Isfahan, Iran). Polyethylene glycol (PEG, MW: 6000, 98% purity) was supplied by Loba Chemicals (Mumbai, India). dimethylformamide (DMF), acetic acid, and hydrochloric acid (HCL) solutions were purchased from Merch (Darmstadt, Germany).

2.2. Membrane preparation

2.2.1. Synthesis of the membrane support

First of all, the PAN copolymer was dissolved in DMF solvent placed on a magnetic stirrer for 8 h at 80 °C. Afterward, PEG was stepwise added and stirred for 12 h at room temperature to achieve a homogeneous solution. The final solution has 12% PAN and 20% PEG. After degasification, the solution was casted in the glass plate and immersed in a water coagulation bath and kept overnight to remove remained solvents.

Table 2
The polymeric membranes based Chitosan.

Binary compounds (wt%)	Support layer	Selective layer	Modified crosslinking	Separation factor	Flux ($kg \cdot m^{-2} \cdot h^{-1}$)	Temperature (°C)	Ref
H_2O/ethanol (10/90)	Chitosan	Chitosan	Sulfuric acid	1791	0.427	60	[10]
Ethanol/H_2O (10/90)	Chitosan	Chitosan	Glutaraldehyde	127	0.201	50	[11]
H_2O/IPA (10/90)	PVA/chitosan (40/60)	PVA/chitosan (40/60)	UFS solution to cross-linked	8562	0.149	30	[12]
H_2O/IPA (10/90)	PTFE	PSSA-g-PTFE/chitosan	GPTMS to cross-linked	1490	0.409	25	[13]