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Comparison of the pervaporation performance of various types of carbon nanotube-based nanocomposites in the dehydration of acetone

Qian Wen Yeang [a], Sharif Hussein Sharif Zein [a], Abu Bakar Sulong [b], Soon Huat Tan [a,*]

[a] School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan 14300, Nibong Tebal, Pulau Pinang, Malaysia
[b] Department of Mechanical & Material Engineering, Faculty Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia

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ABSTRACT

The present work focuses on the functionalisation of multi-walled carbon nanotubes (MWCNTs) with poly(vinyl alcohol) (PVA) in order to improve the compatibility and dispersion of MWCNTs in a chitosan (CS) matrix. The resultant PVA–MWCNT/CS nanocomposite membranes were crosslinked with glutaraldehyde. Pervaporation performances of the resultant membranes in dehydration of acetone were evaluated in terms of water permeance and selectivity towards water. The water permeance of the crosslinked nanocomposite membrane increased while the selectivity decreased compared to the crosslinked pure CS membrane. In addition, the selectivity and water permeance of the crosslinked nanocomposite membrane decreased while the water permeation flux improved with increasing feed temperature. Furthermore, crosslinking of the membranes was found to improve the selectivity of the membranes but lower the water permeance. In another approach, PVA functionalised MWCNT was bulk aligned on the poly(vinylidene fluoride) (PVDF) membrane by a simple filtration method and further coated with CS to form a novel three-layer nanocomposite membrane. This membrane showed immense improvement on the water permeance and selectivity. Upon comparison, the three-layer nanocomposite membrane was found to demonstrate the best separation performance among the membranes described here. Furthermore, the three-layer nanocomposite membrane emerged as a potential solution to the trade-off problem often faced by pervaporation membranes.

1. Introduction

Acetone, the simplest example of the ketones, is an organic compound that is colourless, mobile, flammable, and miscible with water. It is one of the most widely used chemicals in the production of plastics and other chemicals as well as a common solvent in the pharmaceutical industry. Although acetone does not form an azeotrope with water [1], a strong reflux is required to distill large amounts of solution, which requires a large column and high energy costs. Hence, pervaporation has emerged as an attractive alternative to the conventional energy intensive techniques such as distillation, due to its higher separation efficiency and potential savings in capital and energy. Pervaporation is a membrane-based process where the feed liquid mixture is brought into contact with one side of the membrane in which one of the components will be preferentially transported through the membrane and removed from the other side of the membrane as a low pressure vapour.

In the dehydration of organic solutions through pervaporation, chitosan (CS) is one of the most often employed biodegradable polymers because of its excellent hydrophilicity, good mechanical, chemical and thermal stability and good film formation. However, it is reported that CS membranes suffer from excessive swelling, especially when operating under a high portion of water in the feed mixtures [2]. Therefore, an appropriate chemical or physical alteration is essential to overcome this restraint. To solve this problem, various methods were proposed in the literature such as thermal modification, crosslinking, blending with different polymers, formation of a multilayer composite membrane and incorporation of a filler [3–9].

The incorporation of nanofillers such as carbon nanotubes (CNTs) into the polymer matrix as a reinforcing agent has gained a great amount of interest among researchers in the last decade due their extraordinary mechanical, electrical and thermal properties [10,11]. The most common and crucial problem faced in the fabrication process, however, is the dispersion efficiency of CNTs into the polymer matrix as the CNTs tend to agglomerate due to the strong Van der Waals interactions between them [12]. To overcome this problem, various techniques such as surface oxidation, attaching functional groups onto the surface of the CNTs, functionalisation by chemical agents, non-covalent surface coating with surfactants and long polymer chains and non-covalent adsorption of hydrophilic non-charged polymer chains have been widely explored to homogeneously disperse CNTs in a polymer matrix and improve the CNT adhesion to the polymer [13–17].

* Corresponding author. Tel.: +60 4 5996475; fax: +60 4 5941013.
E-mail address: chshtan@eng.usm.my (S.H. Tan).

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Throughout the years, various approaches to the preparation of pervaporation membranes have been carried out by researchers worldwide. A three-layer composite membrane comprised of a thin top layer of dense CS crosslinked with glutaraldehyde (GA) supported on a microporous polyacrylonitrile (PAN) and an intermolecular crosslinking layer in between the dense and the microporous layers was fabricated by Wang and co-workers [18]. In another approach, polyelectrolyte multilayer membranes were prepared by adopting a layer-by-layer self-assembly process [19–21]. Peng et al. [9] prepared nanocomposite membranes (PVA–CNT/CS) by incorporating CS-wrapped multi-walled carbon nanotubes (MWCNTs) into a poly(vinyl alcohol) (PVA) matrix via homogeneous dispersion. Recently, Ong et al. [22] successfully synthesised aligned poly(3-hydroxybutyrate) (PHB)-functionalised MWCNT/CS in a specific pattern by a simple filtration method. Initially, PHB functionalised MWCNTs were aligned on a membrane filter template through a filtration process followed by solution casting of CS onto the template to produce PHB–MWCNT/CS nanocomposite membranes.

In this study, unlike the previous studies, a three-layer nanocomposite membrane was synthesised by bulk aligning the PVA functionalised MWCNTs (PVA–MWCNTs) on a polyvinylidene fluoride (PVDF) membrane by a simple filtration method followed by coating with a thin CS layer. PVA is a hydrophilic, non-toxic and degradable synthetic polymer [23] which is miscible with CS [9]. The oxidised MWCNTs are able to interact with PVA as they both contain hydroxyl (OH) groups to form PVA–MWCNTs [24]. In addition to the three-layer nanocomposite membrane, a homogeneous PVA–MWCNT/CS nanocomposite membrane was formed by blending PVA–MWCNTs with a CS solution followed by a solution casting technique.

2. Experimental

2.1. Materials

MWCNTs manufactured by the chemical vapour deposition method (CVD), which involve a decomposition of gaseous hydrocarbon feedstock in a presence of catalyst, were supplied from Shenzhen Nanotechnologies Port Co. with diameters in the range of 40–60 nm and lengths of 5–15 μm. PVA, 95% hydrolysed, (Mw = 95,000) was purchased from Acros Organics. Low molecular weight CS (Mw = 50,000–190,000) was purchased from Sigma Aldrich. The degree of deacetylation for the low molecular weight CS was approximately 75–85%.

2.2. Preparation of PVA–MWCNTs

Raw MWCNTs were oxidised with 3 M sulphuric acid (H_2SO_4) followed by 3 M hydrogen peroxide (H_2O_2) at 60 °C for 2 h in order to shorten the MWCNTs and enable the attachment of carboxyl (COOH) and OH groups to the surfaces of the MWCNTs. The oxidised MWCNTs were recovered by filtration using a 0.22-μm PVDF membrane and washed with distilled water until a constant pH was achieved. The recovered MWCNTs were dried in the oven at 110 °C for 24 h. The oxidised MWCNTs were then added to a 5 wt.% PVA solution and sonicated for 15 min followed by stirring overnight to homogeneously disperse the MWCNTs in the PVA solution. Subsequently, the solution was filtered through a PVDF membrane and washed with distilled water to remove excess PVA. The recovered functionalised MWCNTs were dried in the oven overnight at 60 °C.

2.3. Preparation of crosslinked homogeneous PVA–MWCNT/CS nanocomposite membranes

PVA–MWCNTs were dispersed in 3 wt.% CS solution via tip sonication for 15 min followed by room temperature stirring overnight. The solution was cast onto a Petri dish and dried at room temperature for 3–4 days to eliminate the solvent. Next, the dried PVA–MWCNT/CS nanocomposite membrane was subjected to alkaline treatment by immersion in an alkaline solution (3 wt.% sodium hydroxide, 47 wt.% ethanol, 50 wt.% water) for 24 h followed by washing with de-ionised water and drying at ambient temperature. The resultant PVA–MWCNT/CS nanocomposite membranes were crosslinked by dipping them into a solution consisting of 0.5 wt.% glutaraldehyde (GA) and 0.05 wt.% H_2SO_4 in 80% acetone solution for 20 min and then thoroughly rinsed with de-ionised water to remove any contaminants [25].

2.4. Preparation of three-layer CS/PVA–MWCNT/PVDF nanocomposite membranes

Two types of three-layer CS/PVA–MWCNT/PVDF nanocomposite membranes were prepared: (i) a thin layer of PVA–MWCNTs supported on PVDF (thin PVA–MWCNT/PVDF) coated with a selective layer of CS (CS/thin PVA–MWCNT/PVDF) and (ii) a thick layer of PVA–MWCNTs supported on PVDF (thick PVA–MWCNT/PVDF) coated with a selective layer of CS (CS/thick PVA–MWCNT/PVDF). Firstly, the PVA–MWCNTs were dispersed in water by tip sonication for 15 min followed by filtration through a 0.22-μm PVDF membrane. The bulk-aligned PVA–MWCNTs on PVDF was then left to dry at ambient atmosphere. After that, the dried bulk-aligned PVA–MWCNT on PVDF membrane was scraped off using a spatula to remove the excess PVA–MWCNT before coating with a thin layer of CS solution. Eventually, a three-layer CS/thin PVA–MWCNT/PVDF nanocomposite membrane was formed after drying at room temperature for 3–4 days. The resultant three-layer nanocomposite membrane was subsequently immersed in alkaline solution as mentioned previously for 24 h and then rinsed with de-ionised water. Finally, the three-layer nanocomposite membrane was dried at room temperature. A similar procedure was carried out in the fabrication of the three-layer CS/thick PVA–MWCNT/PVDF nanocomposite membrane, except without scraping off the excess amount of PVA–MWCNTs on the PVDF membrane before coating it with a thin layer of CS solution.

2.5. Characterisation

Thermogravimetric analysis (TGA) was carried out with a TA Thermogravimetry SDT Q600 V20.9. Specimens in powder form were placed in an alumina crucible and heated at a rate of 10 °C min^{-1} from room temperature to 800 °C under air. The thermal stability of raw MWCNT, oxidised MWCNT and PVA–MWCNT were investigated via TGA. Fourier transform infrared (FTIR) analysis was carried out using a Perkin Elmer spectroscope equipped with an attenuated total reflection (ATR) to investigate the presence of functional groups on raw MWCNT, oxidised MWCNT and PVA–MWCNT. The samples in powder form were mixed with potassium bromide (KBr) to form pellets and scanned in the range between 4000 and 400 cm^{-1}. The existence of surface chemical bonding was recorded. The surface and cross-sectional morphologies of the membranes produced were observed via the Quanta 450 FEG Scanning Electron Microscopy (SEM) apparatus. To view the cross-sectional morphology of the membranes, they were dipped into liquid nitrogen and fractured to prevent deformation of the polymer. Based on the SEM images, the dispersion of the PVA–MWCNT in CS polymer matrix was investigated.

2.6. Determination of mechanical properties

The mechanical properties of crosslinked pure CS and crosslinked PVA–MWCNT/CS membranes were studied using the universal testing machine Instron 5567. The Young's moduli of