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Removal of 2-propanol from water by pervaporation using poly(vinylidene fluoride) membrane filled with carbon black

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ABSTRACT

In the present study, several filled poly(vinylidene fluoride) (PVDF) membranes by the addition of various weight fractions from carbon black (CB) to the casting solution were prepared for the removal of 2-propanol from aqueous solution in pervaporation process. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray diffraction (XRD), contact angle and swelling degree measurements were used to study morphology and properties of the prepared membranes. Separation experiments were carried out at a feed temperature of 45 °C and a permeate pressure of 18 mmHg. The results demonstrated that the addition of carbon black filler resulted in formation of the membranes with denser structure; lower permeation flux and degree of swelling; and higher crystallinity, separation factor, contact angle, and pervaporation separation index.

1. Introduction

In industry, organic solvents are often used as cleaner [1]. Alcohols such as ethanol, isopropanol, and n-butanol are the common solvents which are used in this area [1]. Isopropanol is an important solvent and cleaning agent which is widely used in semiconductor, microelectronic, and pharmaceutical industries [2,3]. The industries discharge this organic solvent as a waste, and consequently recycling of wasted isopropanol is essential from environmental and economical point of view [1,3].

Treatment of wastewater containing low level of volatile organic compounds is quite difficult [4]. Pervaporation is a membrane-based separation process which can be used for removal of trace amount of organic compounds from water [5]. Pervaporation is a promising separation technique and also an alternative to distillation due to being economical, energy efficient and environmentally benign [6,7]. When the permeating species is present in low concentrations, pervaporation is economical and attractive [5]. In pervaporation, the minor component is preferentially transported through the membrane which is selected on the basis of its affinity for this component in terms of hydrophilic or hydrophobic nature [5]. Selective removal of alcohols from water by pervaporation process has attracted significant attention over the years [8].

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer which has gained popularity in industries and academies as a suitable membrane material for pervaporation and other membrane processes [9]. PVDF has advantages such as good processability for membrane preparation, mechanical strength, thermal stability, chemical resistance, and hydrophobicity which are very important for the actual application of membranes [9–13].

As a semicrystalline polymer, PVDF membrane formation during phase inversion process is governed by two mechanisms which are named liquid–liquid demixing and solid–liquid demixing (crystallization) [9,10]. Liquid–liquid demixing usually dominates in the rapid phase inversion process and produces the membranes with a relatively dense skin layer and a cellular network structure with macrovoids [9]. In contrast, when a slow phase inversion rate occurs, the solid–liquid demixing takes place to form a macrovoid-free sponge-like porous membrane with interlinked crystalline structure [9,14].

Jian et al. [15] adapted the mixed solvent system with dual mixture of high and low boiling point solvents to prepare integral asymmetric PVDF membranes using phase inversion method for the separation of organic compounds from dilute organic-in-water feed solutions by pervaporation process. Ong et al. [9] stated that the phase inversion rate should be optimized in PVDF membrane formation by a proper choice of mixed solvent system and coagulant bath in order to minimize macrovoids formation formed by rapid phase inversion and avoid interlinked spherulitic crystal structure created most likely by a slow phase inversion. Liu et al. [10] reported that the addition of solvent into a water bath might

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Nomenclature

List of symbols

A	effective surface area of the membrane (m^2)
ΔH_f	melting enthalpy (J/g)
ΔH_f^*	melting enthalpy of fully crystalline PVDF (J/g)
J_i	component flux (Kg/m^2h)
J_t	total permeation flux (Kg/m^2h)
M_d	mass of dry membrane (g)
M_s	mass of swollen membrane (g)
PSI	pervaporation separation index
Q	mass of the permeate (Kg)
T_m	nominal melting temperature (°C)
T_m^f	final melting temperature (°C)
T_m^{on}	onset melting temperature (°C)
ΔT_m	difference between onset and final melting temperatures
t	experiment time (h)
W_p	weight fraction of the polymer
x	mass fraction of species at the feed
y	mass fraction of species at the permeate

Greek letter

β	separation factor

Abbreviations

CB	carbon black
DMAc	N, N-dimethylacetamide
DSC	differential scanning calorimetry
PDMS	poly(dimethylsiloxane)
PEBA	poly(ether block amide)
PVDF	poly(vinylidene fluoride)
SEM	scanning electron microscopy
XRD	X-ray diffraction

induce delayed liquid–liquid demixing and eventually result in the formation of membranes with sponge-like structure.

In the recent years, some research works have been focused on the preparation of organic-inorganic hybrid membranes to modify the membrane properties for the pervaporative separation of mixtures such as alcohol/water ones [10,16]. Filled membranes combine the favorable features of polymers and fillers and have been proved to be the promising materials for pervaporation process [17]. The presence of the dispersed inorganic nanoparticles in the membrane structure can improve the membrane performance by enhancing mass transfer in pervaporation process as well as modification of selectivity and mechanical properties [10].

In order to preparation of modified pervaporation membranes, the incorporation of carbonaceous materials into the polymeric pervaporation membranes was investigated [18–22]. Shi et al. [18] investigated pervaporation characteristics of the poly(dimethylsiloxane) (PDMS) membrane filled with carbon black for the separation of ethanol from water. Their results indicated that the flux was remarkably increased without reducing the selectivity in the certain ranges of the composition. Panek and Konieczny [20,21] prepared PDMS and poly(ether block amide) (PEBA) membranes filled with carbon black for the pervaporative separation of toluene from the aqueous solutions. They observed that the mentioned filler had a relevant influence on the total permeate flux. In the case of the filled PEBA membranes, the permeate flux and separation factor were increased and decreased, respectively. However, in the case of the filled PDMS membranes the permeation (mainly the permeation of water) was reduced and the efficiency indexes of the process were improved.

The purpose of the present study was to develop a hydrophobic membrane with proper overall pervaporation performance. Therefore, the PVDF membranes filled with CB particles were prepared and used for the separation of 2-propanol/water mixture by pervaporation process.

2. Experimental

2.1. Materials

PVDF supplied by Zibo Yichi International Trading Co. Ltd., was used as polymer. N, N-dimethylacetamide (DMAc, 99%, Merck) and acetone (extra pure, Mojallali Chemical Industries Complex Co.) were applied as solvent. Carbon black powder (CB, N330 grade) with the average primary particle size of 30 nm was kindly supplied by Pars Carbon Black Company. Furthermore, distilled water was used as nonsolvent in coagulation bath. For preparation of pervaporation feed, distilled water and 2-propanol (≥99.5%, Merck) were used.

2.2. Membrane preparation

The PVDF membrane without filler was mainly prepared using a procedure that was reported by Jian et al. [15]. PVDF polymer was dissolved in a mixed solvent system consisting of acetone and DMAc which have a low and high boiling point, respectively. Casting solutions were prepared using PVDF (10 wt.%), DMAc (40 wt.%), and acetone (50 wt.%), which were stirred for 2–3 h at room temperature. After the removal of gas bubbles, the solution was cast onto the glass substrate and then the resulting film was air dried for 10 min. Three precipitation baths were used for the membrane formation. The first bath was composed of 50 vol.% of water, 40 vol.% of acetone, and 10 vol.% of DMAc. The second bath was composed of 60 vol.% of water and 40 vol.% of acetone. The film with glass plate was immersed in the first bath for 15 min and the membrane was separated from the glass plate. Afterward, the membrane was submerged for 15 min in the second bath and then for 30 min in a third bath containing distilled water and finally was exposed to air for drying at room temperature.

The typical procedure for preparation of the filled PVDF membranes was as follows: At first, a predetermined amount of CB filler was added to DMAc solvent and the mixture, 40 wt.% of final casting solution, was stirred under room temperature for 30 min. Then, PVDF powder (10 wt.%) and acetone (50 wt.%) were added into the resultant solution, respectively. The recent mixture was stirred under room temperature for 4–5 h to ensure complete dissolution of the polymer powder. Next, the final solution was allowed to degas overnight before the casting process. Membrane casting procedure is similar to the unfilled PVDF membrane preparation. Four different weight percentages (0.5%, 1%, 1.5%, and 2%) of CB filler were applied in preparation of the filled membranes. Using more than 2 wt.% of CB resulted in preparation of heterogeneous and brittle membranes which could not be characterized.

2.3. SEM test

In order to investigate the surface and cross-sectional morphology of the prepared membranes, the samples were photographed using a scanning electron microscope (LEO 1450VP). For the cross-sectional views, before SEM tests, all the samples were fractured in liquid nitrogen to obtain smooth cross-section.

2.4. DSC test

DSC studies were conducted for the unfilled PVDF membrane and the PVDF membranes filled with 1 wt.% of CB to examine the