Hybrid Nanocomposite Membranes of Polyvinylalcohol/3-Glycidyloxypropyl Trimethoxysilane Incorporated With Chemically Modified Phosphotungstic Acid Used In Pervaporative Dehydration of Methanol

Seema. S. Pattanshetti & G. S. Gokavi
Department of Chemistry, Shivaji University, Kolhapur 416 004, India

Abstract: Novel hybrid nanocomposite membranes of polyvinyl alcohol (PVA)/3-glycidyloxypropyl trimethoxysilane(GPTMS) incorporated with 3, 6 and 9 wt. % of cesium salt of phosphotungstic acid (Cs-PWA) were prepared by solution casting using sulfosuccinic acid (SSA) as a cross-linking agent. Membranes were characterized by thermogravimetric analysis(TGA), contact angle, universal testing machine(UTM) to study their efficiency in methanol dehydration in terms of the concentration of Cs-PWA filler as well as feed water composition and temperature. The membrane characterization to understand their morphology and adherence during the pervaporation(PV) operations.

Key words: Phosphotungestic acid, 3-glycidyloxypropyl trimethoxysilane(GPTMS), Pervaporation, water-methanol mixture.

1. Introduction

Hybrid nanocomposite polymeric membranes prepared by incorporating inorganic fillers into the host polymer matrix have been widely explored in pervaporation (PV) separation of aqueous-organic mixtures [1-3]. Majority of nascent (unfilled) polymeric membranes find limited applications due to excessive swelling, thereby leading to performance failure. Inorganic compounds like polyoxometalates (POMs) in nanoparticulate size range possess acidity more than a mineral acid that are hydrated to a large extent and efforts have been made to incorporate these into the host polymer matrix [4]. In this category, polyvinylalcohol (PVA) is a widely studied membrane material in liquid separation due to its hydrophilicity, stability, compatibility and good film forming properties [3], but high swelling tendency of PVA restricts its application. The terminal oxygens of POMs can easily interact with hydroxyl groups of PVA and water molecules to accelerate the separation performance. In order to improve the membrane performance of PVA, precursors like phenyltriethoxysilane [6] and γ-glycidoxypropyl trimethoxysilane (GPTMS) [7] have been tried that can prevent macro-phase separation during membrane formation, thus offering enhanced compatibility between organic and inorganic phases, since GPTMS contains organically modified alkoxide moiety containing epoxy ring.

In order to suppress swelling and improve the separation performance of PVA, herein we report preparation of hybrid nanocomposite membranes of PVA/3-GPTMS incorporated with 3, 6 and 9 wt. % of Cs-PWA nanoparticles (180-190 nm) by solution casting cross-linked by sulfosuccinic acid (SSA) to achieve methanol dehydration. The leaching tendency of nascent phosphotungstic acid (PWA) can be avoided by converting it as cesium salt Cs-PWA), which when incorporated into the host polymer matrix could considerably reduce its solubility in water. Also, by cross-linking PVA with sulfosuccinic acid (SSA) in the presence of silica domains, dense membranes can be obtained to provide enhanced barrier performance over that of nascent PVA membrane during methanol dehydration. The nano composite membranes were characterized by contact angle measurement, TGA & UTM.

2. Experimental

2.1. Materials

Polyvinylalcohol of MW = 125,000 was received from SRL, Mumbai, India. Cesium carbonate, methanol and phosphotungstic acid (PWA) were procured from s.d. fine Chemicals, Mumbai, India; 1,3-glycidoxypropyl trimethoxysilane was obtained from Hi Media, Mumbai, India and sulfosuccinic acid was purchased from Aldrich, Mumbai, India. All other chemicals were of reagent grade samples used without further purification. Double-distilled water was used throughout the study.

2.2. Membrane preparation

Cesium salt of phosphotungstic acid [8, 9] incorporated PVA–GPTMS hybrid nanocomposite membranes were prepared by solution casting. First, PVA solution was prepared by dissolving 6 g of PVA in 100 mL double distilled water at 90°C.
The solution of GPTMS was prepared by dissolving required quantity in 25 mL of ethanol with 0.1N HCl and stirred for 2 h. Both PVA and GPTMS solutions were mixed and the resulting solution was filtered to get clear solution after constant stirring for 24 h. In situ cross-linking was done by adding 0.5 mL of sulfosuccinic acid (SSA) to the filtered solution. The cesium salt of phosphotungstic acid (Cs-PWA) in amounts of 3, 6 and 9 wt.% with respect to weight of the polymer were added as filler and the resulting solution was cast as a film of uniform thickness onto a clean glass plate in a dust free environment.

The membranes obtained were dried at 80°C for 6 h and peeled off from the glass plate. The thickness was measured using a micrometer screw gauge found to be around 50±3 µm. Membranes were designated as: M-0(without Cs-PWA), M-3, M-6 and M-9, respectively containing 3, 6 and 9 wt. % of Cs-PWA.

To analyze the effects of annealing on physicochemical structure and permeation performance the hybrid composite membrane was annealed at 100°C and 120°C for 12 h in vacuum oven maintained at 100°C C for 3, 6 and 9 h, respectively. The PV performance of the membranes was found to be not affected by the temperature of annealing.

Feed and permeate samples were analyzed by gas chromatography (Model Ultima 2100, Netel India Ltd, Mumbai) installed with a thermal conductivity detector (TCD) by maintaining the oven temperature at 100°C, while the injector and detector temperatures were maintained at 150°C. The sample injection volume was 1 µL and pure hydrogen was used as a carrier gas at a pressure of 1 kg/cm². The GC response was calibrated with the known compositions of methanol - water mixtures and calibration factors were fed into the software to obtain the correct analysis for unknown samples.

Pervaporation (PV) unit consists of a stainless steel cell [5] provided with water circulating jacket for maintaining a constant temperature. The feed mixture in the cell was stirred using a three-blade stirrer at 200 rpm speed by applying a downstream vacuum pressure of 6 mbar using a vacuum pump (Model ED-21, Hindhivac, Bangalore, India). Effective surface area of the membrane was 26.03 cm² and the liquid volume capacity of the PV cell was 200 cm³. Test membrane was equilibrated for 3 h with the feed mixture before performing the PV experiments. Permeate was collected in cold nitrogen traps and weighed on a digital microbalance at ±0.01 mg after attainment of ambient temperature. The concentrations of water and ethanol of the feed and permeate were estimated by gas chromatography.

The PV performance of the membranes was assessed by calculating total permeation flux (J) and separation factor (β) using:

\[ J = \frac{W_t}{A \times t} \quad \text{(kg/m}^2\text{h)} \]

(1)

Where \( W_t \) is weight of permeate (kg), \( A \) is effective area of the membrane (m²) and \( t \) is permeation time (h).

\[ \beta = \left( \frac{P_w}{P_m} \right) \times \left( \frac{F_m}{F_w} \right) \]

(2)

Here, \( P_w \) and \( P_m \) are wt. % of water and methanol, respectively in permeate; \( F_m \) and \( F_w \) are wt. % of water and methanol in the feed. The membranes remained intact even if continuously used in PV experiments up to 8 h.

Mechanical properties of the membranes were measured using universal testing machine (UTM) (Model H25 KS Hounsfield, Surrey, United Kingdom). Test dumbbell shaped test specimens were prepared as per ASTM D-638 standards. Membranes of gauge length of 50 mm and 10 mm width were stretched at the crosshead speed of 10 mm/min.

TGA thermo grams were obtained using SDT 2960 (TA Instruments, USA). Measurements were performed at the heating rate of 10°C/min in a nitrogen atmosphere. Static contact angles between water and membranes were measured using contact angle meter (Rame-hart, Model 500-F1, USA) at 27°C. Static contact angles between water droplet and membrane were measured by contact angle meter (Rame-hart, Model 500-F1, USA) at 27°C.

Equilibrium swelling was performed gravimetrically at 27°C on circularly cut membrane sample (3cm dia). Dry samples were weighed on a single-pan digital microbalance (model AE 240, Mettler, Switzerland) and these were placed in water-methanol mixtures (vol.20 cm³) containing 10, 15, 20 and 25 wt. % of water at 27°C in airtight test bottles. Swelling was also measured in pure water and methanol. Test bottles were transferred to oven maintained constant at 27°C for 48 h. The swollen membrane samples were weighed immediately after blotting off the liquid droplets by pressing between the filter paper wraps and % equilibrium swelling. \( DS \) was calculated as:

\[ \text{Equilibrium Swelling} \times 100 = \left( \frac{W_e - W_d}{W_d} \right) \times 100 \]
Where $W_s$ and $W_d$ are weights of swollen and dry membranes, respectively. The sorption selectivity, $\alpha_s$ was calculated as:

$$
\alpha_s = \frac{M_w}{M_m} \times \left( \frac{F_w}{F_v} \right)
$$

(4)

Where $M_w$ and $M_m$ are, respectively mass fraction of water and methanol in the membrane; $F_w$ and $F_v$ are those of water and methanol in the feed. Diffusion selectivity, $\alpha_d$ was calculated using the solution-diffusion theory [10].

$$
\alpha_d = \left( \frac{\alpha_0}{\alpha_s} \right)
$$

(5)

Here, $\alpha_0$ and $\alpha_s$ refer to real selectivity and sorption selectivity, respectively. Considering the volatile nature of methanol, sorption experiments were repeated thrice and the results obtained within ±3% of standard errors were considered for further analysis.

Membrane density was measured by benzene displacement method. Initially, empty and benzene filled specific bottles were weighed and then a weighed quantity of the membrane was introduced into benzene-filled bottle. Excess benzene was wiped out using a soft tissue paper to measure the weight of bottle plus benzene and the membrane. Density of the membrane was calculated from the difference in weights and volume of the bottle.

**Results and Discussion**

Realizing that surface property of the membrane reflects its PV performance, and in order to quantify whether the membrane surface acquired higher hydrophilicity at higher concentration of Cs-PWA, we have measured water contact angle, $\theta$ that represents surface tension of a liquid and a solid in addition to interfacial tension. The $\theta$ values measured (Table 1) between water droplet and membrane surface show increasing trends with increasing Cs-PWA concentration, indicating increase of membrane hydrophobicity.

TGA curves measured under the flow of nitrogen gas shown in Fig.1 show first weight loss for all the membranes at 150°C due to the loss of absorbed water molecules that might exist in a bound state [11]. The second weight loss occurred at 470°C, due to the residue of PVA and Cs-PWA hybrid nanocomposite membranes containing silica precursor at 475.09°C that was higher than the pristine membrane at 468.16°C with a weight loss of 33.09% (or 3.433 mg). In addition, the weight residue of membrane at 475.09°C was higher than M-0 due to higher degree of cross-linking. However, increasing concentration of Cs-PWA induces high cross-link density of the PVA matrix, leading to increased residual char at 475.09°C with a weight loss of 44.34% (or 4.670 mg). These results suggest that degree of cross-linking as well as introduction of silica and Cs-PWA nanoparticles into PVA chains would enhance thermal stability of the membrane matrix.

In order to understand the mechanical strength properties of the membranes, tensile strength of pristine and hybrid nanocomposite membranes were measured using universal testing machine(UTM). For M-0, M-3, M-6 and M-9, the observed increasing values of tensile strengths of 14.2, 20.8, 22.9 and 23.2 (N/mm²), respectively indicate improved strength properties after loading with Cs-PWA nanoparticles; enhancement in mechanical strength properties may not only be due to the addition of CS-PWA, but also presence of silane particles in the PVA matrix. The high chain-segmental mobility of M-3, M-6 and M-9 membranes exhibit lower elongation-at-break of 3.41%, 3.32% and 1.92%, respectively compared to pristine membrane for which it is 3.44%, due to ionic cross-linking of the polymer matrix. Another evidence for this observation may be restriction in chain mobility of the polymer as result of electrostatic interactions, resulting in increase of rigidity or tensile strength. The corresponding Young’s modulus values are 18.3, 27.1, 29.7 and 53.5, respectively for the nanocomposite membranes, indicating increased mechanical strength with increased filler loading. Intra and inter molecular bonding interactions involved in the polymeric matrix besides the formation of interpenetrating polymer network upon cross-linking by filler nanoparticles are also responsible for such increased mechanical strength.

Table 1 displays the flux and separation factor values at azotropic mixture composition (96 wt. % Methanol + 4 wt. % water) at ambient temperature along with contact angle. The data shows a systematic decrease in flux at increasing loading of Cs-PWA as in case of M-3, M-6 and M-9 compared to M-0 membrane. This is due to increased interaction of polymer chains with water giving higher separation factor with a decrease in flux. At high filler loading, the membrane becomes rigid, causing a reduction in free volume, thereby resulting in a reduced flux. It is also noticed that with increasing temperature, separation factor values increase, but the flux values decrease in comparison to M-3, higher separation factor values are observed for M-6 and still higher values for M-9.

In a PV process, permeation flux and selectivity are dependent on membrane swelling that occurs due to the sorption phenomenon as a
result of interactions between membrane and transporting liquid molecules. Equilibrium swelling (sorption equilibrium) of the membranes was measured and these data at ambient temperature are shown in Table 1. The data of Table 1 show higher equilibrium swelling with respect to water than methanol, due to increased interactions between water and OH groups of the membrane that are capable of forming H-bonds with water molecule. These interactions seem to be prominent for water at which amorphous regions of the membrane may be highly swollen such that polymer chains become more flexible. This would facilitate easy transport of water molecules through membrane, but the presence of Cs-PWA might decrease the flux and increase the separation factor.

Conclusions

In this work, we have developed hybrid nanocomposite membranes having good thermal properties and enhanced mechanical strengths. The membranes are effective to dehydrate methanol. Membrane performance was enhanced at the highest loading of 9 wt. % of Cs-PWA, suggesting their successful application in PV dehydration at ambient temperature.

Acknowledgement

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References:

Fig.1. Thermo gravimetric analysis (TGA) curves of M-0, M-3, M-6 and M-9 membranes.

![Thermo gravimetric analysis (TGA) curves of M-0, M-3, M-6 and M-9 membranes.](image)

Table -1 Result of contact angle, mechanical properties & pervaporation performance of the membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact angle (θ)</th>
<th>Equilibrium swelling in water (N/mm²)</th>
<th>Tensile strength (N/mm²)</th>
<th>Young’s modulus (N/mm²)</th>
<th>Elongation at break (%)</th>
<th>Flux J (kg/m²h)</th>
<th>Separation factor (βij)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-0</td>
<td>66</td>
<td>115.9</td>
<td>14.2</td>
<td>18.3</td>
<td>3.44</td>
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<td>7958</td>
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<tr>
<td>M-3</td>
<td>78</td>
<td>107.4</td>
<td>20.8</td>
<td>27.1</td>
<td>3.41</td>
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<tr>
<td>M-6</td>
<td>83</td>
<td>87.3</td>
<td>22.9</td>
<td>29.7</td>
<td>3.32</td>
<td>1.565</td>
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<tr>
<td>M-9</td>
<td>88</td>
<td>76.4</td>
<td>23.2</td>
<td>53.5</td>
<td>1.92</td>
<td>1.561</td>
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