Synthesis of Polypropylene/ Polyethylene based composite and its Application

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Received 6 August 2018; revised 4 January 2019; accepted 16 June 2019

At present juncture Membrane separation is an emerging area of research and is being widely used in different kind of industrial applications. Among the different processes, pervaporation process has a lot of advantages as compared to others. In this paper, synthesized membrane is used for separation of ethanol-water mixture. Polyethylene (PE)/polypropylene (PP) blend composite membrane was synthesized using solution casting in situ polymerization method. To enhance the properties of the composite membrane various crosslinking agents and fillers are added. In this paper, the results are presented for membranes that are preferentially permeable to ethanol and also for those that are preferentially water permeable.

Keywords: Polyethylene/polypropylene composite, Pervaporation, Ethanol-water mixture, Membrane

Introduction

In Modern era, Pervaporation has emerged as one of the most efficient separation technique for several industrial applications. Pervaporation, a membrane-based separation technology, provides advantages such as energy efficiency, selective separation, removing liquid at low concentration as compared to other conventional separation techniques such as distillation and absorption processes in separating azeotropic mixtures, thermally sensitive compounds and organic–organic blends, as well as in removing dilute organic compounds from different constituents. For pervaporation, the hydrophilic membranes were the first one to achieve the industrial applications and were used for the organic solvent dehydration. In pervaporation, currently, hydrophobic membranes are used for separating volatile organic compounds from the body of water. The membrane only allows permeating the volatile organic compound and rejects water molecule due to its hydrophobic nature. Zhang et al. used PIM-1/PDMS hydrophobic membrane for separation of butanol-water mixture. Some authors used polyethylene/polypropylene composite membrane for improving the thermal stability of Lithium-Ion battery and desalination application. Some authors have also used reinforcing agents such as human hair, nanosilver and porcelain for enhancing the mechanical stability of the polymer composite. In this study, a polyethylene/polypropylene composite membrane is prepared using different cross-linking agents and fillers for enhancing the properties. Moreover, prepared composite membranes have been tested separation of ethanol-water mixture using pervaporation technique.

Experimental

Materials

Polyethylene (HDPE) granules of 0.95 g/ml were procured from Alfa Aesar India. Polypropylene was purchased from OTTO Chemicals India and solvents like xylene, toluene and trichlorobenzene were procured from Avra Synthesis Private Ltd. Ethanol and distilled water was used for pervaporation. All chemicals were used without further purification. 1,2,4 Tri Chlorobenzene was used as a solvent. Different fillers and cross-linking agents such as Nanoclay, Titanium dioxide and Silica were used. Diethyl Phthalate was used as a plasticizer. Ethanol-water mixture was used to study the performance of the prepared membranes.

Preparation of polyethylene/polypropylene membranes

The solute polyethylene/polypropylene and the solvent tri-chlorobenzene were mixed at a temperature of 150°C and stirred in a magnetic stirrer for 5 hours for uniform dispersion. The sample was sonicated for an hour and the sample was cast on a flat plate and allowed to dry in an open atmosphere for 24 hours. Then the sample was heated at a temperature of 160 °C for 15 minutes. The sample was dried in open atmosphere and detached from a
flat plate. To enhance the properties of the membrane different kind of cross linking agents and fillers were added\(^9\). The Table 1 below shows the composition of solvents and fillers added.

**Analytical methods**

**Scanning Electron Microscopy (SEM) analysis**

Scanning electron microscopy was used to know the surface morphology of all prepared polyethylene/polypropylene membranes using a Zeiss EVO 18 scanning electron microscope.

**Fourier Transform Infrared (FTIR) analysis**

FT-IR of permeates collected after the pervaporation experiment was carried out. It was used to identify the functional groups and to know the changes in the hydrophobic character. FT-IR spectra were obtained using Nicolet 5700 spectrometer in transmittance mode from 400 to 4000 cm\(^{-1}\) wavelength.

**Pervaporation**

The above flow sheet in figure 1 depicts pervaporation membrane setup which was designed and fabricated for ethanol-water separation. The mixture of ethanol-water was stored in the feed tank. The solution before being sent to the membrane module is preheated to the desired temperature, generally around 45-50°C with the help of heater. The membrane module, where the membrane is fitted with two airtight steel plates with the help of screws and bolts is shown in figure 1. Membrane module contains three ports upper side which may or may not be used depending on our need and one port on the bottom side. On the upper side one port is the inlet feed port from where the feed enters into the module. Second port is for bypassing the retentate liquid. There is an outlet port for permeate at the bottom of the module which is placed in a condenser. The vacuum pump is connected to the downstream side to maintain the downstream pressure less than 5 mm Hg. The condensed permeate vapors were finally collected in the permeate collector.

**Refractive index test (RI) analysis**

The refractive index (RI) was determined for permeate samples. For this calculation, a different ratio of Ethanol-water samples was prepared and find out the refractive index for each sample using Abbe Refractometer (RSR-1, Rajdhani Scientific instrument Co., India). A reference graph was plotted for RI with a change in the mass fraction of ethanol.

**Results and Discussion**

The membrane is an essential component of a membrane separation process. Five samples of membrane were prepared by solution casting method involving various fillers and composition. Results of investigations carried out are presented in the sections to follow.

**Scanning electron microscopy (SEM) analysis of polyethylene/polypropylene membranes**

The SEM shows the surface of the polymer composites (Figure 2). In the "scanning" process, the electron beam interacts with the surface region and generates secondary electrons from the composite. Figure 2(a) depicts the plain surface with some polypropylene found at the surface of polyethylene/polypropylene blend membrane. The membrane was mainly non-porous. To enhance its properties fillers and crosslinkers were used. Figure 2(b) shows irregular structure of the polyethylene/polypropylene membrane/diethyl phthalate membrane. Figure 2(c) exhibits the roughness of nanoclay reinforced polyethylene/polypropylene/diethyl phthalate membrane. It can be seen that the surface became harder and rough as compared to pure polymeric composite membrane. Nanoclay was added to enhance the membrane strength of polymeric membrane. Diethyl Phthalate was added as the plasticizer to enhance the plasticity and reduce the viscosity. Figure 2(d) represents the fractured surface of silica reinforced polyethylene/polypropylene membrane. Figure 2(e) shows agglomeration of particles occurred at surface of polyethylene/polypropylene/titanium dioxide membrane.

Fig. 1 — Schematic diagram of experimental setup
Pervaporation studies

The ethanol-water mixture was passed through the different membranes at different feed concentrations and the performance was noted. Several compositions of the ethanol-water mixture were used to measure the flux of ethanol across the membrane in order to study the performance of prepared membranes. Table 1 shows the change in flux of different membranes concerning change in concentration. The membranes were subjected to feed concentration of 15%, 40% and 60% respectively. From the figure, it can be concluded that the flux of the membranes are in the order of

SL5>SL4>SL3>SL2>SL1

The membranes are made of different crosslinkers and fillers. A particular membrane is passed through three different concentrations. It can be seen that on increasing the feed concentration the flux of the membranes increases. Also, it can be revealed that the flux increases with the change in the filler added. The membrane SL1 made of polyethylene-polypropylene shows the least amount of flux. On addition of the plasticizer diethyl phthalate the membranes plasticity increases and the viscosity decreases. Thus the flux is increased. This can be observed in membrane SL2 which showed enhanced property compared to SL1.

The membrane SL3 was made by the addition of nanoclay. This gives excellent roughness surface and hence the flux was further enhanced. The membrane prepared by the addition of silica is SL4. The presence of silica provided a barrier to the movement of water, but the flux increased on account of the increase in the amount of ethanol collected. Similarly, the addition of Titanium dioxide led to an increase in flux because of the increase in the amount of permeates collected. It was found that on using membranes of higher concentration of fillers the flux further decreased because the fillers acted as a barrier for swift movement of the permeate at higher concentrations. The water flux also varied through these membranes. Thus the selectivity increases with the increase in concentration of feed, but the degree of separation decreased at higher ratios.

**Fourier-transform infrared spectroscopy (FTIR) analysis of permeates**

The primary objective of the present work is to determine the best membrane for permeation as the membrane which gives the maximum flux may not necessarily provide the maximum amount of ethanol. To determine the functional group present in the samples, FTIR analysis of permeates was done. The ethanol-water mixture was passed through the membrane and based on the amount of permeate

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**Table 1 — Compositional details for synthesized all polymeric membranes, Flux variation with different alcohol-water concentration change and Mass fraction of ethanol in Permeates**

<table>
<thead>
<tr>
<th>Membrane name</th>
<th>Base polymer(g) (PE)+(PP)</th>
<th>Solvent(ml) TCB</th>
<th>Filler(g)</th>
<th>Flux for different Alcohol-water concentration (wt%)</th>
<th>Mass fraction of ethanol in Permeates</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL1</td>
<td>2 + 0.5</td>
<td>20</td>
<td>Nil</td>
<td>5.98 7.37 9.89</td>
<td>0.0422</td>
</tr>
<tr>
<td>SL2</td>
<td>2 +0.5</td>
<td>20</td>
<td>0.2 (Diethyl Phthalate)</td>
<td>7.11 11.18 16.54</td>
<td>0.0772</td>
</tr>
<tr>
<td>SL3</td>
<td>2 +0.5</td>
<td>20</td>
<td>0.2(Diethyl Phthalate)+0.2 (Nanoclay)</td>
<td>8.16 12.97 17.33</td>
<td>0.7464</td>
</tr>
<tr>
<td>SL4</td>
<td>2 +0.5</td>
<td>20</td>
<td>0.5(Silica)</td>
<td>9.71 13.34 18.67</td>
<td>0.2183</td>
</tr>
<tr>
<td>SL5</td>
<td>2 +0.5</td>
<td>20</td>
<td>0.25 (TiO₂)</td>
<td>10.42 14.81 19.47</td>
<td>0.5352</td>
</tr>
</tbody>
</table>
collected, FTIR of permeate gave peaks of ethanol and alkanes. From the figure 3(a), we can see peaks at wavenumber 1647.8 cm⁻¹ for all membrane samples. This shows the presence of alkanes. The peaks of O-H stretching can be found in the range of 3400 cm⁻¹ to 3640 cm⁻¹. From the graphs, we can deduce that curve of the membrane SL3 consist of the widest –OH group curve. A small peak is found at 1026 cm⁻¹. This is followed by the presence of small peaks at 2258 and 2973 cm⁻¹. All these peaks show the alcohol alkene stretch.

Refractive index test (RI) analysis of permeates

The refractive index was measured to determine the mass fraction of permeates using a reference plot (Figure 3(b)). The results of mass fraction obtained from the refractive index test analysis confirm that the membrane in decreasing order of ethanol composition is:

SL3>SL5>SL4>SL2>SL1

Thus we can conclude that membrane SL3 is best for pervaporation process of the ethanol-water mixture.

Conclusions

In this paper, Hydrophobic Polyethylene Polypropylene membrane samples were used for Ethanol-water mixture separation with varying fillers concentration. Ethanol-water mixture was used as the feed and permeated collected was examined. The ethanol flux through the membrane increased with the increase in crosslinker to pre-polymer ratio, but at higher concentrations, it creates defects in the membrane giving increased water flux together with high ethanol flux. The membrane prepared with TiO₂ filler gave the maximum flux. Also, the membrane prepared by adding plasticizer diethyl phthalate and nanoclay gave the best pervaporation result for 60% concentration of the feed. FTIR analysis and refractive index of permeate confirmed the above results.

References

