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Pervaporation of Ethanol/Water Mixtures by Polyethylene based Fly Ash Composite Membranes

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In this study new cross-linked polyethylene based membrane was prepared by solution casting method in the presence of solvent Xylene using different proportions of fly ash particles. These composite membranes showed good selectivity and flux towards organics separation as compared to pure polymer membrane. Membranes were used in a lab scale pervaporation setup to separate 10 wt. % of ethanol water mixture. Membrane sample M4 with 10 wt. % of total polymer content showed the highest flux during experiments i.e. 873 gm/m^{2}h and separation factor was also best for this sample.

Keywords: Alcohol Water Separation, Fly Ash, High Density Polyethylene, Pervaporation

Introduction

Pervaporation is an energy-efficient process of separating mixtures by membrane permeation and evaporation in its most accessible form. For a multitude of procedures, it is regarded as an appealing alternative to other techniques of separation. With the low temperatures and pressures engaged in pervaporation, for instance, it often has cost and efficiency benefits in separating constant-boiling azeotropes. Pervaporation is also used to remove organic solvents from aqueous streams and to dehydrate organic solvents. Furthermore, pervaporation has appeared as a good option for products susceptible to heat separation. The implementation of membrane separation processes in the separation of alcohol-water is increasing quickly. Conventional separation methods such as distillation, adsorption, liquid-liquid extraction, and crystallization are often inefficient and insufficient. Contemporary membrane technology can save process expenses because energy consumption is small, raw materials and nutrients can be retrieved and recycled, fermentation procedures can be performed continually, and disposal issues can be decreased or eliminated.[1]

Many studies have been carried out on the separation of alcohol-water from its solution by pervaporation. Several membranes have also been used for the separation process. Membranes produced by using various polymers like polyethylene[2], polydimethylsiloxane[3], polyvinyl alcohol[4], polyamide[5], polyvinyl chloride[6], cellulose acetate[7], and polystyrene[8] are commonly used depending on the demands. The method of separation relies on the type of membrane and the circumstances of the process. Prior studies have shown that Polyethylene membrane had very good separation efficiency because of its properties like high tensile and excellent resistant to most of the solvents.

However, a good pervaporation method is also evaluated from other dimensions. Here a fresh type of membrane is prepared using polyethylene, with fly ash as filler to improve characteristics. It provides great density to membrane structure and efficiency of separation. Various cross-linking agents have also been introduced to improve the characteristics. Fly ash characterization was performed through x-ray diffractometer (XRD) and scanning electron microscope (SEM) and SEM was also used for study for membrane morphology. The experiment of pervaporation was performed, and gas chromatography analysis of the final products was carried out to check that which membrane was more efficient in separation. After the blend is separated, the best membrane is determined based on the separation achieved, and the flux acquired. Ethanol-water is the model compound chosen for pervaporation.

Materials and Methods

Materials

The solute high-density polyethylene is selected, which was purchased from Alfa Aesar India. The

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density of the polymer is 0.95 g/cm^3. Xylene is selected as the solvent for the preparation of the membranes. Polyethylene glycol (PEG) was bought from HPLC, Mumbai and used as a crosslinking agent between polyethylene and fly ash. Fly ash is used at different composition (Table 1), to see the effect of fly ash on the membrane and the pervaporation process. This is collected from Panki Thermal Power Plant, Kanpur, India.

Filler Preparation

The collected fly ash was screened and washed properly. Then it was dried in the oven for 72 hours at 1000°C. After these two basic steps, the sample was separated in various parts for calcination at different temperatures such as 500, 600, 700, 800, and 900°C. After that various characterizations were made to study the physical changes in filler after calcination.

Membrane Preparation

Membranes were prepared by thermal induced phase separation method.[9] The solute and the solvent were mixed at a temperature of 150°C and stirred in a magnetic stirrer for 5 hours for uniform dispersion and then heated again 1 hour without stirring to remove any air trapped due to vigorous stirring. The sample was further casted on a flat plate and allowed to cool in an open atmosphere for 24 hours. Then the sample was heated at 160°C for 15 minutes. Then the sample was dried in an open atmosphere to get the final film.

Performance Study

Pervaporation separation of the ethanol-water blend was performed with the prepared membranes. An experiment with the configuration was conducted, as shown in the Fig 1. In the membrane module, the membrane was sliced and clamped. Care was taken to ensure that the module was airtight. The permeate container was kept in a chiller to guarantee that the vapours were condensed. Ethanol-water feed mixture was heated at 50°C. The respective membrane region has been calculated. Using the vacuum pump, the permeate pressure was kept below 5 mm Hg. Ethanol composition was held with water at 10 %. The vapor permeates across the membrane was condensed in a condenser with the assistance of a chiller and eventually gathered in the permeate stack. The experiment was repeated with separate membranes in order to obtain the finest membrane by determining which membrane provides the highest permeate effectiveness gathered. The mean of final results were taken.

Table 1 — Composition of composite membranes

Membrane	HDPE (g)	PEG(g)	Xylene (ml)	Fly ash (g)
M1	2	0.5	50	0.00
M2	2	0.5	50	0.05
M3	2	0.5	50	0.15
M4	2	0.5	50	0.25
M5	2	0.5	50	0.35

Characterization

The thickness of the membrane was measured by the Absolute Digimatic CD-6 CSX Vernier Calliper. The scanning electron microscope was used to visualize the morphology of membrane surface .all the analysis is done using instrument EVO - Scanning Electron Microscope MA15 /18, CARL ZEISS MICROSCOPY LTD. The X-ray diffractometer Rigaku Miniflex 600 Desktop X-Ray Diffraction System, RIGAKU Corporation used for analysis was equipped with monochromatic Cu-Kα radiation (λ=0.154 nm).Nicolet iS5, Fourier Transform Infrared Spectroscopy (FTIR) instrument, made by Thermo Electron Scientific Instruments LLC, Fitchburg, USA used for obtaining FTIR spectra of samples.

Solutes Uptake Ratio of Membranes

Membrane samples (diameter = 5 cm) were dried at 70°C in the oven for 3 days to let any possible mass change occur. The dry mass was denoted as m_1. Then the membrane was immersed into ethanol at room temperature for 3 days. The samples were removed from the solution, external liquid was wiped softly and the weight of swollen sample was measured. The sample was then returned to the solution for 6 hour, removed and weighed again. In all cases, the second mass measurement was within 0.1% of the first measurement, indicating that 3 days immersion was

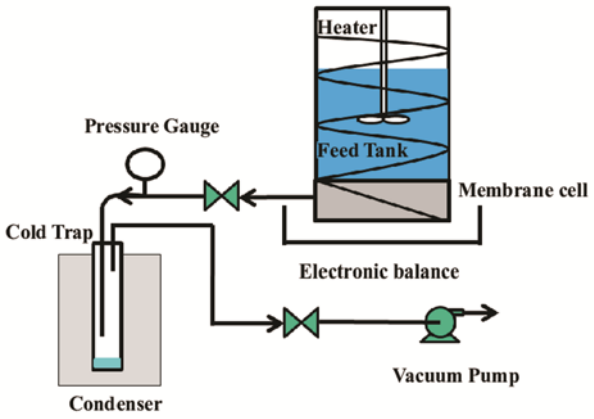

Fig 1 — Schematic diagram of pervaporation experimental set up

sufficient to reach equilibrium. The mass of sample with fluid uptake was denoted as m_2. All experiments were repeated three times for each liquid. The solute uptake ratio, U, is defined as

$$U = \frac{m_2 - m_1}{m_1} \times 100\% \quad \ldots (1)$$

Performance Study

Pervaporation tests were conducted on a lab scale setup using a 10 wt. % ethanol-water model mixture at 50°C. The effective membrane area was 19.625 $*10^{-4}$ m^2. The composition of the permeate collected was calculated by gas chromatography. The total flux J and separation factor α are defined as follows:[10, 11]

$$\text{Total flux (J)} = \frac{Q}{AT} \quad \ldots (2)$$

Where Q (gm) is the total mass of permeate collected in T hours, and A (m^2) denotes the effective area of the membrane.

$$\text{Separation factor } (\alpha) = \frac{Y_A \times X_B}{Y_B \times X_A} \quad \ldots (3)$$

Where X_A and X_B represent the ethanol and water concentrations (wt. %) in the feed solution respectively, and Y_A and Y_B represent the ethanol and water concentrations (wt. %) in the permeate.

Result and Discussion

Scanning electron microscopy was used for morphological studies of fly ash particles and prepared membranes samples. As it is shown in Fig. 2, SEM results revealed that fly ash particles are spherically shaped and are lumped together. However, calcination has distorted the lumps ad particle size was reduced. It is shown in Fig. 2(d) that after calcination at 800°C, lumps were reduced and particles were in decent shape within 2–20 µm size range. Fly ash calcinated at 900°C had shown the similar particle size and structure. So by SEM, analysis it was concluded that fly ash sample S4 was appropriate to use as filler for preparation of HDPE composite membranes.

XRD patterns of all different fly ash sample calcinated at different temperatures are presented in Fig. 3. It was observed that all samples showed sharp and narrow peaks, which verified that elements present in the fly ash were of crystalline nature. Such nature is commonly exhibited by inorganic materials like metals. So XRD spectra verified the presence of different metal oxides in fly ash samples.

After preparation of different HDPE based fly ash composite membrane sample, these were further characterized by SEM to verify the non-porous structure of membranes. The SEM images of different membrane samples M1, M2, M3, M4, and M5 respectively are shown in Fig. 4. All membranes

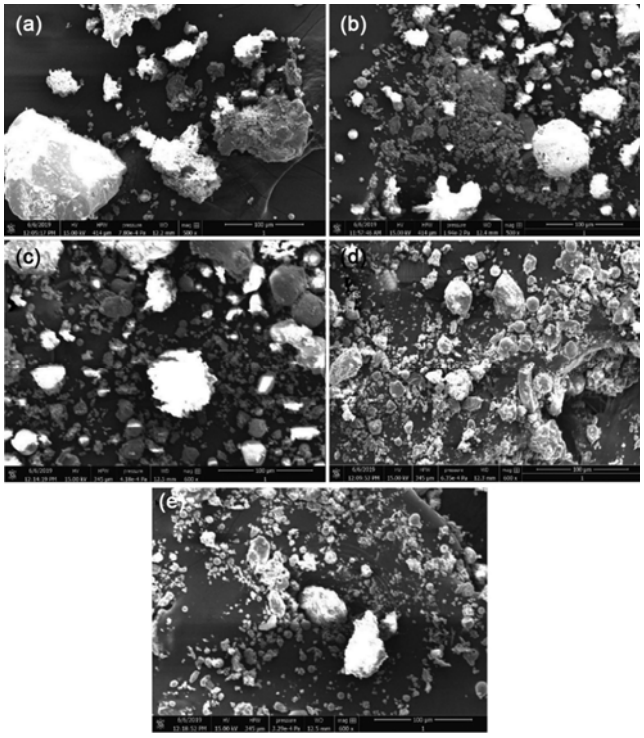

Fig. 2 — SEM images of fly ash particles after calcination at (a) 500°C, (b) 600°C (c) 700°C, (d) 800°C and (e) 900°C

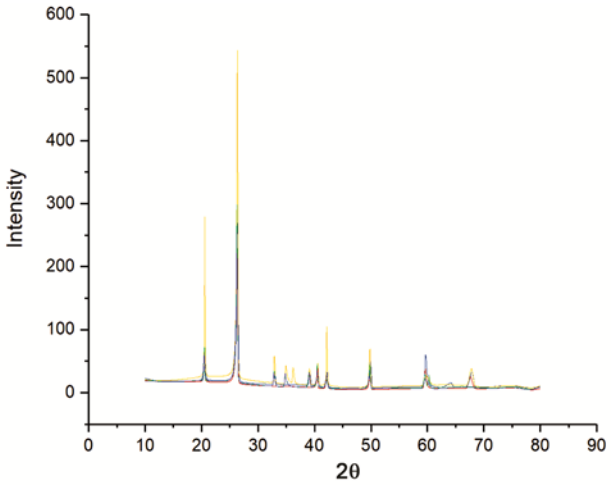

Fig. 3 — XRD spectra of fly ash samples calcined at different temperatures 500–900°C

samples are majorly non-porous in nature, which is required for pervaporation processes. Few spots are visible in SEM images of samples which are not pores, and these spots were created by air bubbles present in the casting solution. The thickness of membrane samples was measured by digital vernier caliper and was found between 60–100 µm ranges.

The solute uptake ratio, U (%), of membrane samples were 11.43, 12.05, 13.22, 14.21, and 14.96%, respectively for ethanol. This shows that ethanol has significant solubility in HDPE, and it was increased with addition of fly ash content into the membrane structure.

Pervaporation Studies

To study the application of the polyethylene composite membrane pervaporation was done. To check the membrane's separation performance ethanol-water mixture was used as feed. The aqueous mixture of 10 wt. % of ethanol was passed through the different membranes and the performance was noted in terms of flux and separation factor. It was found in the experiments that total flux was improved with addition of inorganic fly ash particles within the membrane.

As it is shown in Fig. 5, almost 50% flux was hiked with addition of fly ash in membrane M2 as compared to pure polyethylene membrane M1. Flux across the membrane depends on two factors viz. selective sorption and selective diffusion of solute across the membrane. Presence of fly ash particles have been improved the sorption into membrane body and eased the diffusion at the permeate side. Therefore such enhancement in flux was observed. With a higher amount of fly ash content in membranes M3 and M4, flux was increased to and was highest for M4, i.e. 873 g/m^{2}h. Membrane M5, however, showed a decline in flux. It can be estimated that fly ash addition than an optimum value hander the diffusion through the membrane and intern reduces the flux. Such a phenomenon was similar to the studies of other researchers also.[12–19] Similarly, separation factor was also highest for membrane M4 as shown in Fig. 5.

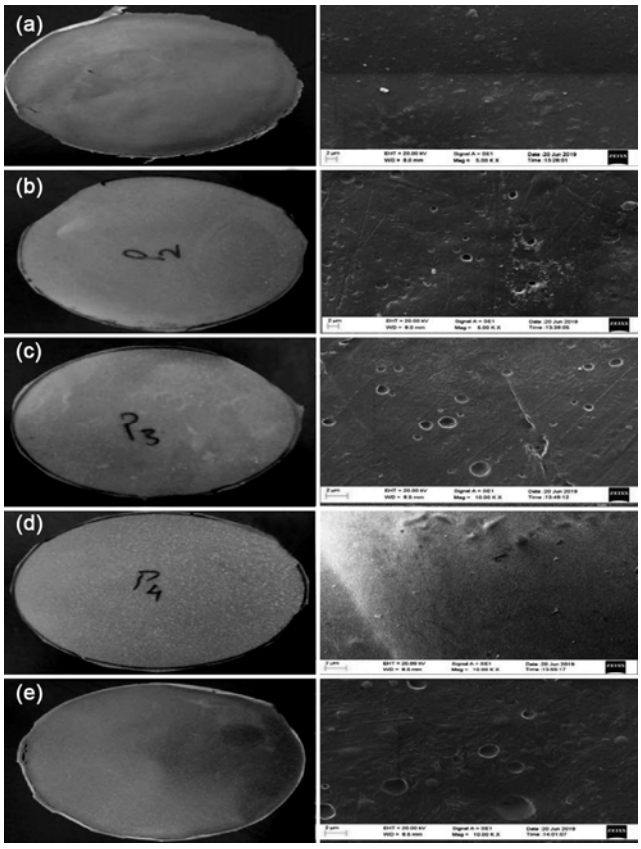

Fig 4 — Normal and SEM images of different membrane samples M1, M2, M3, M4 and M5

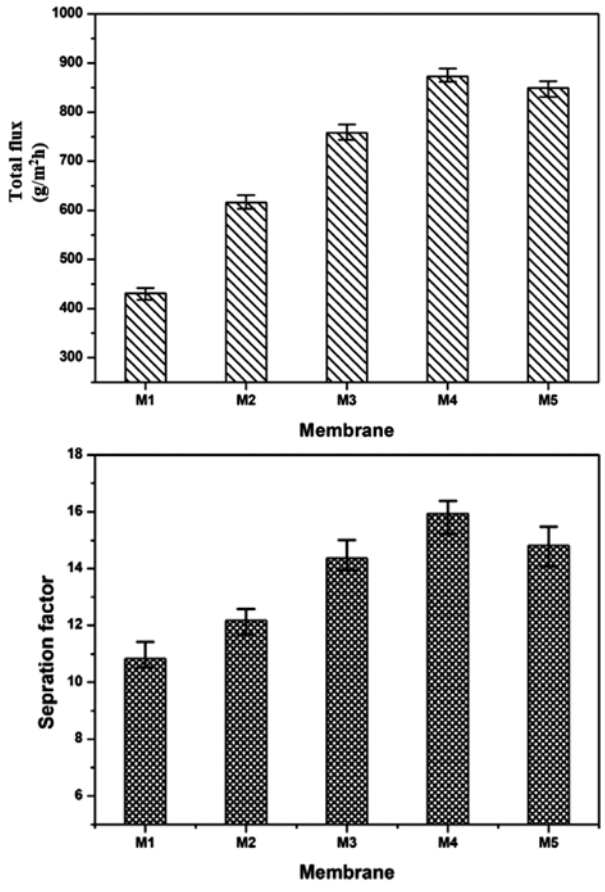

Fig. 5 — Total fluxe and Separation factor for different membrane samples M1, M2, M3, M4 and M5

Conclusions

Composite membranes based on polyethylene were prepared by thermal induced phase separation method using an waste filler material such as fly ash. Five membranes samples were fabricated and characterized by scanning electron microscope to study surface morphology of the synthesized membranes. It was observed that all membranes were non-porous and composite membranes had a good distribution of fly ash into the membrane body. Membranes were further used in a lab-scale pervaporation setup to separate 10 wt. % of the ethanol-water mixture. Membrane sample M4 with 10 wt. % of total polymer content showed the highest flux during experiments and separation factor was also best for this sample i.e. 15.93.

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