

Carbon Black Loaded Composite Poly(Dimethyl Siloxane) Membrane Preparation and Application for Hazardous Chemical Removal from Water

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Industrial waste-water contains hundreds of hazardous chemical components such as volatile organic compounds. Several of the chemicals, such as acetone, are soluble in water. These chemicals pose a threat to the human health and ecosystem. The governments are interested in decreasing the concentration of these chemicals in waste-water by making environmental regulations. Most of the chemical industries have their own waste-water treatment units. These units can separate impurities down to ppm level. After that point, more complicated and costly methods are required. Alternatively, membrane separation methods, such as pervaporation can be used for selective separations of the volatile organic compounds. Pervaporative separation system is defined as environmentally friendly, cost effective process to separate azeotropic and water soluble mixtures. The membrane is the main constituent of the pervaporation and the performance of the separation is directly affected by the membrane selection. In this study, carbon black loaded poly(dimethyl siloxane) mixed matrix membrane was prepared to separate acetone from water by pervaporation. Thermal gravimetric analysis was applied to determine the thermal behavior of the membrane. Inorganic distribution was monitored by means of polarized electron microscopy. Contact angle measurement was applied to determine the effect of filler incorporation on the polymer hydrophobicity. Effect of temperature and feed molar ratio on acetone selectivity and flux were determined.

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1. Introduction

Membrane separation methods are very important for chemical industry to remove many of impurities from the fresh or waste-water [1, 2]. Filtration type membrane separation processes, such as microfiltration and ultrafiltration are prevalent. In these systems, porous membranes are used to retain micro or macro contaminants. However, these membranes cannot separate the ion and dissolved chemicals from the water selectively. At this point, more selective and efficient membrane process is required.

Pervaporation (PV) is a non-porous membrane separation method that is used commercially to separate the dissolved organics from waste-water. Based on the non-porous membrane usage, separation occurs according to the solution-diffusion model. Thanks to the selective character of the pervaporation membrane, it is possible to remove dissolved component from the water in terms of the affinity of the membrane. The performance of the system directly depends on the membrane selectivity, productivity and stability. Membrane is the main constituent of the system, that defines the efficiency of the PV. Therefore, the academic studies have been focused on the appropriate membrane preparation.

Polymeric, inorganic or mixed matrix membranes can be used in PV, according to the component to be

separated. Polymeric membranes are handled easily. However, chemical, thermal and mechanical stability of these materials are relatively lower compared to the inorganic membranes. Inorganic membranes have good stability. Yet, the manufacturing process of the inorganic membranes is complicated. The basis material of the inorganic membrane is expensive and brittle.

Inorganic particle incorporated polymeric membranes, in other words mixed matrix membranes, have the positive properties of both polymeric and inorganic materials [3–5]. They offer such advantages, as easy processibility, easy preparation, and higher chemical, thermal, and mechanical stability. In accordance with the nature of the solvent to be separated, they can be prepared with different polarity.

Based on the water and organic selectivity of the polymer, membranes can be divided into two classifications as hydrophilic and hydrophobic. Hydrophobic materials are appropriate to separate small amounts of organics from the waste-water. Poly(dimethyl siloxane)(PDMS), natural rubber and polyurethane, are well-known types of the rubbery hydrophobic materials. Among them, PDMS is commercially used as pervaporation membrane [4–7].

In this study, selective separation of the acetone from water was aimed. For this purpose, poly(dimethyl siloxane)(PDMS) was selected as membrane matrix. Carbon black (CB) filler was incorporated into the PDMS matrix in order to balance the hydrophobicity of the PDMS, increase the thermal stability of the membrane, and enhance the flux of the permeated solvent. CB has same backbones, as the most organic compounds. It has

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a hydrophobic nature and shows high affinity to the organic compounds over the water [8]. Characterization test was done to determine the thermal and surface behavior of the pristine and mixed matrix PDMS membrane. Pervaporation experiments were performed with different concentration of acetone-water mixtures at different temperatures. System performance was evaluated as a function of total flux, acetone separation factor and pervaporation separation index.

2. Materials and methods

2.1. Membrane preparation

Vinyl terminated PDMS (Silastic New GP30) was kindly supplied by Dow Chemical Company. The pristine and carbon black loaded PDMS membranes were prepared by phase inversion method. Approximately 10 wt.% PDMS was dissolved in chloroform at 50 °C. After a homogeneous phase had been obtained, 5 wt.% CB was added to PDMS solution at room temperature. At the end of the three hours, benzoyl peroxide was added as cross-linking agent. The homogeneous polymer solution was cast onto a Teflon plate and allowed to dry at room temperature. After the membrane had formed, it was cured in an oven to complete the cross-linking reaction.

2.2. Characterizations

Membrane characterizations were done to determine the physical and structural properties of the pristine and carbon black loaded membrane. In order to determine the CB distribution in the membrane, characterization was made by means of Nikon Electron Microscope and KVS Attension contact angle measurement equipment. The thermal behavior of the pristine and CB loaded membrane was analyzed by Mettler Toledo thermo-gravimetric analysis. Fourier-Transform Infrared (FTIR) spectra of the pure polymer and cross-linked PDMS membranes were analyzed by means of Perkin Elmer Pyris 1 FTIR.

2.3. Pervaporation

Pervaporation experiments were carried out with different acetone concentrations, in range from 3 wt.% to 10 wt.%, at different temperatures. The experimental system is shown in Fig. 1.

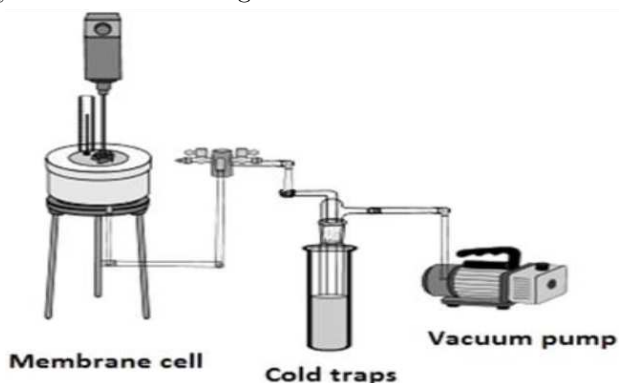


Fig. 1. Experimental pervaporation unit.

The upstream side of the membrane was kept at atmospheric pressure. In the downstream side, vacuum was applied and the pressure was 30 mbar. The total volume of the mixture was kept constant at 200 ml. The effective separation area of the membrane was 19.625 cm². Pervaporation performance was evaluated as function of flux J . Acetone separation factor and pervaporation separation index were defined elsewhere [9].

3. Results and discussion

3.1. Characterization results

The surface images of the CB loaded membrane are shown in Fig. 2. Figure 2a shows the smooth surface of pristine PDMS membrane. Figure 2b, c, and d shows the CB loaded surface of the mixed matrix membrane. Because of the good compatibility of the CB with the PDMS matrix, there were no contact-free regions between the CB and PDMS. CB particles were homogeneously distributed inside the PDMS matrix.

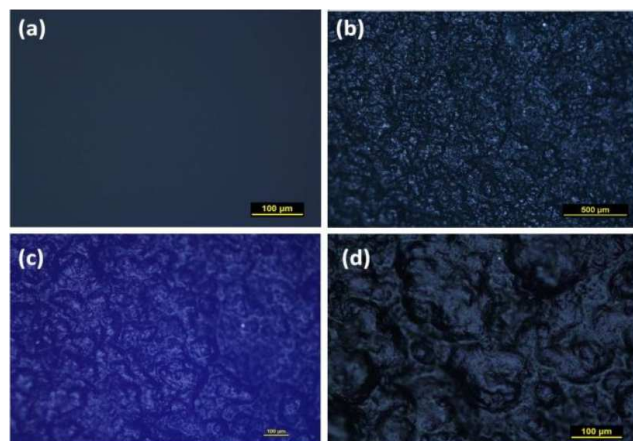


Fig. 2. Microscope images of pristine (a) and CB loaded (a, b, c) membranes at different magnifications.

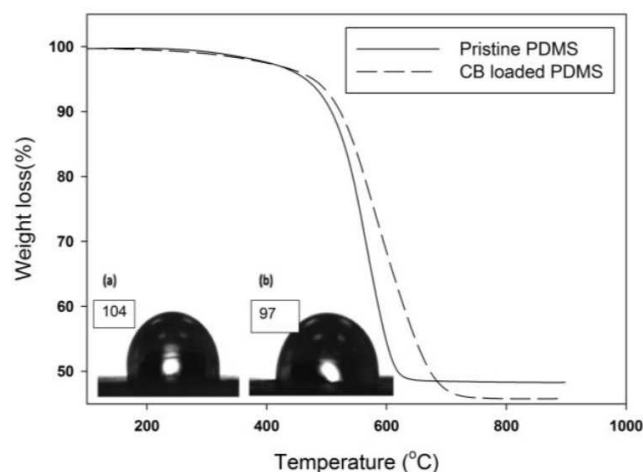


Fig. 3. TGA curves and contact angle measurements of pristine (a) and CB loaded (b) membrane.

Figure 3 represents the thermal behavior of the pristine and CB loaded membrane. As seen in the figure, thermal degradation period was slightly decelerated by CB addition. TGA result of the pristine and loaded membrane shows that there is no weight loss below 400 °C and this temperature was quite above the operating temperature of the pervaporation experiments. As can be seen in Fig. 3, the weight loss was decreased by the CB addition.

Figure 3 also shows the hydrophobicity of the pristine and carbon black loaded membrane in terms of water contact angle measurement. Because of the organic-water sorption capacity of the CB, the contact angle between the membrane and water decreases with CB addition. The hydrophobicity of the membrane surface decreases and the wettability of the membrane increases. An increment in flux value with the CB addition was expected based on this result.

Figure 4 shows the FT-IR spectra of the PDMS membrane before and after the cross-linking reaction. Cross-linking procedure was very important to restrict the excess enlargement of the void spaces of the PDMS matrix.

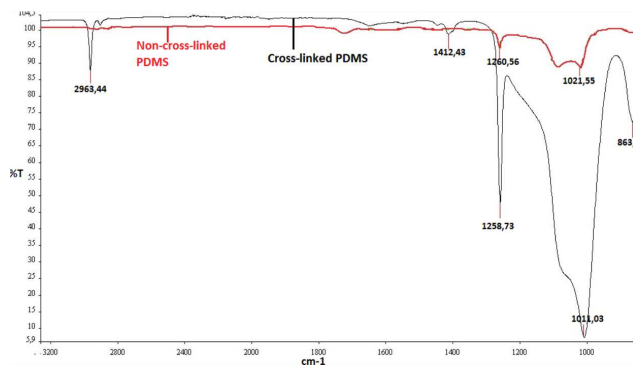


Fig. 4. FT-IR curves of pristine and CB loaded membrane.

It is well known that the PDMS has very flexible chain structure and the segmental motion of PDMS was very effective during the separation process. In order to increase the acetone selectivity, the segmental motion should be restricted by cross-linking. FT-IR analysis helped us to evaluate the cross-linking efficiency. As seen in the figure, the peak at 2963 cm^{-1} region is attributed to the $-\text{CH}_2$ end groups of PDM. This peak had disappeared in the cross-linked PDMS curve, as the result of the cross-linking reaction maintained by peroxide radicals.

3.2. Pervaporation results

Temperature has directly increased the vapor pressure of the component. Therefore, the driving force between the sides of the membrane has increased. Temperature has also affected the mass transfer rate directly. Both solution and diffusion capacity of the solvent were accelerated by the increased temperature and flux. From the structural point of view, temperature was also effective for improving the segmental structure of the polymer.

Due to the increasing chain mobility of the polymer, the frequency of the free volume in polymer matrix would be enhanced and the flux would enhance. Therefore, the temperature dependent flux increase was the prevalent result for polymer based pervaporation membrane [10, 11]. As seen in Fig. 5a and b, temperature has directly affected the flux and acetone separation factor. When temperature had increased from 30 °C to 60 °C, both flux and separation factor had increased.

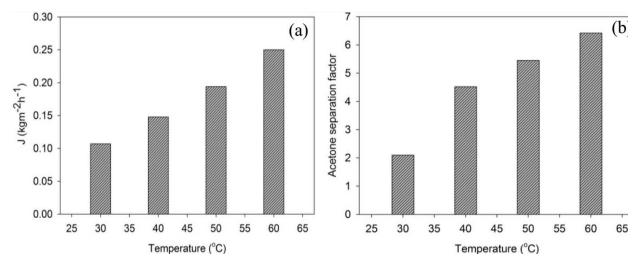


Fig. 5. Temperature dependent flux (a) and separation factor (b) results (3 wt.% acetone).

In the most of literature studies, there was a trade-off trend between the flux and separation factor, depending on the separation temperature. Because of the structural properties of the polymeric membrane and the physicochemical properties of the solvents, separation factor was decreased by the temperature. While the flux was improved by temperature, the selective character of the polymer has suffered and the pervaporation separation index was caught up at a certain value [9].

In this study, CB black addition has increased the tortuous pathway throughout the membrane. Therefore, even at high temperature, CB particles contributed to exhibition of organic selective character of PDMS. In fact, acetone molecules were retained in the feed side at low temperature due to the higher kinetic diameter of the acetone. When the temperature increased, expanded chain structure allowed acetone transition and separation factor had increased, as seen in Fig. 5b.

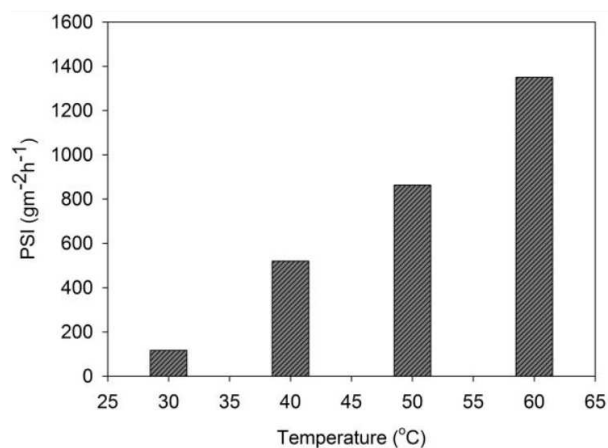


Fig. 6. Temperature dependent PSI results (3 wt.% acetone).

In order to evaluate the performance of the different membranes or conditions, flux and separation factor are estimated simultaneously and the pervaporation separation index (PSI) is defined by researchers. PSI is a quantitative multiplication of flux and separation factor. As seen in Fig. 6, similar to the separation factor and flux, PSI was also improved by the temperature.

4. Conclusions

In this study, carbon black loaded mixed matrix membrane was prepared to be used for acetone removal from model-waste solution. Surface characterization shows that CB was compatible with PDMS. Inorganic distribution was homogeneous and there was no contact-free region between the polymer and CB particles. Carbon black addition has retarded the thermal degradation rate of the membrane. Temperature has positively affected the flux, as expected. Separation factor and pervaporation separation index were also positively affected by the temperature. Characterization experiments and separation results have shown that the CB loaded PDMS membrane was very effective for acetone separation.

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