International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 09 Issue: 03 | Mar 2022 www.irjet.net p-ISSN: 2395-0072

A Study Effect of Perambilty and Selectivity on Mixed Matrix Membranes Made with Zeolite 4A in Polyethersulfone (PES)/Polysulfone (PSF) for Gas Separation

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Abstract: Mixed matrix membranes (MMM) with moderate filler loading have been shown to improve the transport properties of polymers and their blends for many gas separations. Currently, the main focus of the research is to invent new membranes materials and their combinations for gas separation. PES/PSF (80/20%) blend with dispersed inorganic porous zeolite 4A MMM were fabricated at 10, 20, and 30% ZIF-4A loading For the pure gas permeation, the effect of zeolite 4A loading at 2 bar on permeability (Barrer) and selectivity were investigated. The addition of 10 % zeolite 4A into the polymer blend, increased the permeability about two times for gases O_2 and N_2, while the ideal selectivity shows a slight increase for pure PES/ PSF blend membrane. For the higher zeolite 4A loadings (≥ 30 %) permeability's were oxygen increasing but Nitrogen started to reduce rapidly due to agglomeration of nanoparticles, but it was found that still, the selectivity improved and increase with the addition of filler into the glassy polymer blend up to 25% and 30% loading

Keywords: Mixed Matrix Membrane, Zeolitic4A, Gas separation, Permeability, selectivity.

1. Introduction

Mixed matrix membranes (MMMs) are heterogeneous membranes consisting of inorganic fillers embedded in a polymer matrix [1–20]. MMMs are very effective in the separation of gases. The inorganic fillers used in MMMs are porous molecular-sieve-type materials. MMMs offer an advantageous blend of the properties of polymer matrix and filler particles. [1-3] the incorporation of molecular-sieve type fillers in polymer matrix generally leads to higher permeability, higher selectivity, or both compared to the polymeric membrane. Furthermore, MMMs are easy to process and manufacture as compared with inorganic membranes.[4] The molecular-sieve type fillers used in MMMs are capable of discriminating between different molecules present in the feed mixture, usually on the basis of the size and shape of molecules. For example, in the separation of oxygen-nitrogen mixture Zeolite 4A is very effective as a molecular-sieve filler. Zeolites are porous alumino-silicates composed of AlO4 and SiO4 tetrahedra, which build up a network of cages/cavities interconnected by precisely sized apertures in the range of few Angstroms. Zeolite 4A possesses an eight-sided aperture with an effective aperture size of 3.8 Å. [6]As this aperture size falls between the lengths of O2 (length = 3.75 Å) and N2 (length = 4.07 Å) molecules, Zeolite 4A acts as a molecular sieve for O_2/N_2 gas pair. Zeolite 4A has an O_2/N_2 selectivity of 37 and an O_2 permeability of approximately 0.77 Barrier at 35 ∘C [2]. Carbon molecular sieves (CMS) are also important as inorganic filler materials for MMMs. In this paper, a study effect of Perambilty and selectivity on mixed matrix membranes made with zeolite 4A in Polyethersulfone (PES)/Polysulfone (PSF) polymer matrix for oxygen and nitrogen separation

2. Materials and Methods

The PES/PSF/ zeolite 4A based asymmetric flat sheet mixed matrix membranes were prepared by loading 0 to 30% of filler zeolite 4A using the solvent-evaporation method at a blend ratio of 80/20 (wt.%) of PES/PSF. Initially, for the preparation of PES/PSF/ zeolite 4A (10%, 20 % and 30 % zeolite 4A) (M1, M2, M3) blend mixed matrix membrane, also As we all know the membrane is of various types of membrane modal used in gas separation such as flat sheet, hollow fibre, spiral wound, etc. Among them, a hollow fibre membrane is used for gas separation. This type of membrane allows a high membrane surface area to be contained in a compact module. This means large volumes can be filtered, while utilizing minimal space, with low power consumption and shape, with different % Zeolite 4A filler [8]

3 Separation of single gases:

The feed tank was initially filled with the penetrant gas, which was pure O_2 and N_2, and the permeability tests were carried out at 35 ^{0}C. To assess the effectiveness of the membranes, pure O2 and N_2 single gases were passed through a PES/PSF mix (80/20%) and a PES/PSF blend (80/20%) with Zeolite 4A filler (10%) at 1 bar to 9 bar pressure and 35^{0}C temperature. The change in pressure on the downstream side (permeate side) of the membrane holder was measured over time to compute permeability and selectivity, as well as to investigate the influence of Zeolite 4A filler loading on membrane performance. [7]

4. Gas permeation

4.1 Estimation of single gas permeability

To characterize the membranes, single gas permeation experiments are typically performed. It is useful to gain a general understanding of membrane performance, the following equation was used to calculate the permeability 'P' of gases.[8]

$$Pemeability(P_{O_2}) = \frac{\text{Gas flow rate } (V_{CO_2}) \times \text{Membrane thickness } (l)}{\text{Area } [A] \times \text{Pressure drop } (\Delta P)} \quad 4.1$$

The effective membrane area is 'A' (cm^2), the time of permeation is 't' (s), and the trans membrane pressure drop is 'p' (cm. Hg) [9]. The volumetric gas flow rate is measured in cm^3 (at S.T.P.) per sec, and the unit of Permeability is Barrer.[9-10]

$$Barrer = 1 \times 10^{-10} \frac{cm^3 [STP]\ cm}{cm^2\ s\ cmH\ g} \quad 4.2$$

Using Equation 4.3 Selectivity was obtained

$$\propto_{i/j} = \frac{(y_i/y_j) permeate}{(x_i/x_j) feed} \quad 4.3$$

5. Results and discussion

The impact of Zeolite 4A loading on permeability (Barrer) and selectivity at 1 bar pressure at 35^{0}C was examined for pure gas permeation. Figures 4.1 and 4.2 illustrate the effect of Zeolite 4A loading on the single gas permeability of O_2 and N for PES/PSF blend mixed matrix membranes (M0, M1, M2, and M3), respectively. It was discovered that the permeability of both O_2 increased and N_2 decreased when the filler loading (Zeolite 4A) increased. It's also worth noting that O_2 has a higher permeability than N_2. The addition of the Zeolite 4A filler enhanced the overall performance of the mixed matrix membranes by up to 30%. The selection, however, as shown in Figure 4.3, the selectivity for O_2/N_2 rapidly increases the filler loading Zeolite 4A increased. This might be attributable to the aggregation of Zeolite 4A filler particles. These observations and discoveries of permeability and selectivity were used for further testing of the mixed matrix membranes for binary gas separation at greater pressures by increasing the Zeolite 4A loading.

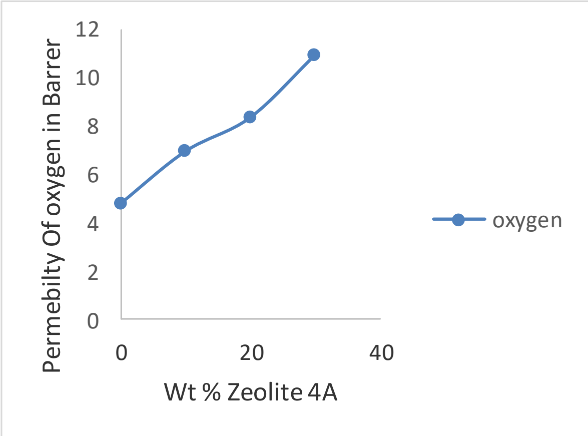

Figure 4.1: Effect of Zeolite 4A loading on O_2 gas permeability at 35^0 C and 2 bar pressure

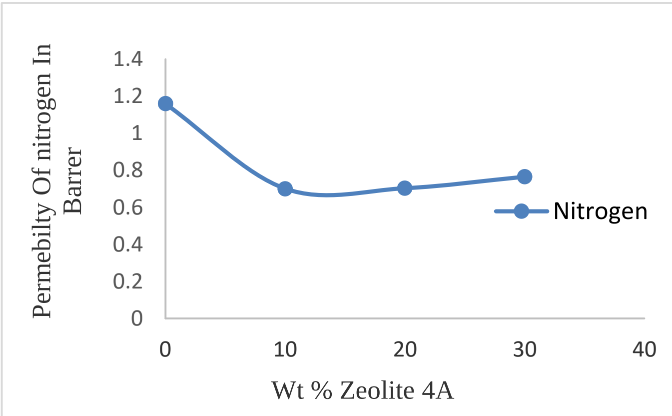

Figure 4.1: Effect of Zeolite 4A loading on N_2 gas permeability at 35^0 C and 2 bar pressure

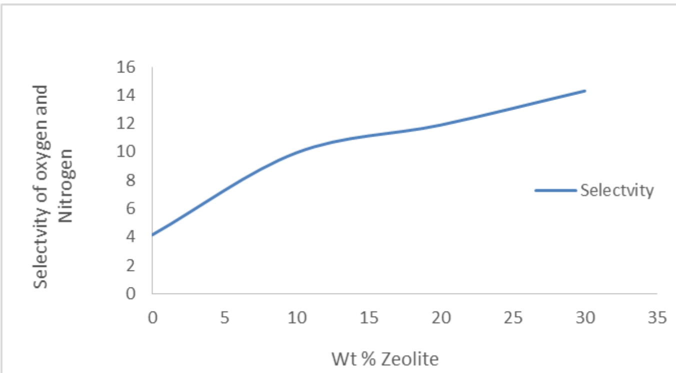

Figure 4.3: Effect of Zeolite 4A loading on O_2/N_2 selectivity at 35^0 C and 2 bar pressure

5. Conclusion

The incorporation of synthesized Zeolites 4A crystals into continuous PES/PSF blend polymer matrix resulted in high-performance gas separation membranes with uniformly good dispersion of fillers at acceptable limits and high improvement of permeability with considerable ideal selectivity. The permeability of gas increased with Zeolites 4A loading, while the ideal selectivity showed an increase compared to the neat PES/ PSF blend membrane. The addition of 20 to 30 % Zeolites 4A was selected as optimum filler loading for membrane formulation considering the permeation performances at 2 bar pressure. At higher loading, some agglomeration of Zeolites 4A was observed

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