

Synopsis of the thesis entitled
**STUDY OF GAS PERMEATION FOR POLYMER BLEND &
COMPOSITE MEMBRANES**

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1. Introduction

Study of gas permeability for polymer blend & composite membrane been studied extensively over the past few decades due to their improved physical and chemical properties. Membranes science and technology leads to the industrial applications such as microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas transport, and pervaporation which has been developed technologies. Not only in the industrial era but also in the medical field membrane technology has brought an attention for applications such as artificial lungs, artificial kidney and controlled drug delivery system [1,2]. The separation process concerns for the material having some specific properties (chemical or physical) that can exist under the operating conditions [3]. Polymer membranes are widely used to perform mass transport process in chemical industry due to wide range of applications in fluid separation. Additionally, the polymer membrane can be produced cost efficiently and the separation process based on membrane is environment friendly [4]. The flow of gas molecules across the membrane is influenced several factors: feed gas properties, material used to design the membrane, morphology of membrane structure and operating conditions [5].

The rising potential of new type of membrane material composed of organic frame and inorganic filler, full fills the future applications in mixed matrix membrane. In the nanocomposite membrane, the particle loading not only promotes gas transport properties but also influence selectivity up to some extends [6]. The filler is preferred at nanoscale and it is chosen such a way that it would serve better contributively to respected field application. The incorporation of SiO₂ nanoparticles in to the host polymer matrix alter the intermolecular chain packaging of polycarbonate membrane which results in the change of morphology along with polymer structures[7,8]. Carbon dioxide being polar molecule, at higher pressure results in plasticization with some glassy polymers having polar pendent groups. Due to the plasticization of membrane material its permeability is changed which can modify separation ability of the membrane. The plasticization is penetrant induced phenomenon which relay on the nature of penetrant, nature of material and the penetrant material interaction. Plasticizing potential of CO₂ with glassy polymers having polar group promotes the permeability of gas molecules

through the membrane material [9]. Specific modifications performed such as irradiation, thermal rearrangement, grafting changes the internal chain arrangement which results to improve the separation factor of the membrane.

1.1. Transport Phenomenon

The permeability of gas through dense polymer membrane depends on solubility and diffusivity of reentrant. Gas transport phenomenon for glassy polymers membrane is explained by solution diffusion mechanism. Gas permeation is the flux of gas molecules through an object normalized to the pressure gradient. The driving force behind the transport of gas molecules which involves sorption, diffusion and permeation is mainly due to pressure difference between two phases.

1.2 Gas Permeability and Selectivity

Gas permeability coefficient P , of a pure gas for polymeric membrane is given by following formula:

$$P = \frac{JL}{P_2 - P_1}$$

Where, J is the steady state flux across the membrane L is the membrane thickness, P_2 is the upstream pressure and P_1 is the downstream pressure [4]. Permeability is expressed in barrers, where 1 barrer = 10^{-10} [cm^3 (STP) $\text{cm}/(\text{cm}^2 \text{ s cm-Hg})$].

The selectivity of a polymer membrane for gas pair A and B is defined as the ratio of their permeability:

$$\alpha_{AB} = \frac{P_A}{P_B}$$

2. Experimental Techniques

2.1 Materials

In this chapter, it is proposed to prepare hybrid membranes by metal coating and nanocomposite using inorganic filler. PC membrane of about 180 (± 2) μm thickness was purchased from General Electrical Co, USA. Standard vapor deposition sputtering technique has been used to prepare layered composite membranes at ICMB facility of University of Texas at Austin, TX, USA. Silica nanoparticles (stock number 4860MR),

20 nm in average diameter, were supplied by Nanostructure and Amorphous Materials, Inc, USA. A thin layer of metal was deposited on bisphenol-A polycarbonate using standard vapor deposition sputtering technique. The Pt-Pd alloy and iridium were used for deposition to make layered composite membranes. Silica nanoparticles were used as filler to synthesize polycarbonate nanocomposite membranes by solution casting method with various loading concentrations. Some additional modifications such as blending and blending with nanocomposites have been performed to prepare different types of hybrid polymer membranes.

2.2 Experimental Techniques

A constant pressure variable volume system is also developed to measure permeate flux in terms of height gain of mercury slug by the mercury flow meter attached to the gas permeability cell. Constant volume variable pressure system is also used to measure permeate flux by monitoring the pressure increase of collected permeate gas in a closed volume using a pressure transducer. Characterizations such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) are also applied to analyze the properties of the membrane. Some other characterization techniques may also be included during the time of thesis submission.

3. Gas Transport through Layered Polymer Nanocomposite Membranes

3.1 Gas permeability of various gases by metal coated polymer membrane

In this chapter, the transport behavior of different gases across the metal coated membrane has been studied and compared with that of standard polycarbonate membrane. Deposition of nanolayer affects the transport properties due to the modification in sorption-diffusion process. A Pt-Pd alloy thin film of around 8-10 nm was coated on thick polycarbonate substrate using sputtering technique to make layered polymer nanocomposite membrane. The tests were carried at constant upstream pressure 30 psi. Gases used for the present study were He, H₂, CO₂, O₂, N₂ and CH₄ and the selectivity was calculated for particular gas pairs. Pure gas permeability coefficients were calculated using constant volume/variable pressure method at 35 °C temperature. Permeation behavior was found in following order: He > H₂ > CO₂ > O₂ > N₂

> CH₄ for both the pure and Pt-Pd layered PC membrane. There is marginal change which can be acceptable due to leakage in the permeability of pure PC.

3.2 CO₂ plasticization effect for metal coated polymer membrane

Transport behavior of CO₂ across the metal coated membrane has been studied and compared with that of standard polycarbonate membrane as a function of feed pressure. As CO₂ is a plasticizing agent, at definite pressure it gives plasticizing effect depending on the properties of material. The tests were carried at different upstream pressures i.e. in the range of 30 psi to 230 psi for PC/Pt-Pd at 35 °C temperature. Moreover, the selectivity of CO₂ was also determined with O₂ and N₂ at 30 psi as well 130 psi upstream pressures. CO₂/H₂ selectivity was also determined from 30 psi to 180. The metal coating plays a vital role for enhancement of solubility factor which is responsible for gain in permeability.

4. Hydrogen Transport through Metal Coated and Nanofiller Polycarbonate

In this chapter, the transport behavior of H₂ across the different metal coated and nanocomposite membrane has been studied. Transport properties changes due to the modification in the composition of nanofiller. A Pt-Pd alloy thin film of Pt-Pd metal alloy and iridium thin film of around 8-10 nm was coated on polycarbonate substrate using sputtering technique to make layered polymer nanocomposite membrane. Moreover, SiO₂ nanocomposites with 10 wt% and 15 wt % were prepared by solution casting method and the tests were carried at constant upstream pressure 30 psi and at constant temperature 35 °C using constant volume/variable pressure method. The alteration in the transport of hydrogen molecules reflects the performance of these modified membranes in terms of permeability along with selectivity. Metal coating provide better gateway to the penetrant to make them soluble in the membrane material which finally also reflect as an increment in permeability. Selectivity factor is also maintained by the hybridization which is applicable to separate H₂ from gas mixture.

5. Gas Permeation through Polymer Blend and Composite Membranes using SiO₂ Doping Agent

The blending of polymers has been studied in different amount for different polymers. However, very few works has been reported for mixture of inorganic nanoparticles with blending of two different polymers. In this work we have used polycarbonate (PC) and polysulfone (PSf) to prepare blend membrane with different weight percentage of polycarbonate and SiO₂ nanoparticles mixed with the blended mixture. The membranes have been fabricated by solution casting method using sonicator. There are total 12 samples synthesized by solution casting method with different polymer ratios. The membranes were tested for oxygen transport rate (OTR) from Lab think (Packing Safety Testing Center, Jinan, China). Nanofiller plays vital role to improve oxygen permeability in both PC and PSf membranes. Gas permeability experiment for H₂ was performed by constant pressure/ variable volume set-up for the same samples. Gas permeation of O₂ and CO₂ may be included by this developed system at the time of thesis submission.

6. Conclusion and Future Scope

This chapter is an accomplishment of whole work done in the thesis and also future perspectives of different hybridization will be discussed.

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