Chapter 7

Nano-Silica Embedded PDMS Membranes and their Performance

This chapter deals with the synthesis of nanocomposite membrane using the same amorphous SiO_2 nanoparticles synthesized from bamboo leaves which acted as support media in the previous chapter. The SiO_2 nanoparticles are used as filler by incorporating them in the polymeric matrix to enhance its separation efficiency. Effect of particle loading on membrane performance is studied in detail. Characterization techniques like X-ray diffraction (XRD), high resolution scanning electron microscope (HRSEM), dispersive X-ray spectroscopy (EDX), and Fourier transform infrared (FTIR) spectroscopic are used to study the morphology and surface characteristics of membranes. Hydrophobicity is measured using contact angle analyzer. Effiicacy of the nano-composite PDMS membrane for pervaporation is evaluated using acetic acid-water mixture. It was observed that the presence of SiO_2 nanoparticle significantly improved the pervaporation flux as well as thermal stability.

7.1 Introduction

Separation processes using membranes are considered as one of the most cost effective and energy saving methods in comparison to conventional processes such as distillation or adsorption (Chovau et al., 2010). Among these membrane separation processes, Reverse osmosis (Dong et al., 2020), nanofiltration (Toh et al., 2008), ultrafiltration (Arif et al., 2019), gas permeation (Chung et al., 2007) and pervaporation (Arif et al., 2018) are widely used in commercial applications due to their ease of operation, eco-friendliness and energy

saving aspects. Among all the separation processes, pervaporation is a separation process in which dense polymeric membrane is used for selective permeation of one or more components from a liquid mixture. It is an energy efficient process for the separation of energy intensive, azeotropic, closely boiling and temperature sensitive liquid mixture (Chapman et al., 2008).

Polymeric membrane materials for Pervaporation like, poly(dimethylsiloxane) (PDMS) (Zhan et al., 2010), polyether block polyamide (PEBA) (Mohammadi et al., 2008), crosslinked poly (acrylate-co-acrylicacid) (Roualdes et al., 2003) and polyvinylidene fluoride (PVDF) (Arif et al., 2019) are largely used and among them PDMS is considered good because of its flexibility, amorphous molecular structure and rubbery state at ambient temperature (Tg = −123 °C). It has been found PDMS has a higher selectivity for ethanol (Xiangli et al., 2007).

Researchers globally have witnessed the improvement in pervaporation performance and physicochemical properties of polymer membranes by addition or incorporation of inorganic fillers like, polyphosphazene nanotube (Huang et al., 2009), nano-silica (Zhou et al., 2010), carbon nanotube (Peng et al., 2006), zeolite (Li et al., 2008), nano-iron (Chen et al., 2008), TiO_2 (Yang et al., 2009) and carbon black (Panek et al., 2007) into the PDMS polymer casting solutions. In the recent years because of its low cost, availability in pure form, nontoxic nature, bio-compatibility, mechanical and chemical stability up to high pressures and temperatures, and ability to functionalize with a range of polymers nano-silica filled polymer matrix composites has drawn the attention of researchers and showcased significant improvement in physicochemical stability and separation performance of membranes.

The synthesized SiO_2 nanoparticles as discussed in chapter 6 are incorporated in the PDMS polymer membrane matrix prepared by the solution casting method. Morphology and chemical nature of synthesized nanocomposite membranes are ascertained with the help of various characterization techniques i.e. XRD, FTIR, SEM-EDAX, and Contact Angle analysis. Different weight % of SiO_2 nanoparticles are loaded in PDMS hydrophobic polymer to enhance its selectivity which is tested through pervaporation experiments conducted using acetic acid-water mixture.

7.2 Materials and methods

7.2.1 Materials

Poly (dimethyl siloxane), hydroxyl terminated with a density of 0.97 g/ml is purchased from Sigma-Aldrich Co., Ltd, St. Louis, USA. Toluene (solvent) is purchased from Sisco Research Laboratories Pvt. Ltd. India. Tetraethylorthosilicate (TEOS), dibutyltindilaurate (DBTOL) are purchased from Otto Chemie Pvt. Ltd. India. Synthesized silica nanoparticles (15 ± 3nm, $250m^2g^{-1}$)

7.2.2 Preparation of Dense Membrane

Both pure PDMS and PDMS incorporated with silica nanoparticles are synthesized by solution casting method. The Liquid hydroxy terminated polydimethylsiloxane as a base polymer, a crosslinking agent(TEOS) and curing agent dibutyltindilaurate(DBTDL) is mixed with the solvent in the ration of 5:1:0.3(in weight). First, the desired amount of polydimethylsiloxane is mixed with an organic solvent (toluene) in a beaker followed by continuous stirring using magnetic stirrer for 1 h to achieve homogeneous solution. In the mean time for better dispersion of silica nanoparticles in PDMS matrix, silica nanoparticles

and toluene are mixed simultaneous but separately in a beaker with proper stirring for an hour and then sonicated for 15 min. The prepared solutions are mixed followed by continuous stirring for 1h then the tetra ethyl ortho silicate (TEOS) a crosslinker is introduced at ambient temperature. After mixing for 15 min, the dibutyltindilaurate (catalyst) is added at room temperature and stirred to obtain viscous solution. After this, the viscous mixture is poured to a glass plate and kept for degassing at room temperature for 24 h. Solvent evaporation takes place, and the same material is placed in an oven for 3 h, at 85°C for proper crosslinking reaction along with remaining solvent evaporation. Finally, the PDMS −Silica nanocomposite membrane peeled from the glass plate for the required application. Silica-filled PDMS composite membrane with different percentages of silica is prepared to investigate the effect of incorporation of silica nanoparticles on properties and pervaporation performance of the PDMS membrane. Membrane sample is named as P for pure PDMS and P1, P2, P3 for PDMS/SiO$_2$ with 2%, 4%, and 6 % silica nanoparticles respectively.

7.2.3 Characterizations of Nano-particles and Membranes

Hydrophobic nature of the membranes is described using water contact angle. This is measured for all membranes using a KRUSS DSA 25 (KRUSS, Hamburg, Germany) drop shape analyser using the sessile drop technique with a 0.2-μl volume of water. FTIR spectra is used to know the presence of functional groups. The FT-IR spectra of the sample is obtained using the Nicolet- iS5 spectroscopy (Thermo Fisher Scientific, Waltham, MA, USA) in the range of 500–4000 cm−1 at a resolution of 6–32 scans. XRD pattern of the SiO$_2$ nanoparticles, PDMS, and PDMS/silica membranes is obtained using a Rigaku

Miniflex 300/600 X-ray diffractometer (Tokyo, Japan). The diffractograms are measured at a scanning speed of 10 deg/min, using a tube voltage of 40 kV and tube current of 15 mA.

7.2.4 Pervaporation Experiment

Laboratory scale batch type simple pervaporation experiment is carried out with the pure PDMS membrane and PDMS membrane incorporated with 2, 4 and 6 wt % silica nanoparticles. Effective membrane area is 19.625 cm^2. This membrane is cut down and clamp in the membrane module as shown in Figure 7.1. The pervaporation module is equipped with the corresponding membrane and the screws are tightened. The permeate pressure is kept below 5 mm Hg with the help of a vacuum pump. Vapor which permeates across the membrane is condensed in a condenser with the help of a chiller and finally collected in the permeate collector. The collected sample is analyzed using a gas chromatographic technique of GC-NUCON with flame ionisation detector (FID) equipped with Carbowax-20M column. Here nitrogen (N_2) is used as the carrier gas at a flow rate of 35 mL/min, also hydrogen (H_2) and oxygen (O_2) are set at 27 and 250 mL/min, respectively to ignite the flame and the oven temperature is programmed at 100 °C at ramp rate of 20^0 C/min while injector and detector temperature are maintained at 210 and 240 °C respectively. The concentration of acetic acid at permeate is find out from the standard plot prepared separately. Before any analysis calibration is performed with a standard aqueous solution and each concentration determination is based on 3–4 injections. The experiment is repeated two to three times for each membrane to reduce experimental errors and the final results are averaged for better evaluation. In the Pervaporation experiment, permeate flux

(J$_P$) and separation selectivity (α) are determine by equations (7.1) and (7.2) respectively (Panek and Konieczny, 2007).

$$J_p = \frac{m_p}{At} \tag{7.1}$$

Here,

m$_p$ is the mass of permeate in kg; A = cross-sectional membrane area in m^2, and is the time of permeation in an hour.

$$\alpha = \frac{Y_{pw}X_{fw}}{Y_{pa}X_{fa}} \tag{7.2}$$

Here Y$_{pw}$ and Y$_{pa}$ are mass fractions of component water and acetic acid in permeate side respectively. Similarly, X$_{fw}$ and X$_{fa}$ are a mass fraction of acetic acid and water in the feed side respectively.
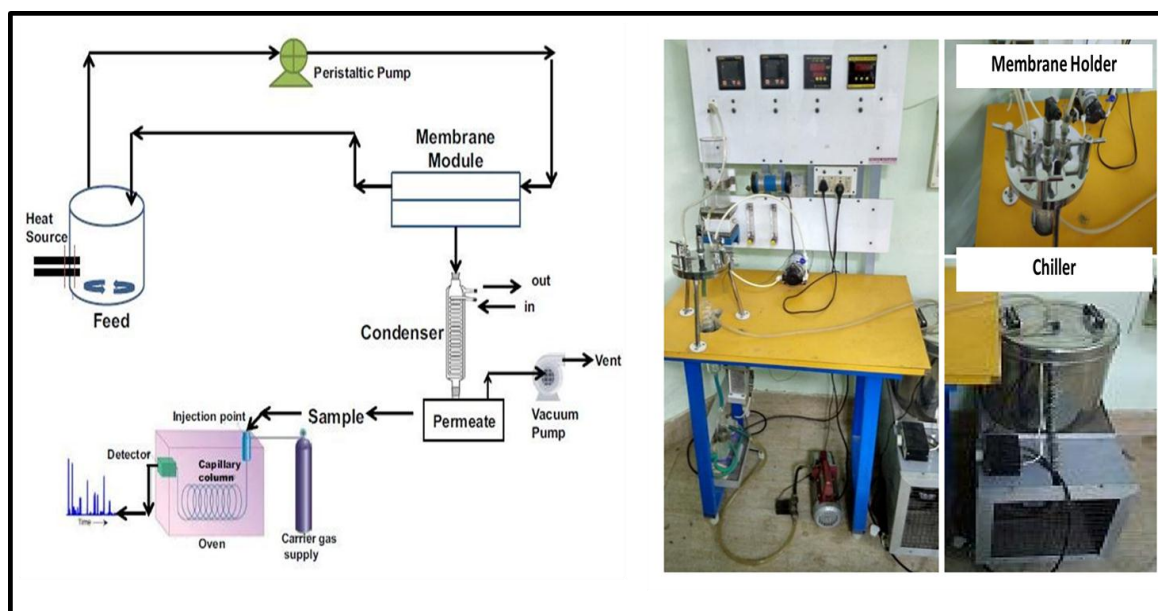

Figure 7.1 Pervaporation setup

7.3 Results and Discussion

7.3.1 FTIR Analysis

The Fourier Transform infra-red Spectroscopy as shown in Figure 7.2(a) & 7.2(b) provides information about functional groups present in the synthesized SiO_2 nanoparticle as well as polymeric matrix. From the Figure 7.2(a) peak corresponding to 463 cm^{-1} signifies bending vibrations of Si-O-Si part. The peak at 802 cm^{-1} shows the presence of Si-O bending vibrations (Hernandez and Pierre, 2000). The broad peak at 1089cm^{-1} has been designated to asymmetric Si-O-Si bonding structure of O and Si atoms (Moncada et al., 2007), and the peak at 3023 cm^{-1} is due to the Si -OH groups. As calcination caused the Si-OH groups to disappear, the band at 3023 cm^{-1} represent the deformation and O-H stretching vibrations of weakly-bound water (Wang et al., 2003, Soria et al., 2010). The OH groups are still observed because moisture was adsorbed by the sample from the air after calcination.

The FTIR spectra of pure PDMS and PDMS incorporated with different percentages of silica nanoparticles is shown in Figure 7.2(b). The peak at 2961.3 cm^{-1} shows asymmetric stretching vibrations of the CH_3 groups of PDMS. The absorption peaks at around 1072 and 1008 cm^{-1} in the filled membranes are corresponded to stretching vibration of Si-O-Si. The peak at 1257 $cm^{-1}$is assigned to deformation vibration of the two-methyl linked with Si (Sun et al., 2013). Figure 7.2(b) depicts that all membranes had very similar peaks at a wave range from 500 cm^{-1} to 4500cm^{-1} which demonstrate that SiO_2 nanoparticle is physically blended in the PDMS polymeric matrix (Li et al., 2008).
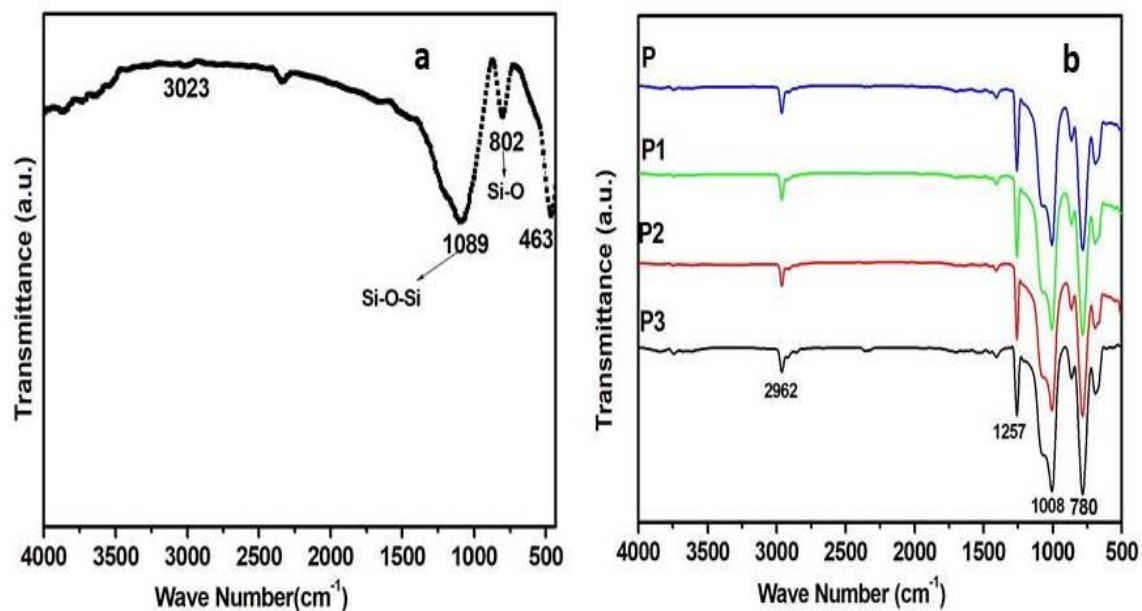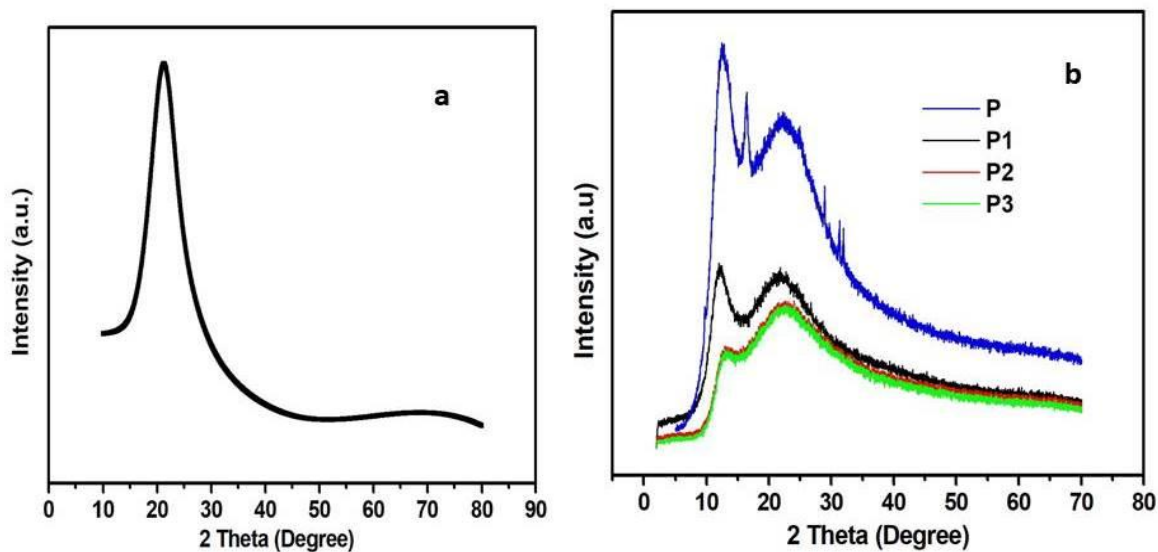
Figure 7.2 FTIR Spectra of (a) synthesized silica nanoparticles and (b) pure PDMS and

PDMS composite with different % of Silica nanoparticles

7.3.2 XRD Analysis

The crystalline and amorphous character of the SiO_2 nanoparticle and the membrane is studied by X-ray diffraction measurement. X-ray diffraction spectra proved the high percentage of amorphous SiO_2NPs with wide band at 2θ of $22°$ (Chen et al., 2014, Liou and Yang, 2011) is obtained as shown in Figure 7.3(a). Absence of any other sharp peaks confirms the amorphous nature of synthesized SiO_2 NPs. XRD pattern of pure PDMS and PDMS incorporated with different percentages of silica nanoparticles is shown in Figure 7.3(b). A broad semi-crystalline peak is observed for all PDMS membranes at a diffraction angle (2θ) of $12°$ (Hong et al., 2011). Visible decreasing in intensity with increase in

percentage loading of silica as shown in the Figure 7.3(b) benefits membrane process ability and application.


Figure 7.3 XRD patterns of (a) synthesized silica nanoparticles and (b) pure PDMS and PDMS composite with different % of silica nanoparticles

7.3.3 HRSEM-EDAX Analysis

The HRSEM analysis is done to determine the average size and shape of the synthesized SiO_2NPs from bamboo leaf along with morphology of synthesized membrane. Figure 7.4(a), depicts the formation of SiO_2NPs with an average particle size of 20 nm. It is visible in the image that SiO_2NPs are slightly agglomerated. The X-ray Energy Dispersive Spectrometer (EDX) is employed to know the elemental composition of the synthesized SiO_2 NPs. The EDX spectrum is shown in inset of Figure 7.4(a), which confirmed the presence of both Silica (Si) and oxygen (O) without any impurity in the sample with weight percentage, 52.25%, and 47.75% respectively. Figure7.4 (b) depicts a smooth surface which signifies the characteristic of dense pure polymer membranes. The EDAX result shows a small intensity peak of silica in pure PDMS membrane due to the addition of tetra

ethylorthosilicate (TEOS) during the membrane preparation. In case of PDMS membranes with silica nanoparticles, the distributed microsphere of silica particle is observed in PDMS as shown in Figure7.4(c) and strong intensity peak of Si compare to pure PDMS confirmed the presence of silica nanoparticle.
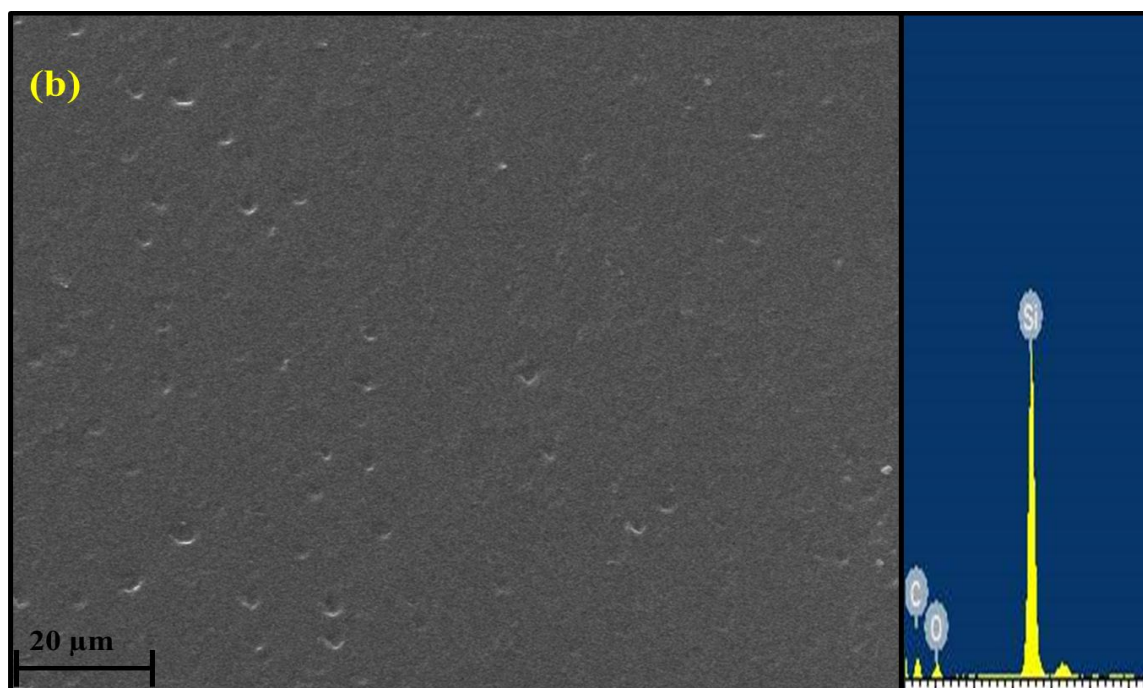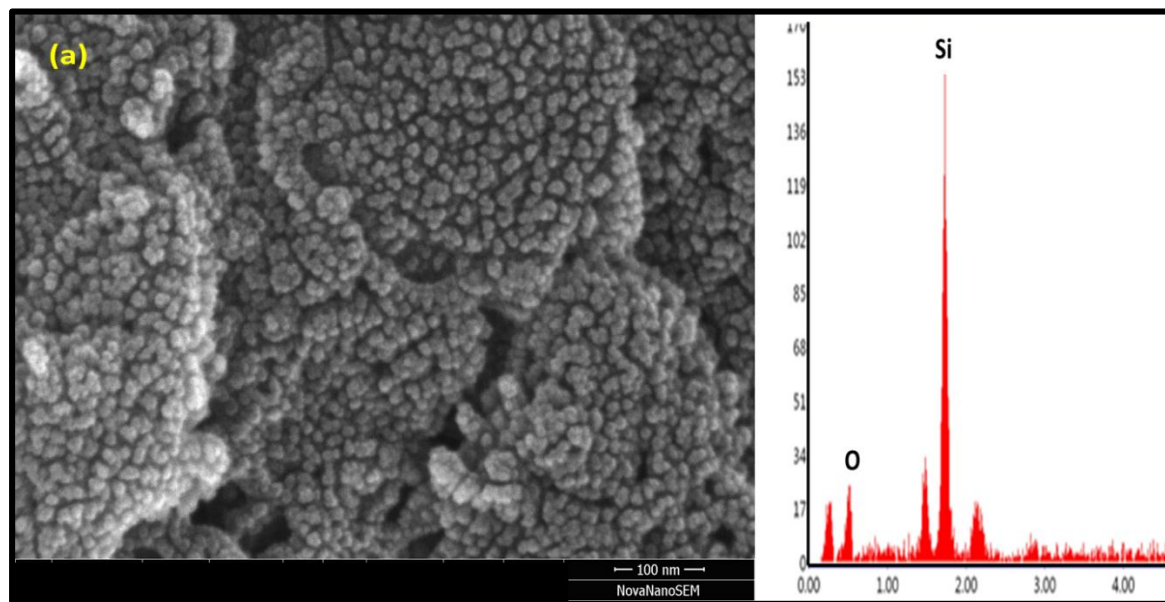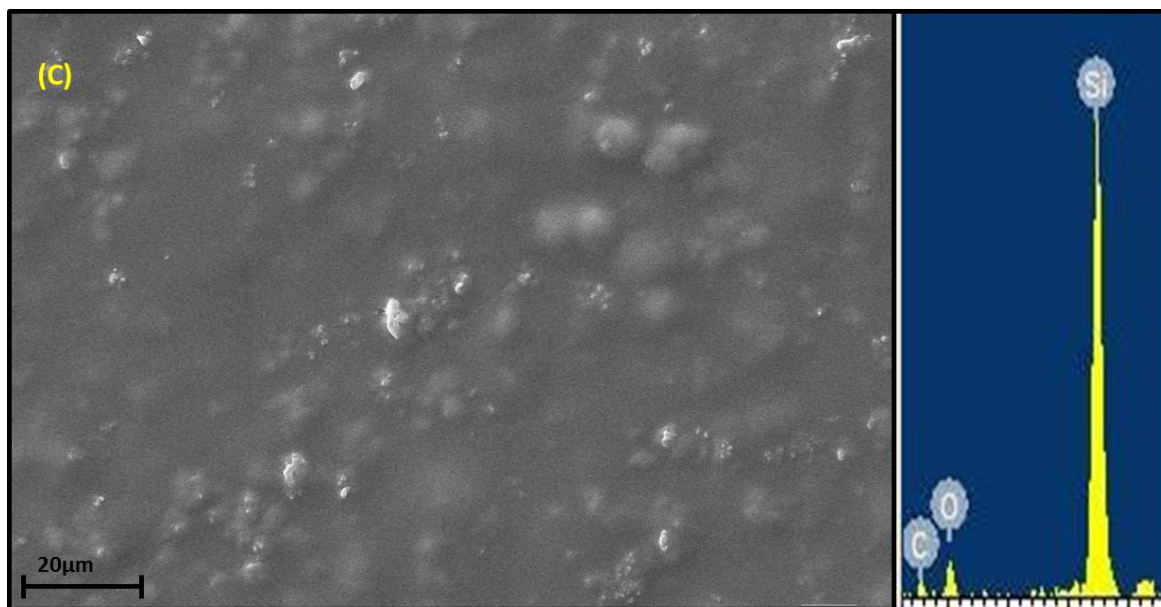
Figure 7.4 HRSEM –EDAX image of (a) synthesized Silica nanoparticles and (b) pure PDMS and (c) PDMS with silica nanoparticles

7.3.4 Contact Angle analysis

Results of the contact angle test is shown in Figure 7.5. As silica content increases the contact angle of the membrane is decreased. The contact angle is a well-known property for determining the surface characteristics of any polymer/membrane. It provides information about surface wettability by giving a geometric measurement of angle θ formed at the intersection of the liquid and solid phase. The water contact angle is measured to check the hydrophilic /hydrophobic nature of membranes (Le et al., 2011). From the contact angle analysis results it is revealed that as the wt% of silica increased from 0% to 6%, the contact angle at the surface of the composite membrane decreased from 118.6º to 99.0°. This is attributed to the presence of OH functional groups on silica nanoparticles which improved the hydrophilicity of PDMS-SiO$_2$ membrane. More concentration of SiO$_2$ nanoparticle in the polymeric matrix, more the surface roughness of the membrane which decreases the

contact angle (Liu et al., 2018). Even though hydrophobicity is slightly reduced from P1 to P3, the composite membrane still remains hydrophobic.
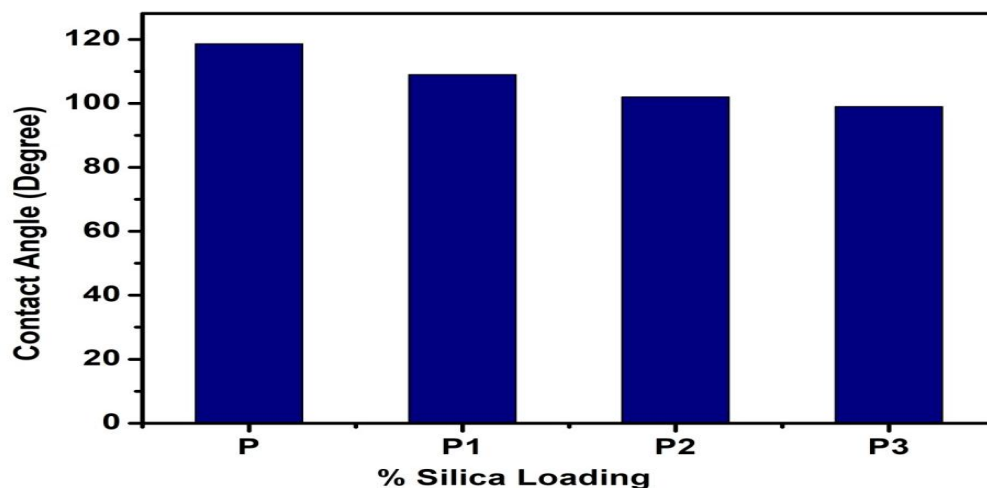

Figure 7.5 Contact angle analysis of PDMS and PDMS with silica nanoparticles

7.3.5 Pervaporation performance

The flux of acetic acid in case of silica filled PDMS membrane increases with increase in the silica content in the membrane as shown in Figure 7.6(a). As reported in the literature incorporation of silica nanoparticles led to an increase in the free volume of PDMS membrane and because of this diffusion coefficient of molecules through membrane increases which enhances the permeation of components through the membrane (Tang et al., 2007). On the other hand, increase in the silica content slightly decreases the selectivity of PDMS membrane as shown in the Figure 7.6(b) because of aggregation of silica particles on the membrane surface or may be due to generated defect (cavities) on the membrane surface. Thus the total flux is also significantly affected by the presence of defects on the membrane surface (Peng et al., 2011, Gomes et al., 2005)

7.3.5.1 Effect of Feed composition

Feed composition has a greater impact on membrane selectivity and total permeation flux. Figures 7.6(a) and 7.6 (b) shows the effect of feed composition on permeation flux and selectivity. By increasing the acetic acid concentration, the total permeation flux increases while the separation factor decreases slightly. The pervaporation is governed mainly by diffusion and sorption. In any binary mixture if there is one target component and if polarity between the target component and membrane material is low compared to that for the other component, then membrane swells more by the target component and shows preferential selectivity for it. In the case of acetic acid-water mixtures, membranes have preferential selectivity for acetic acid. With an increased acetic acid concentration in the feed, the interaction between acetic acid and the cross-linking phase of PDMS becomes stronger. The membrane swells more and it permits high mobility of permeating species. By enhancing the chain mobility, thermal motion of these segments also increase and gives a high diffusion rate, hence increased permeation flux. However, the diffusion rate of water being more than that of acetic acid due to the smaller molecules of water, slightly decreases the separation factor (Gongping et al., 2011).
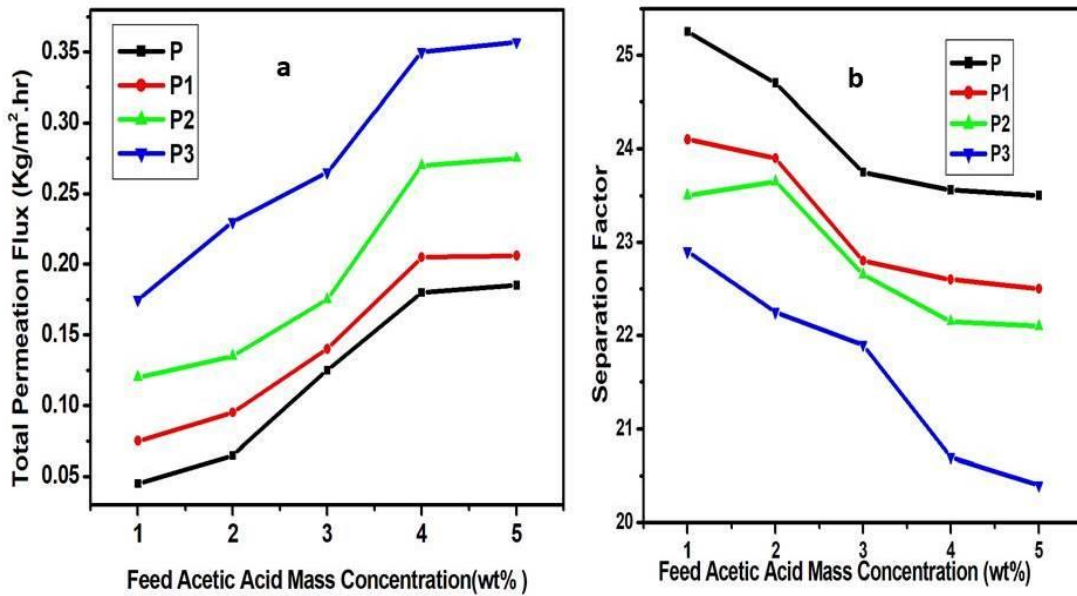
Figure 7.6 Effect of Acetic Acid concentration on the pervaporation performance (a) Total Permeation Flux (b) Separation Factor

7.3.5.2 Effect of Operating Temperature

Both solubility and diffusivity are temperature dependent. Since pervaporation transport involves these two properties, the separation performance is significantly affected by the temperature. Generally, the permeation flux as a function of temperature follows the Arrhenius type of relationship (Tang et al., 2007),

$$J_p = C_o exp(-E_P/(RT)) \tag{7.3}$$

Where J_p = total flux, C_o = constant, E_P = activation energy for permeation, T = operating temperature in Kelvin, and R = gas constant.

As the temperature is increased from 25°C to 40°C the total permeation flux increases from 0.212 kg/m^2.hr to 0.368 kg/m^2.hr for pure PDMS membrane and from 0.248 kg/m^2.hr to

0.396 kg/m^2.hr to the membrane filled with 2 to 6 % silica contents as shown in Figure 7.7. Increase in the temperature increases vapor pressure difference which enhances driving force for transport through the membrane (Bai et al., 1993). Diffusion of acetic acid and water through PDMS membrane increases and led to high permeation flux (Le et al., 2011).
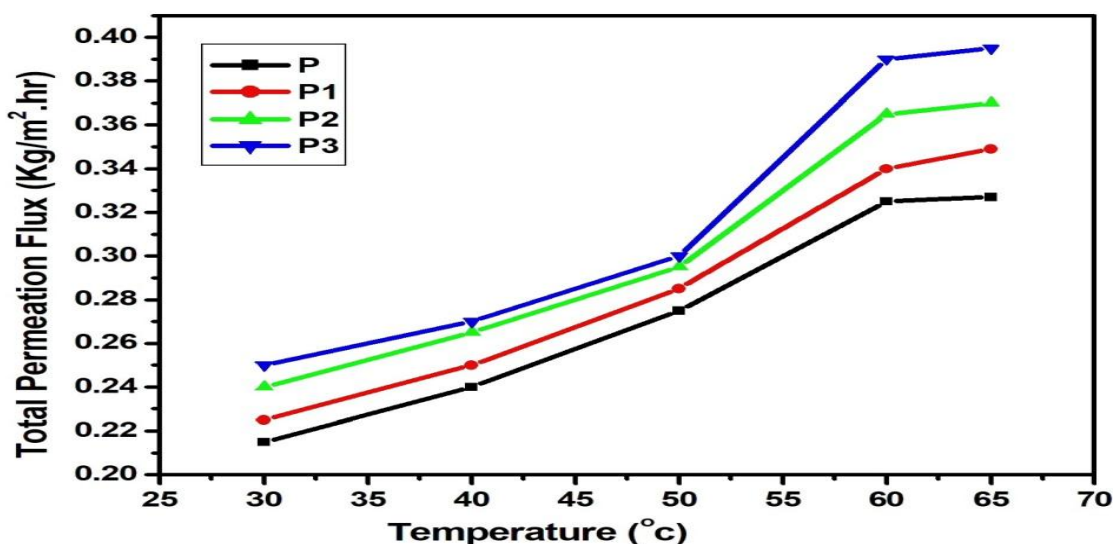

Figure 7.7: Effect of Temperature on total permeation flux

7.4 Conclusion

SiO$_2$ NPs are succesfully used as inorganic filler material to improve the pervaporation performance of polydimethylsiloxane (PDMS) membrane. PDMS is incorporated with different percentage of silica nanoparticles (2, 4, 6 wt %) by a solution casting method. Morphology analysis using SEM-EDAX revealed well embedded nano silica in PDMS membrane. Addition of nano silica improved the hydrophilicity of membrane due to presence of OH functional groups in silica nanoparticles as revealed by FTIR analysis. Pervaporation performance evaluation study reveals a significant improvement in

membrane pervaporation flux in SiO_2 NP embedded membranes compared to membranes without nanoparticles. Effect of feed concentration and process temperature on membrane performance is also studied and it is observed that increasing the feed concentration of acetic acid increases the permeation flux, while the selectivity of the membrane slightly decreases and increasing the temperature of the feed solution increases the acetic acid take-up by the membrane. Overall results concludes that the presence of SiO_2 nanoparticle significantly improves the pervaporation flux without compromising selectivity much.