CHAPTER 4

HYDROGEN TRANSPORT THROUGH METAL COATED AND NANOFILLER POLYCARBONATE

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4.1. Introduction

The global energy consumption is predicted to increase in vast amount in upcoming years and it demands for clean and efficient energy sources. The combustion of fluid fuels especially for transportation and heating offers emission of greenhouse gases and large amount of pollutant. To overcome this difficulty, a variety of fuels such as methanol, ethanol, methane gas, hydrogen and synthetic liquid derived from natural gas have been proposed as energy sources. Considering the outcomes of global warming and energy security, hydrogen fuel accommodates the clean and efficient energy demand [1]. For this purpose hydrogen production, separation and purification becomes the necessity of present era. As hydrogen production offers the other byproducts, its separation and purification becomes necessary for energy applications. Membrane separation technologies provide ultrahigh purity hydrogen gas consuming less energy and supports continuous operation process [2-4]. Generally polymer materials are applicable in the membrane fabrication for gas separation but the transport of hydrogen is quite different from metallic lattice compared to other gasses. The multilayer metallic membrane coated with palladium metal improved the separation of hydrogen from helium and argon gas mixture providing ultrapure hydrogen gas [5]. The metallic coating on the polymer substrate can improve gas transport efficiency which has been discussed in the previous chapter but another modification by incorporation of inorganic fillers into polymer matrix also improves gas permeation and selectivity of the particular gas pair. Organic-inorganic MMM composite of TiO_2 dispersed into PVAc matrix by solution casting method increases H_2 permeation with improvement in its separation from N_2. Thermal stability of the composite membrane also enhances due to dispersion of nanofillers [6].

The performance of nanoporous ZIF-8 nnaoparticles into polybenzimidazole (PBI) polymer phase show excellent improvement in the H_2 permeation without loss in its separation with CO_2. Moreover, it shows superior performance when ZIF-7 nanoparticles are incorporated in the polymer matrix instead of ZIF-8 nanoparticels. Such novel nanocomposite membranes are applicable in hydrogen purification and energy related applications [7]. Fabrication of PEO/silica reverse selective MMM is also applicable for hydrogen purification at elevated pressure range. H_2 permeation remains constant and CO_2 permeability improves with operating feed pressure resulting increase in the CO_2/H_2 selectivity. The addition of inorganic filler into PEO matrix enhances mechanical properties as well thermal stability of the resultant membrane which promotes industrial scale applications of hydrogen energy [8]. The nature of nanofiller also plays vital role in the improvement of gas permeation properties. When SiO_2 nanofillers are dispersed into poly(1-trimethylsilyl-1-propyne) (PTMSP) matrix, increases free volume in the MMM increasing the gas permeation. Moreover, if the filler content is increased, it further increases in the membrane free volume and hence promoting gas permeability [9].

This chapter aims to describe H_2 transport across the different metal coated and nanocomposite polycarbonate membranes. Transport of hydrogen gas flux changes due to the modification in membrane matrix. Metal coating was performed using Pt-Pd alloy and Ir. High purity hydrogen gas is required in energy applications where it replaces the conventional fuels. For this purpose Palladium membrane is considered as it can separate high purity hydrogen from the gas mixture. The most promising utilization of palladium as membrane is as a membrane reactor. According to this application, simultaneous purification by separation and chemical reaction occurs. Pure palladium undergoes phase transition below 300 °C, the lattice absorbs hydrogen gas molecules which leads warping and causes embrittlement [10]. In this work Pt-Pd alloy and Ir used due to their good adhesion characteristics with polymer phase [11].

A Pt-Pd alloy thin film and Ir thin film of around 8-10 nm were coated on polycarbonate substrate. Standard vapor deposition sputtering technique was used to develop layered polymer nanocomposite membrane. PC/SiO_2 nanocomposites with 10 wt% and 15 wt% silica nanoparticles loading were prepared by solution cast method. The gas permeability experiment was performed at constant 30 psi upstream pressure and at constant temperature 35 °C using constant volume/variable pressure method. For iridium coated PC, the test was performed at 22.5 °C temperature and at the same operating pressure. The other parameters such as thickness and exposed area of the membrane are provided in section **2.3.1** of **Chapter 2**. Section **4.2** describes the effect of membrane compositions on the hydrogen flux. The analysis of hydrogen permeation is given in section **4.3** and in the next section **4.4**, necessary characterization analysis is described. Selectivity of the membrane material by H_2/CO_2 gas pair is explained in section **4.5** and the last section **4.6** provides summary of the chapter.

4.2. Hydrogen flux through membrane

As hydrogen gas molecules diffuse through the membrane, it gives the gas flux transported from the higher pressure side to the lower pressure side conforming pressure gradient across the membrane. Diffusion is rate determining step for gas permeation through the membrane depends on the nature of membrane and permeated gas flux. Solution diffusion mechanism has been applied for the MMMs and metal coated membranes. H_2 transport through the metal coated polymer film and MMMs follows different routes for gas transportation as explained below.

4.2.1. Rate of H_2 transport across metal coated PC membrane

Hydrogen transport by metallic material is complex mechanism as especially for palladium metal. Palladium is the most permeable materials for hydrogen whereas impermeable to other gasses which in turns to improve permselectivity. Hydrogen permeation through metallic membrane follows solution-diffusion mechanism due to partial pressure across the membrane involving some additional steps. In the first step of the mechanism, as the hydrogen gas molecule is dissolved into the feed side protective surface of the metal, chemisorption takes place. Therefore, a diatomic hydrogen molecule splits is into atomic hydrogen.

$$H_{2\,(\text{molecule})} \xleftrightarrow{\text{Chemisorption}} 2H_{(\text{atom})}$$

The chemisorption of hydrogen gas molecule by metallic compositions is reversible process. The diffusion takes place same way such as according to the solution-diffusion mechanism and during desorption from the bulk metallic volume, hydrogen atoms recombine into the molecular form. These additional two steps are involved in this mechanism for hydrogen permeation through metallic membrane which may affect the transport rate of the gas by the metallic layered [12].

A graph of downstream pressure versus time for H_2 transport by metallic layered PC, SiO_2 doped PC and pure PC is shown in **Figure 4.1**. It was observed that the H_2 gas flux differs as the coating composition changes and also varies according to SiO_2 wt%. Pure PC gives higher transport rate as compared to the PC/Ir and PC/Pt-Pd membranes. The rate of gas flux depends on the other factors such as exposed area, membrane thickness and different test conditions such as operating temperature and upstream pressure. Hence all the parameters effectively control the flow rate. The permeating hydrogen flow rate by PC/Ir membrane was found to be lowest. The metallic coating lowers the H_2 flow rate as compared to that of pure PC. This may be due to the hydrogen dissociation and recombination by metal surfaces. It might also change because of change in sorption nature of different metallic composition. In metallic layered polymer membranes, the feed gas first interact with metal coating which is physiochemical process. The rate determining step of H_2 transport through thin metal layer enhances the gas sorption by the membrane towards upstream side. Thus the metal coating easily achieves solution diffusion mechanism. Furthermore, palladium metal adds resistance which reduces as increase in temperature. Therefore, the vacant sites increases by penetration of gas molecule promoting diffusion rate[13, 14]. Thus PC/Pt-Pd gives better flow rate as compared to PC/Ir. Downstream pressure rate varies for H_2 with operating pressure ranges from 30 psi to 180 psi at 35 ℃ as shown in **Figure 4.2**. The figure indicates the rate of hydrogen gas flux variation with respect to time for PC/Pt-Pd membrane. Hydrogen transportation increases in negligible amount as feed pressure increases. By applying 180 psi feed pressure the slope of downstream pressure versus time gives small increase within 130 seconds for diffusion.

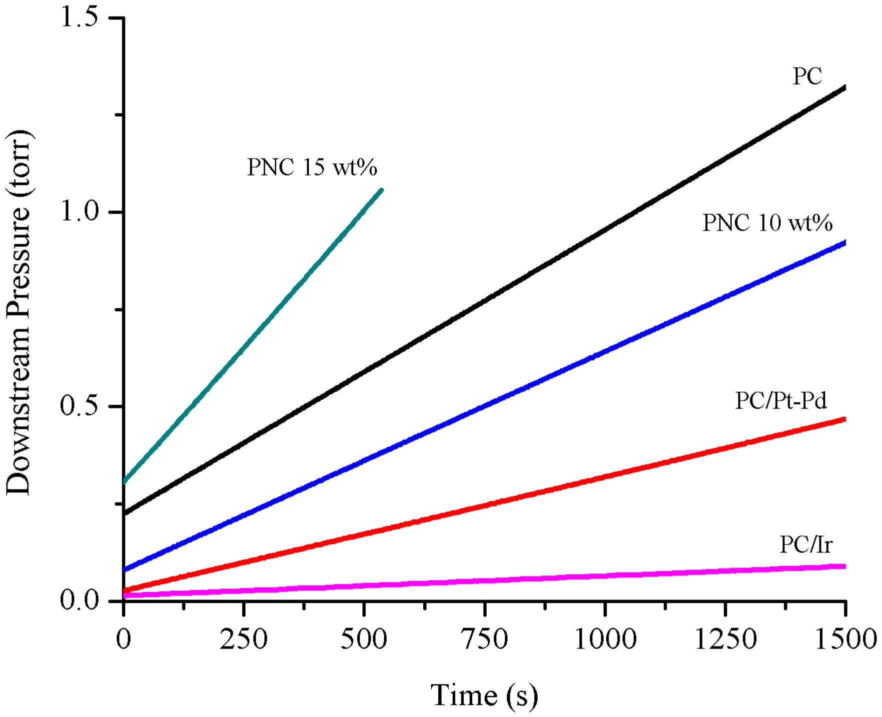

Figure 4.1 Downstream pressure versus time for pure and modified membrane at 30 psi feed pressure

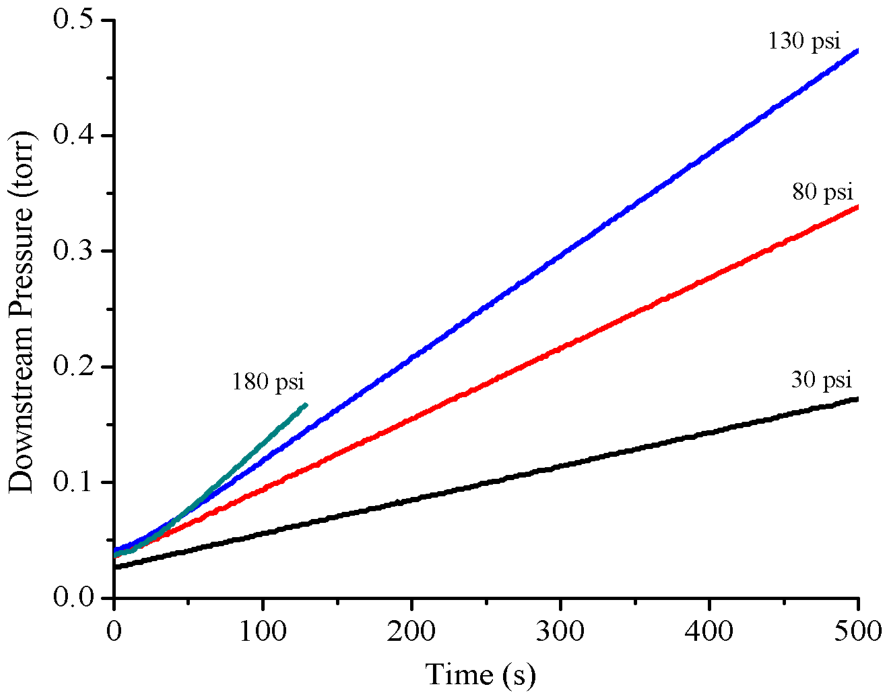

Figure 4.2 Downstream pressure versus time for PC/Pt-Pd at various feed pressures

4.2.2. Rate of H_2 transport across MMMs

The transport of any gas molecules especially through the MMMs depends on different variables such as suitable combination of polymer/inorganic filler, particle size, particle agglomeration and sedimentation and as well the interfacial morphologies. The transport rate of hydrogen gas flux through SiO_2 MMMs is plotted in the **Figure 4.1**. As compared to other membrane materials, 15 wt% SiO_2 fillers in PC matrix show enhancement in transport rate which tends to increase diffusion within the pressure gradient. Gas flux rate through 10 wt% PNC membrane and pure PC are almost parallel depending on the exposed area and the thickness of the film to be tested. The host PC represents better transport rate compared to metal coated and 10 wt% PNC as the gas permeability parameters not only depend on the slope of downstream pressure versus time but also depend on membrane parameters such as exposed area and thickness. By increasing the filler amount in the polymer matrix the flow rate of hydrogen gas molecules is promoted resulting increase in slope.

During the synthesis of MMM, the particle agglomeration is responsible to change the transport parameters of the membrane. SiO_2 nanofillers and PC having different chemical and physical properties, there is possibility to produce inhomogeneous phase in mixed matrix material. Therefore, silica filler can not compile properly with the PC phase resulting in agglomeration. In addition, small voids are formed at the particle-polymer interphase due to poor contact which provides extra path ways for diffusing molecules [15]. Nanofillers also modify the chain packing in the polymer phase causing small pinholes. The gas flux diffused through such a composite membrane may refer the developed non-resistive paths and can easily transport through the film to be tested. The major concern in the hybridization of organic and inorganic compound is the suitability of polymer with filler as particle agglomeration depends on the combination of the compositions. Although, the selection of inorganic filler is major factor affecting the diffusion of gasses but the choice of polymer matrix is also an important concern which determines the performance of the hybridized membrane. It is reported by Duval et al. [16], MMM formed by incorporation of zeolite filler in the various silicone rubber determined the resultant performance as in original membrane such as low permeability and high selectivity. The diffusion coefficient would likely improve in low transport resistance phase of the polymer matrix. The filler size is also a dominating factor for gas transport rate as most of the research work has been done with the filler content in micron size. The disturbance in the polymer chain packing causes more molecular diffusion due to the polymer/particle interface. If the filler size is used in nanorange rather in micron then the interface area can be increased which finally tend to perform better transport rate. The dispersed filler content would be chosen in such a way that it can also enhance the separation of different gas species. There should be proper adhesion between the polymeric material and the nanofillers which can also strengthen the resultant membrane at the higher feed pressure. Generally, the PC and SiO_2 having difference in densities as well chemical composition, inorganic filler tend to agglomerate from the polymer phase and they migrate towards the surface or sediment at the bottom during the film casting process. As shown in the **Figure 4.3** instability is developed during the membrane casting process. The top layer is curved surface due to differences in the surface tension from center to edged volume of the flat bottom petri dish. The small arrows in the figure show the migration of fillers towards central top region. The silica particles are trapped towards higher viscosity top region rather to sediment in low viscosity bottom region. This can be analyzed in the membrane appearance given in section **5.3.1** of **Chapter 5**. This instability during the casting process forms small pinholes within the developed membrane or may cause small nanogaps between PC/SiO_2 interface. Hydrogen molecule being smaller kinetic diameter can easily diffused through the tiny voids or from the interface nanogaps. Although sonication step had been performed during film casting, but small amount of agglomeration was formed in the final MMM.

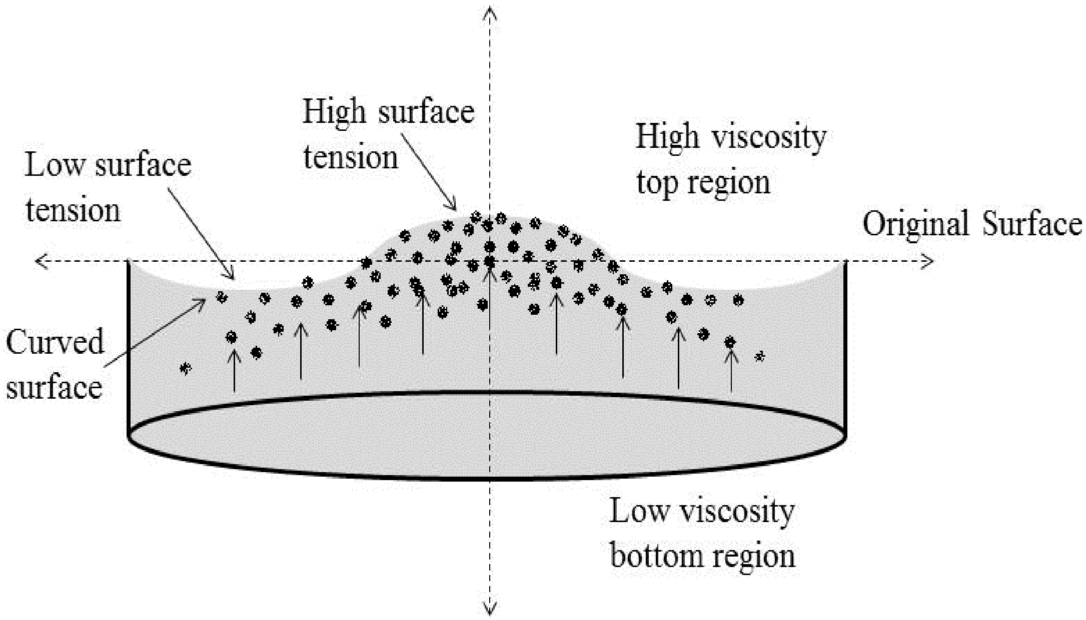

Figure 4.3 Instability developed during membrane casting [15] (Small arrows shows the particles trapped towards high viscosity top layer)

4.3. Hydrogen permeability through the membrane

4.3.1. Metal/alloy coated PC membrane

H_2 permeability is shown in **Figure 4.4** in which metal coated PC membrane provides better transport efficiency relative to that of pure PC polymer. It is observed that permeability obtained by PC/Ir is almost twice than that of PC membrane. Even, Pt-Pd coating also promotes the H_2 permeability as it increases by 17 % relative to the host polymer material. As per the bar graph, iridium coating shows better compatibility for H_2 gas compared to Pt-Pd alloy. This may be due to change in thermal property of exposed surface was changed during metal coating and condensation occurred which affect solubility factor. Permeability is also influenced by solubility of penetrant. Due to the condensation of gas molecules and mixing with polymer segments promotes the solubility which enhances the permeability. **Figure 4.5** describes the effect of feed pressure on H_2 permeation for PC/Pt-Pd. Permeability remains almost unchanged as per increase in upstream pressure. At 30 psi and 80 psi, the scattered values of permeability are almost same and small loss at 130 psi upstream pressure can be recorded. At 180 psi feed pressure small jump in H_2 permeability can be observed. Small marginal variation could have obtained within 130-180 psi range of upstream pressure which is unremarkable.

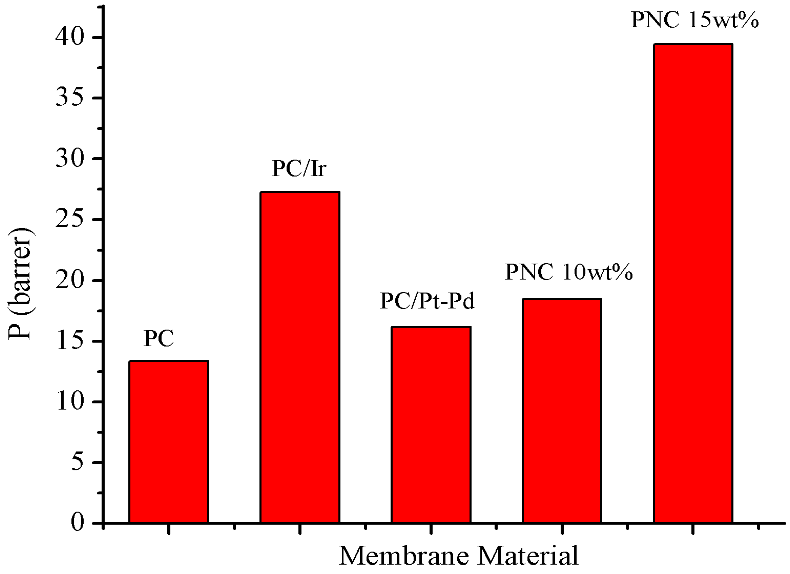

Figure 4.4. Permeability of pure and hybrid polycarbonate

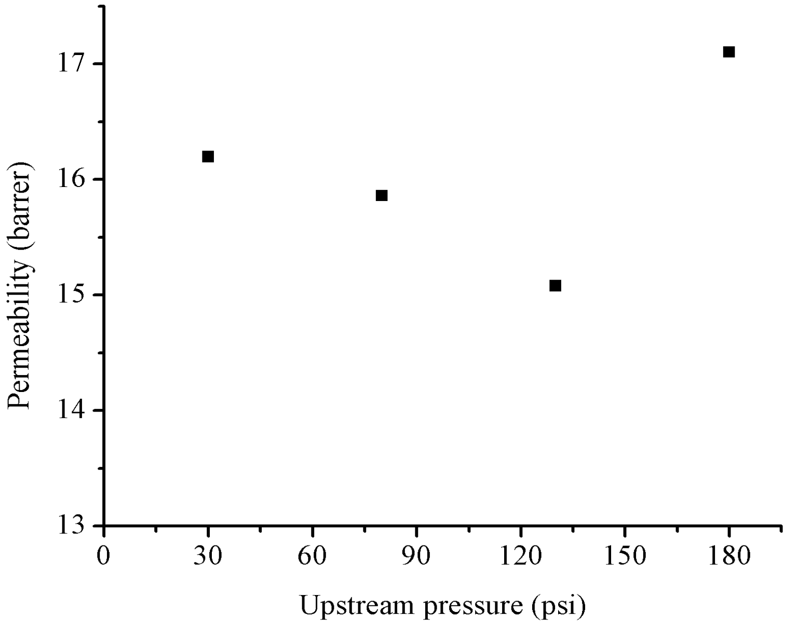

Figure 4.5 Permeability of H_2 for PC/Pt-Pd at 35 °C and different upstream pressure

4.3.2. Mixed Matrix Membrane

As explained in the previous section, the dependence of penetrant on the various factors in MMMs affects the permeability parameters of gas molecules. Permeability obtained in PC/SiO_2 MMMs for different wt% of nanofiller loading is given in the **Figure 4.4**. There is increase in permeability by incorporation of SiO_2 nanoparticles in polycarbonate matrix. MMMs with 10 wt% silica nanoparticles affect permeation of H_2 gas flux up to 27% than that of pure polycarbonate membrane. As the filler amount is increased up to 15 wt%, H_2 permeability enhances up to 66% as compared to pure PC membrane. In general, the gas permeation through the film relies on diffusivity and solubility parameters of the applied penetrant passing throughout the membrane phase. Thus in nanocomposite membrane, mechanism of enhanced gas permeability is based on solubility increase mechanism or free volume increase mechanism. Increase in solubility is due to the interaction between filler material and penetrant where the functional group on the filler surface are going to be interacted with polar gas molecules [17]. In the present work, H_2 is not the polar gas as the increase in the overall gas permeation is caused by the free volume developed due to dispersion of nanofillers. Therefore, solubility increased phenomenon is not responsible for relatively faster gas permeation in the MMM. In the free volume increase phenomenon, nanofillers are interacted with polymer chain segment. Silica nanoparticles dispersed in the polycarbonate matrix modify segmental mobility of polymer chain interrupting polymer chain-packing and results increase in the free volume between the polymer chains. This free volume is responsible for the promotion of penetrant permeability. By increasing the amount of nanofiller there is increase the fractional free volume promoting the H_2 permeability. It is observed from the graph that 10 wt% MMM gives better H_2 permeability than the pure PC membrane and by increasing silica content up to 15 wt% the H_2 permeation was found to be increased [11, 18]. As filler content is raised in the polysulfone matrix, it promotes degree of agglomeration which increases void size which leads to permeability enhancement. A schematic diagram of various nanoscale structures at polymer/particle interface is shown in the **Figure 4.6**. Type (a) structure represents ideal morphology which corresponds to the prediction of Maxwell model. Type (b) structure represents the development of interfacial voids due to the detachment of polymer chains from filler surface. The polymer chains which are in direct contact with filler surface rigidified compared to bulk polymer chains as indicated in the type (c) structure. In type (d) structure, the surface pores of fillers are filled by the rigidified polymer chains [15, 19]. The inter-aggregate void formed between the nanofiller aggregates enlarges at high filler concentration. Thus additional free volume besides fractional free volume exists. Permeability of large gas molecule is increased by addition of silica filler due to increase in the free volume [20].

According to the Maxwell model, gas permeation by composite membrane decreases as per increasing the filler volume fraction but several researchers have scrutinized an increase in permeation of gas component by promoting amount of nanofiller in the polymer matrix [21]. Due to the nature of SiO_2 nanofillers to agglomerate, they do not adhere tightly with the continuous phase of PC matrix forming nanogaps surrounding the filler surface. This narrow gap at the polymer-filler interaction permit gas component to be easily diffuses through it. Thus the diffusion path is going to be shortened resulting increase in the diffusion coefficient. Thus, the addition of SiO_2 nanofiller amount to the PC generates shortcuts to permeate H_2 gas component and allows faster permeation. Therefore, as compared to 10 wt% MMM, 15 wt% MMM results in higher permeability for H_2.

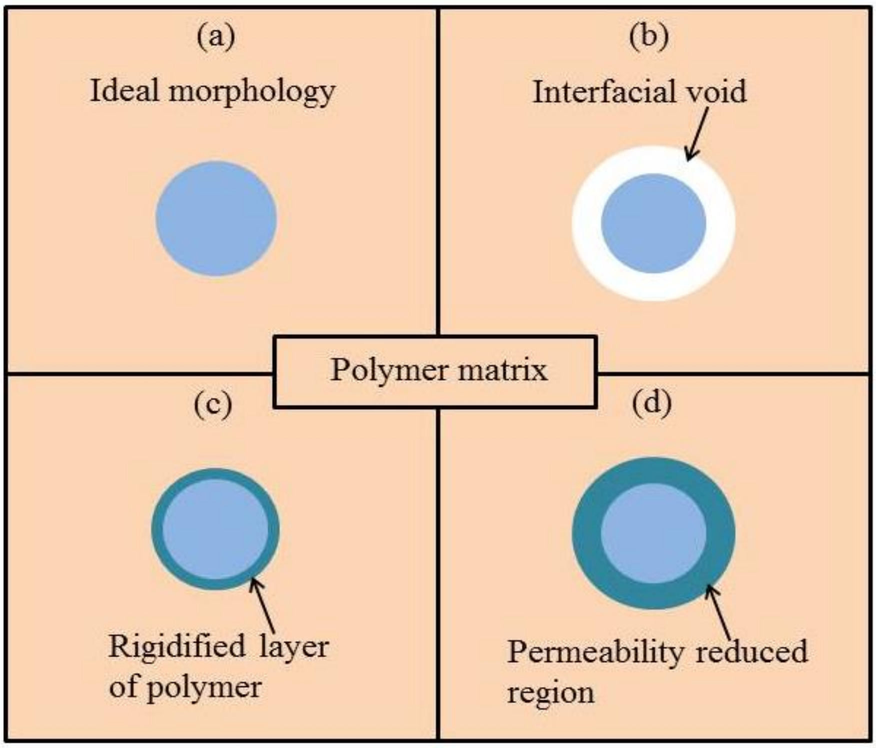

Figure 4.6 Interaction of nanofiller within polymer matrix [15]

4.4. Additional characterizations

4.4.1. Scanning Electron Microscopy (SEM)

The surface morphology of Pt-Pd coated PC is given in the **Chapter 3** and for 10 wt% SiO_2 doped PNC is given by SEM image as shown in the **Figure 4.7**. Filler incorporation into the polymer matrix modified its intermolecular chain packing changing morphological structure. Silica nanofillers successfully generate excessive free space inside polymer matrix but the void size depends on the degree of de-agglomeration. In present study, it is observed that the average free space created is 100-120 nm [18]. It is reported that pure PC membrane shows dense structure given by in FE-SEM image. More agglomeration forms by increasing filler content. Surface morphology of pure PC shows dense structure as reported by Idris et al. compared to MMMs. Free space volume enhances as increase in the filler content [22]. During the solvent evaporation, after membrane casting process, interfacial voids are formed and rigidifies polymer chains due to distinct phase properties and densities of filler and host polymer material. The developed rigid layer around nanofiller is associated by uniform distribution of stress results in the restriction of polymer chain mobility [19, 21]. The formation of interfacial voids is related to the non-uniform stress directions. It also depend on the other factors such as polymer packing distribution, weaker adhesion of filler and polymer, differences in thermal expansion and repulsive forces during membrane drying time period [23].

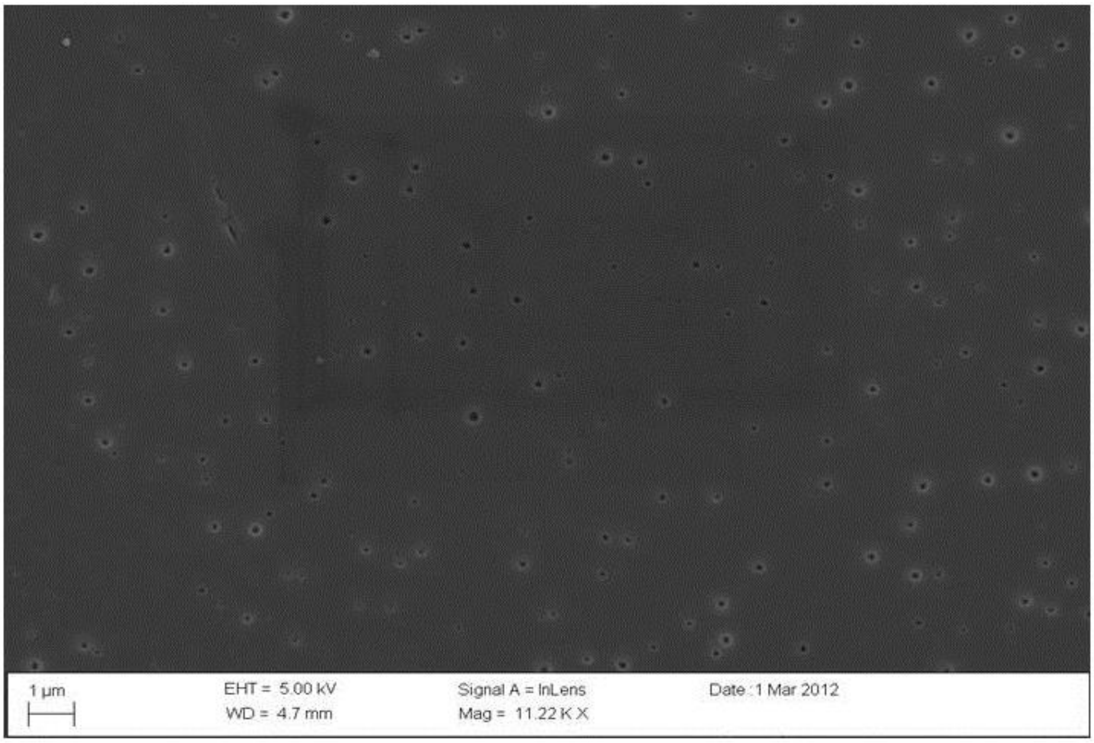

Figure 4.7 SEM image of 10 wt% SiO_2 PNC membrane

4.4.2. Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) analysis of PC and PNC (10 wt% filler content) was estimated by TA universal analysis software which is explained in the **Chapter 2**. **Figure 4.8** shows comparative DSC thermogram of pure PC and PNC. To avoid the effect of impurity, the measurement repetition was extended up to six cycles on true value of T_g due to which end points do not include data. It is found that the T_g for pure PC is 150 °C and it is matched with reported value [24]. The T_g value of PC/SiO_2 is 148 °C. Glass transition temperature reduces slightly for PNC which may be associated with the existence of filler composition in the polymer matrix. The long range segmental mobility within polymer chain is developed by the nanofillers which reduces the T_g [25]. Moreover, the filler concentration may alter the glass transition temperature up to some extent [18].

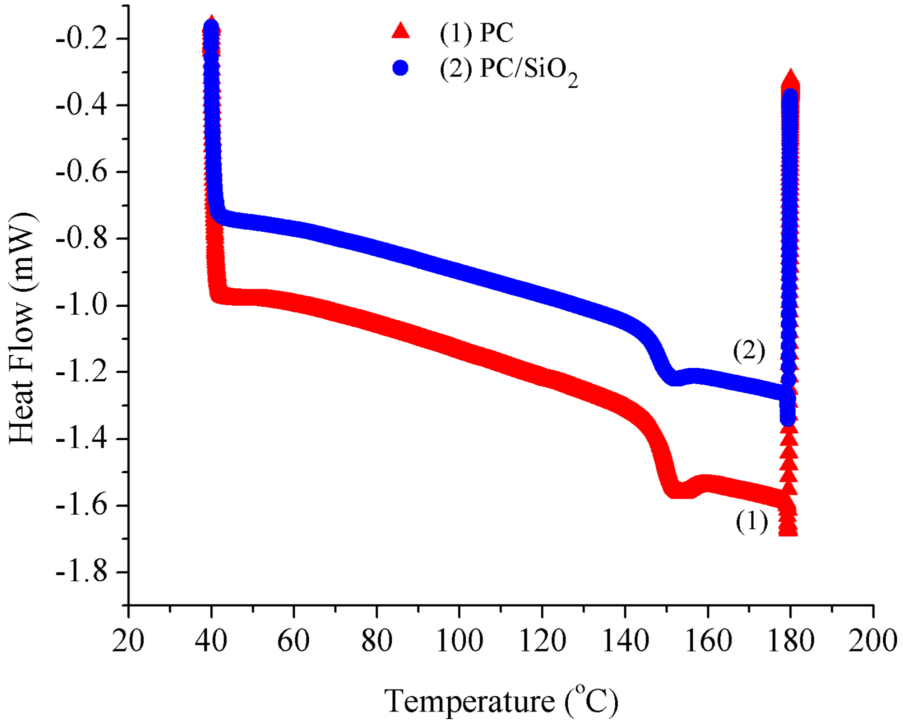

Figure 4.8 DSC thermogram for PC and PNC

4.4.3. Dynamic Mechanical Analysis (DMA)

Figure 4.9 shows stress versus strain curves for pure PC and PC/SiO_2 (10 wt% filler) membranes. Observing both the curves shows clear change in the tangent modulus for membranes. It is found to be 12 MPa and 9.5 MPa for pure polycarbonate and SiO_2 polycarbonate membranes respectively. At 2 % strain modulus for PC it is recorded 24 MPa and for PNC it is 19 MPa of stress applied. The change in the modulus provides the evidence of modification in the membrane structure[26].

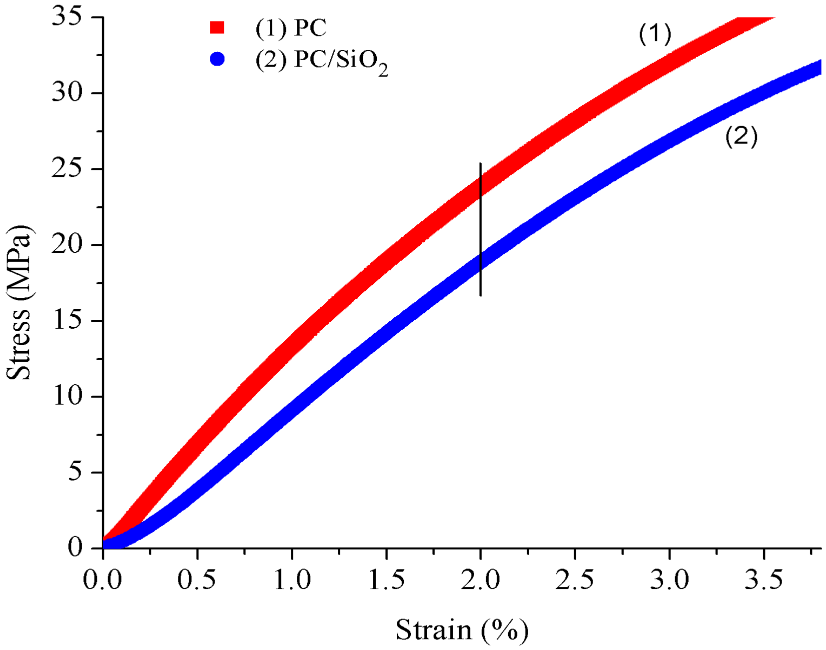

Figure 4.9 Stress versus strain curve for PC and PNC

4.5. Selectivity

Very few literatures are available till the date denoting the difference between the mixed gas permselectivity and an ideal separation factor for palladium membrane. Hydrogen swells the lattice structure of the metal and forms grain boundary space to diffuse other gases which in turn increases separation factor [27]. The selectivity comparison of H_2/CO_2 for pure PC, PC/Pt-Pd and for PC/SiO_2 (10 wt% filler content) is given in graph as shown in **Figure 4.10**. The SEM of metal coated PC provided in **Chapter 3** and the SEM of PNC membrane described in the previous section shows the surface roughness on the membrane where the feed gas is exposed. The roughness parameter is associated to nanofiltration applications. The disorder due to roughness enlarges the effective surface area of the membrane up to some extent resulting change in transport routes for different gas species [15]. Thus separation factor is affected by surface morphology. Hydrogen permeability increases for both the metal coated and nanofiller doped PC membrane in vast amount whereas its selectivity with CO_2 gas remains almost unchanged. Although permeability-selectivity parameters have trade-off nature, but the silica nanofillers maintains selectivity unchanged with increase in permeability which may be attributed to the nanogap hypothesis. As explained in the previous section about the hypothesis, free tiny space or nanolayer is created around the fillers due to poor adhesion with polymer chains. Therefore, short diffusive modes promote penetrant permeation and as the filler surface becomes compatible to polymer matrix, the nanogap shrinks and helps to uphold the separation factor [17].

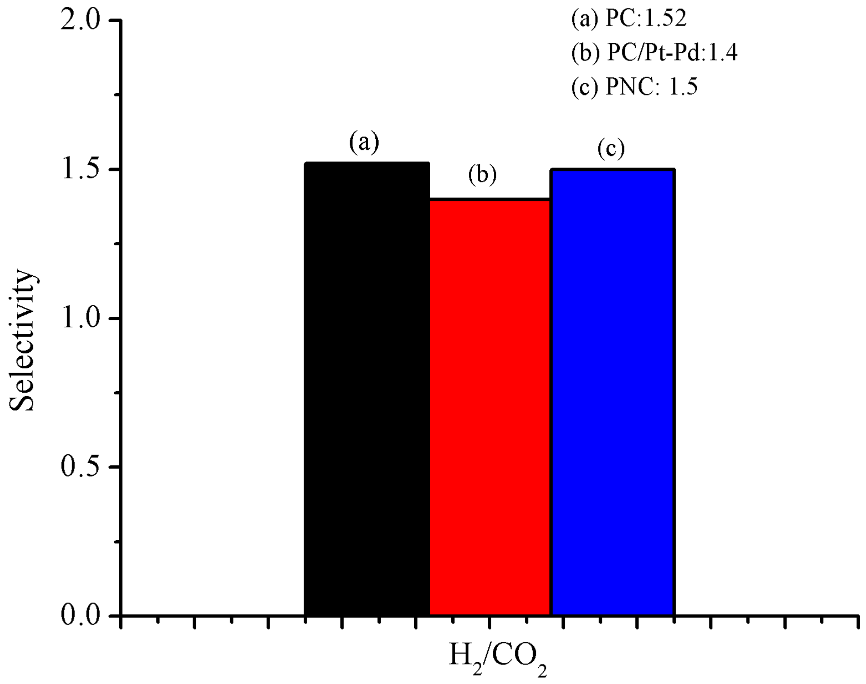

Figure 4.10 Selectivity of H_2/CO_2 by pure PC, Pt-Pd coated PC and 10wt% SiO_2 PNC membranes

4.6. Summary

The composite form of PC membrane improves transport mechanism for hydrogen gas molecules. The alterations in the hydrogen transmission reflects enhancement in permeability coefficient with un-affecting the separation factor. The composite form of PC by filler incorporation play vital role to provide additional routs for hydrogen diffusion. In addition, the filler concentration increases the excessive free space to support the gas permeation. Metal coatings also form new gate way to the hydrogen molecules making them soluble within the membrane matrix. The selectivity factor is maintained by the modification which makes it applicable for separation of hydrogen from the carbon dioxide. The analytic characterizations provide morphological view and thermodynamic information about the members. It provides the information about the responsible factors behind the change in the transport parameter and separation factor.

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