Fabrication and Evaluation of Functionalized Nano-titanium Dioxide (F-NanoTiO₂)/ polysulfone (PSf) Nanocomposite Membranes for Gas Separation

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Abstract

TiO_2 nanoparticles were pretreated with ethelendiamine (EDA) to synthesize amine-functionalized TiO_2. The mixed matrix membranes (MMM) comprised of amin-functionalized TiO_2 inside polysulfone (PSf) matrix were fabricated and characterized for gas separation. The effects of the amin-functionalized TiO_2 loading on the gas permeation properties of the MMM were investigated by varying the amin-functionalized TiO_2 loading in the PSf matrix from 0−10 wt%. The fabricated amin-functionalized TiO_2/PSf MMM were characterized by scanning electron microscopy (SEM), Fourier Transform Infrared spectroscopy (FT/IR) and pure gas permeation test. Gas permeation measurement showed that MMMs embedded with different amount of amin-functionalized TiO_2 exhibited different separation performances. For example, in MMMs containing 10 wt% amin-functionalized TiO_2, the permeability of N_2, CH_4, CO_2 and O_2 increased up to 0.69, 0.8, 3.5 and 1.1 GPU respectively. Due to the higher interaction of amine groups on F-nano TiO_2 with polar gases, amin-functionalized TiO_2 possessed better performances in terms of permeability and selectivity in comparison to pure TiO_2. The results revealed that the functionalization of TiO_2 has improved the gas permeability of prepared membranes.

Keywords: *Gas Separation, Nanocomposite Membrane, Functionalized Nano TiO_2*

1. Introduction

Application of polymeric membranes in gas separation processes is growing rapidly. This is due to low capital and operating cost and low energy consumption, so improving the performance of polymeric membranes for gas separation is considered to be a dominant factor in the field of membrane technology [1]. Generally, for economic consideration, the permeability and selectivity of the membranes should be maximized for

providing commercially attractive separation behavior and achieving more efficient separation [2, 3]. Therefore, mixed matrix membranes (MMMs), defined as inorganic nanofillers dispersed at a nanometer level in polymer matrix have been studied as an alternative approach to improve gas separation performance and overcoming Robeson upper bound limitation [4, 5]. Actually the advantages of polymeric membranes and the superior separation performances of rigid molecular sieves were collected in MMMs [6]. Metal oxide

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nanoparticles such as MgO and TiO_2 are emerging materials due to their potential applications for membrane-based separation purposes. Titanium dioxide (TiO_2) as a filler has received considerable attention because of its excellent chemical and thermal stability, hydrophilicity and gas separation properties [7, 8].

Freeman *et al*. [9] reported that the relative permeability of PTMSP/TiO_2 was improved by increasing the free volume of polymer matrix and void formation at PTMSP–TiO_2 interface. Hu *et al*. [8] shows that the addition of TiO_2 to poly (amide–imide) in the NCM has shown an increase in the selectivity of the gas pairs CO_2/N_2 and H_2/N_2 and the specific interaction of CO_2 and H_2 with the TiO_2 domain has been considered for this. Matteucci *et al*. investigated the influence of TiO_2 particle on the gas transport properties of the MMM based on both glassy [9] and rubbery polymer [10]. Upon the incorporation of TiO_2 into the polymer matrix, the dispersion of these nanoparticles was varied depending on the amount of loading. From this study, the permeability and selectivity of gas pairs consisted of CO_2 and nonpolar gas appeared to increase with increasing particle loading.

The choice of suitable polymer is quite important from the view of compatibility with the inorganic fillers as well as ability to resist plasticization under aggressive feed steams. PSf is considered to be a good candidate possessing not only good thermo-mechanical strength, permeability and selectivity but is also cost effective. Its high resistance to plasticization at a pressure above 30 bar makes it suitable for membrane development [11].

One of the most important parameters in MMMs fabrication is good dispersion of nanoparticles in polymer matrix. The results of previous works show that the small sizes of particles with high specific area disperse appropriately in polymer matrices [12]. Recently, with advances in nanotechnology, addition of chemically modified or functionalized nanoparticles into polymeric materials has become a subject of considerable attention. In this advance, the inorganic particles (such as TiO_2 and SiO_2) are connected with organic coatings (like amine or carboxyl) by physical and/or chemical interactions between the particles and organic modifiers. In the chemical treatment, there is a strong attachment so nanoparticles dispersion is good in polymer matrix.

In the present work, TiO_2 nanoparticles were functionalized by ethylenediamine (EDA) and the amino-functionalized TiO_2 nanoparticles were blended with PSf to prepare mixed matrix membranes. The changes in the structure and gas permeability of the membranes caused by different weight ratio of F-nano TiO_2 were investigated. The single gas permeation and separation performance of gas N_2, O_2, CO_2 and CH_4 were measured.

2. Experimental
2-1. Materials
Polysulfone beads (PSf;Udel P3500, Solvay polymers) as the membrane substrates polymer and 1-Methyl-2-pyrrolidone (NMP, >99.5%, Merck, Germany) as the solvent and TiO_2 (particle size of 25 nm, Degussa) as organic filler, ethanol (>99.9%, Scharlab S. L., Spain), Ethylenediamine (>99.5%,

Scharlab S. L., Spain) were used for functionalization of Nano TiO₂. Oxygen (O_2, 99.9999%) and nitrogen (N_2, 99.9999%) were obtained from Balon Gas Asia Co. Carbon dioxide (CO_2, 99.9999%) and methane (CH_4, 99.9999%) were obtained from Technical Gas Services, Dubai, United Arab Emirates.

2-2. Nano TiO₂ functionalization

EDA was used to functionalize TiO₂ nanoparticles according to the procedure shown in Fig. 1. The proper amount of the nano TiO₂ was added to 50 ml ethanol and dispersed by sonication. After that, ethylenediamine (EDA) was added to the solution [13]. Then, the solution was refluxed under stirring using magnetic stirrer equipped with reflux condenser, thermometer and oil bath for better heat distribution at 65°C for 3 h. After amination the TiO₂-NH₂ was filtered with filter paper. As the final stage, the amine functionalized nano TiO₂ were dried in an oven at 80°C for 24 h to remove the unreacted amine agent and the adsorbed water vapour or other organic vapours.
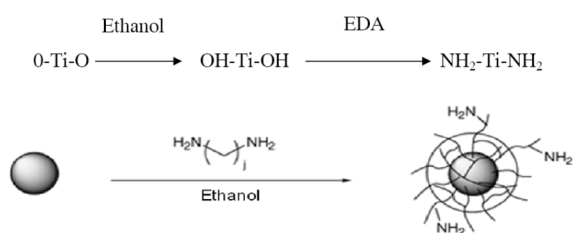

Figure 1. Schematic of amino-functionalization of nano TiO₂ using a EDA

2-3. Preparation of membrane

Phase inversion induced by immersion precipitation technique was applied for preparation of mixed matrix PSf membrane with functionalized TiO₂ nanoparticles at different concentrations (0, 2, 5 and 10 wt%). For preparation of MMMs, a predetermined mass of the nanoparticles was dissolved in NMP. This functionalized TiO₂ nanoparticles solution added to the polymer solution (20 wt%) and the mixture allowed mixing for 6 h at room temperature. The polyester non-woven fabric was attached to a clean glass plate and after 10 min sonication the dope solution was then extended on to the polyester fabric using a casting knife. The thickness of the ready membranes was between 150-175 μm. The whole composite was immersed in the precipitation bath including DI water after a few seconds to start the phase inversion. After that, the membranes were stored in water bath for at least 1 day to leach out the residual solvents completely.

2-4. Characterization of membrane structure and surface properties

Scanning Electron Microscopy (TESCAN, operating at 15 KV) was used to observe morphology, surface structure, cross-sectional images and dispersion of TiO₂ nanoparticles in the membranes. For the cross-section scanning, membranes were fractured in liquid nitrogen. Then, all samples were coated with a gold layer for observation by a sputter coater (BAL-TEC, SCDOOS). ATR–FTIR spectra of the MMMs were recorded with a WQF-510A spectrophotometer in the range of 500–4000 cm^{-1}.

2-5. Permeation test

The pure-gas permeation tests were carried out at room temperature, with the permeation

apparatus shown in Fig. 2. The constant pressure permeation system was used at room temperature. Before the feed side exposure to the selected gas at a specific pressure, the membranes were held under vacuum for about 5min to make a steady state. A circular sample with 28.5 cm^2 effective areas (A) was cut from membranes samples and placed in the cross flow stainless steel membrane module. Digital mass flow meters measured permeate flows while the feed flow rate was controlled by a mass flow controller (ALICAT, 91260 Model). The gas permeability of membranes was calculated by solution-diffusion mechanism [12].
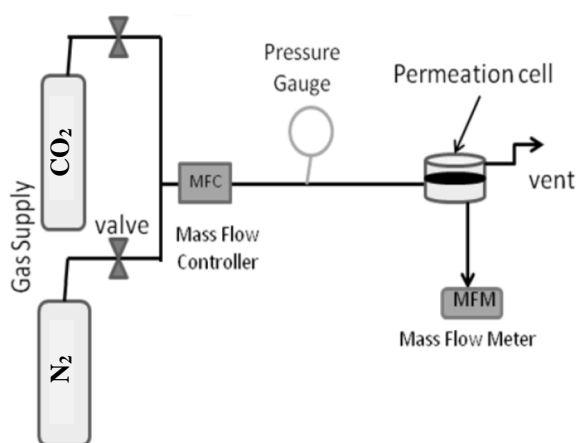

Figure 2. The diagram of the set-up for the permeation measurement.

The permeation coefficient is calculated by using the following equation:

$$\frac{P_i}{L} = \frac{Q}{A \Delta p} \tag{1}$$

Where P_i is the gas permeation through the membrane, which is expressed customarily in GPU (1 GPU= 10^{-6} cm^3 (STP)/cm^2 s cm Hg); Q the gas permeation rate (cm^3 (STP)/s); A the effective membrane area for

permeation (cm^2); and Δp the pressure difference across the membrane (cm Hg) and L the membrane thickness (cm). The ideal separation factor $\alpha_{i,j}$ can be estimated by using the following equation which is the ratio of pure gas i and j permeances:

$$\alpha_{i,j} = \frac{\dfrac{P_i}{L}}{\dfrac{P_j}{L}} \tag{2}$$

3. Results and discussion
3-1. Functionalization of TiO_2 nanoparticle
To confirm the functionalization of nano TiO_2 by EDA, the FTIR spectrum of chemically modified TiO_2 nanoparticles was shown in Fig. 3. The FTIR spectrum of pure TiO_2 nanoparticles was provided elsewhere [14]. A comparison between FTIR spectra of pure and functionalized TiO_2 nanoparticles indicated the formation bands at 2920 cm^{-1} (CH_3) and 3409 cm^{-1} (OH stretching frequency of amino groups), and 1650 cm^{-1} (N-H stretching vibration) which corresponded to the functional groups of EDA. The band at around 1480 cm^{-1} is assigned to vibration of second amine groups (C-N). These bonds prove that the amine group has been chemically attached to the TiO_2 nanoparticles.

3-2. Morphology of F-TiO_2 /PSf mixed-matrix membranes
SEM was used to observe the compatibility between the sieves and polymer matrix. Fig. 4 shows the surface and cross sectional SEM images of 5 wt% F-TiO_2/PSf MMM. From cross section SEM micrograph of MMMs, the particles distributions of F-TiO_2 in MMMs were verified. As can be seen from
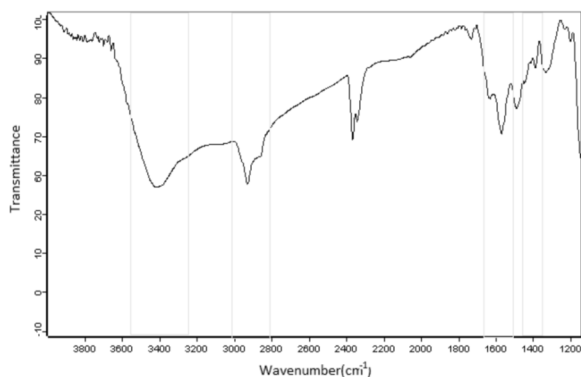
Figure 3. FTIR spectrum of Functionalized-TiO$_2$ nanoparticles.

Fig. 4, the membrane has asymmetric structure consisting of a finger-like porous as a result of the strong affinity between solvent and water in coagulation bath [1]. The surface image of this MMM (Fig. 4a) indicated that F-TiO$_2$ particles were not agglomerated and well distributed along the surface of the PSf matrix. The cross sectional image (Fig. 4b) of the same MMM also discovered that F-TiO$_2$ particles were well dispersed throughout the PSf matrix. Because of the affinity between the PSf matrix and F-TiO$_2$ particles, there were no interface voids or sieve in matrix morphology. Amine group could be used to bond polymer chains onto the F-TiO$_2$ surface, thus increasing good correlation between the TiO$_2$ and the bulk polymer phase. In order to investigate the morphological structure of F-TiO$_2$/PSf MMM at different F-TiO$_2$ loading, the SEM images were carefully examined (Fig. 5). The surface image of 2 wt% F-TiO$_2$/PSf MMM indicated that F-TiO$_2$ particles were well dispersed throughout the PSf matrix (Fig. 5a). No evidence of particles agglomeration or interface void can be found through these images, thus good agreement was suggested between the PSf matrix and F-TiO$_2$ particles. As the TiO$_2$ loading was further increased up

to 10 wt% (Fig. 5c), the titanium dioxide tends to agglomerate and is not well dispersed throughout the PSf matrix. Furthermore, the defects and interface voids around the TiO$_2$ agglomerates could also be found on the surface of this MMM (Fig. 5c). The interface voids are dependent on the content of F-TiO$_2$. These voids increased with increasing F-TiO$_2$ loading ratio. For instance at 2 wt% of F-TiO$_2$, there were no interface voids while in the case of 10 wt%, the voids have been observed.
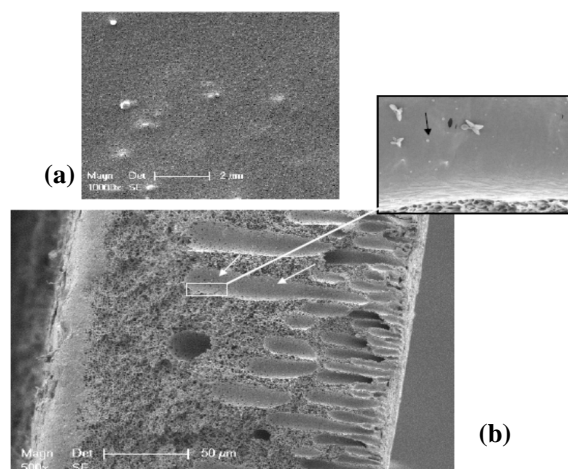

Figure 4. SEM photographs of F-TiO$_2$ (5 wt%) /PSF mixed matrix membrane embedded with amine functionalized TiO$_2$ (a) surface image (b) cross section image.
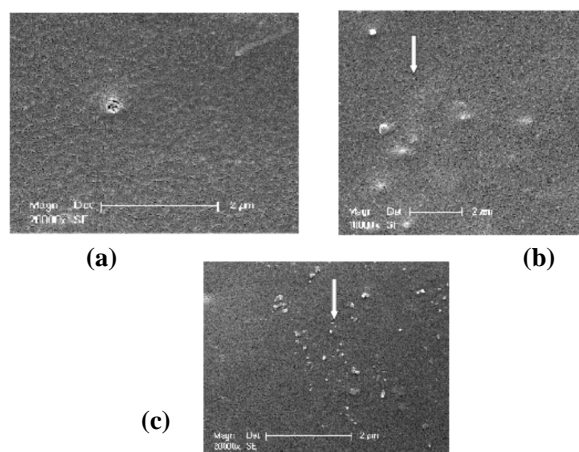

Figure 5. SEM images of surface of F-TiO$_2$/PSf MMM at different TiO$_2$ loading: (a) 2 wt% F-TiO$_2$; (b) 5 wt% F-TiO$_2$; (c) 10 wt% F-TiO$_2$.

Fig. 6 presents ATR–FTIR spectra of the F-TiO$_2$/PSf mixed matrix membrane with different filler loading. The spectral of F-TiO$_2$/PSf mixed matrix membrane exhibits some characteristic absorption peaks of EDA, which means the particles were successfully modified by EDA. In the spectra of mixed matrix membranes, the bands at around 2900 cm^{-1} belong to methyl group [–(CH) n–] [15, 16]. The band at 1658 cm^{-1} is assigned to vibration of amine groups (C-N) in the mixed matrix membranes, which is attributed to functionalization of TiO$_2$. The band at around 3450 cm^{-1} is assigned to vibration of amine bands which overlapped with the OH band at around 3409 cm^{-1} [17]. Additionally, the intensity of peaks increases with increasing F-TiO$_2$ loading in polymer matrix. The presence of amine groups into polymer matrix can affect the gas permeability. CO$_2$ molecules interact with the polar and electronegative groups in the main chain of polymer, during permeation. Therefore, the strong interaction between CO$_2$ molecules and amine groups on the TiO$_2$ surface is one of the important reasons for higher CO$_2$ permeability [18, 19].
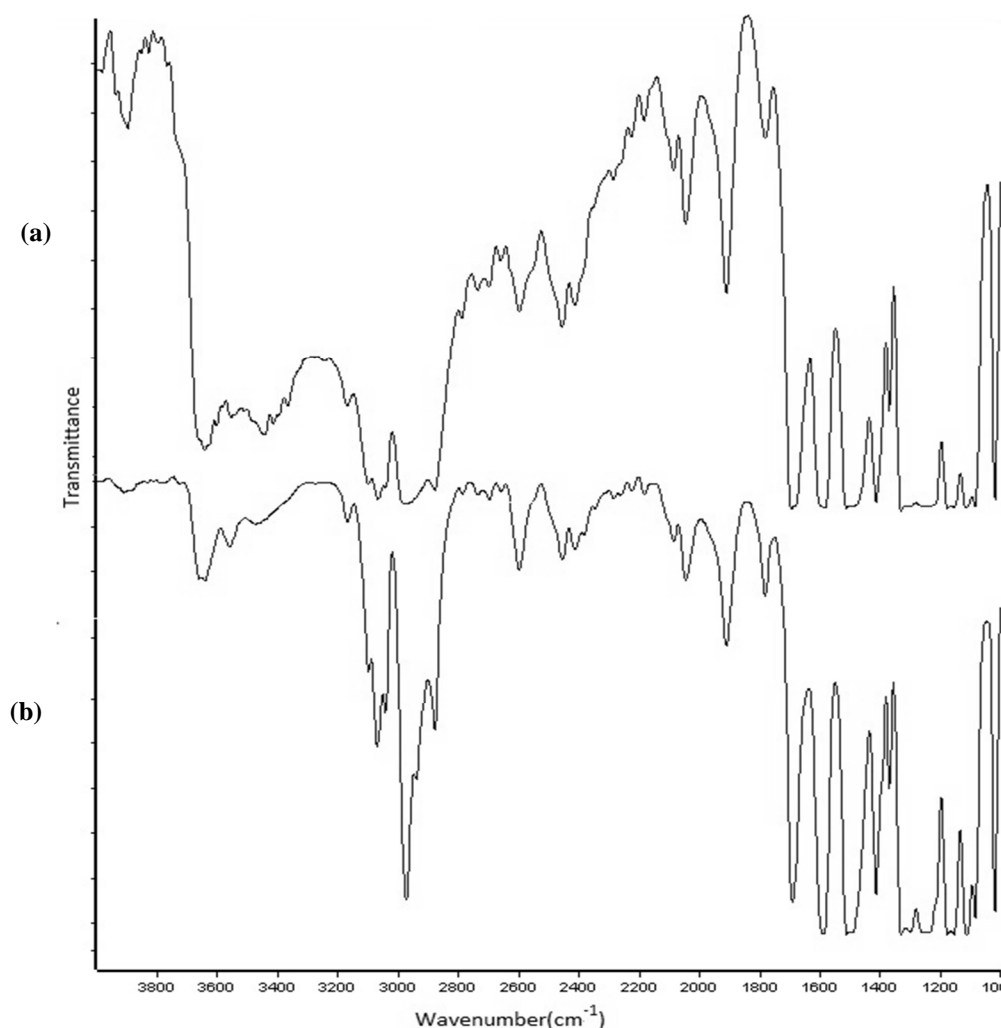

Figure 6. FTIR spectra of F-TiO$_2$/PSf mixed matrix membrane: (a) 5 wt%; (b) 10 wt%

3-3. Gas permeability and selectivity of F-TiO$_2$ /PSf mixed matrix membrane

In order to investigate the effect of F-TiO$_2$ loading on the MMM gas separation performance, F-TiO$_2$/PSf MMM with different F-TiO$_2$ loadings were fabricated. For comparison, neat PSf membranes and TiO$_2$/PSf were also prepared with the same procedure. The single gas permeation experiments showed that the permeability of all gases increased with TiO$_2$ nanoparticles loading from 0 wt% to 10 wt%. This increase might be due to the fact that the number of pinholes increased with increasing TiO$_2$ nanoparticles loading ratio, and consequently diffusion mechanism increased. Furthermore, this increase may be a trend because of the interaction between polymer phase adhered well to F-TiO$_2$ surface. EDA with a reactive end group could be used to bond polymer chains onto the TiO$_2$ nanoparticles surface, thus promoting good adhesion between the TiO$_2$ nanoparticles and the bulk polymer phase which in turn contributes to the high gas permeability [10]. Gases permeability for F-TiO$_2$/PSf membrane is higher than those without functionalized TiO$_2$ loading and increases with increasing TiO$_2$ loading ratio at fixed pressure.
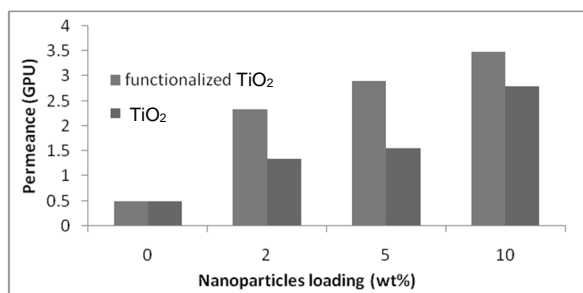

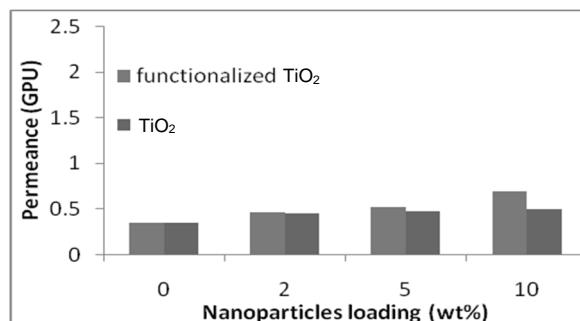**Figure 7.** Effect of Nanoparticles loading on CO$_2$ permeability.

Figure 8. Effect of Nanoparticles loading on N$_2$ permeability.
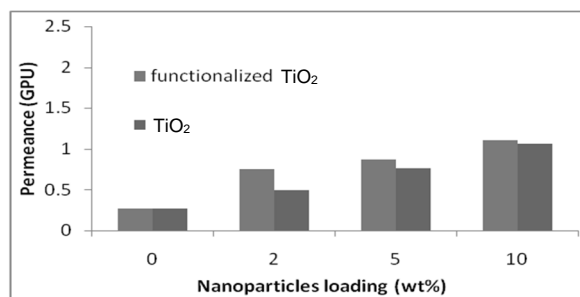

Figure 9. Effect of Nanoparticles loading on O$_2$ permeability.

The CO$_2$ permeability of the F-TiO$_2$/PSf mixed matrix membranes initially increased with increasing F-TiO$_2$ concentrations. The CO$_2$ permeability of the F-TiO$_2$/PSf membrane reached to 2.33 GPU at F-TiO$_2$ loading of 2 wt%. When the F-TiO$_2$ concentration was increased to 10 wt%, the CO$_2$ permeability increased remarkably to 3.4 GPU. The O$_2$ and N$_2$ permeability were increased from 0.60 to 1.1 and 0.45 to 0.69 respectively when the F-TiO$_2$ loading in the polymer matrix was increased from 2 wt% to 10 wt%.

The results suggest that the interaction between polymer-chain segments and F-TiO$_2$ may disrupt the polymer-chain packing and thus enhance the gas diffusion due to more free volumes introduced among the polymer chains and defects at polymer/nanoparticles interface. The amine group, confirmed by

FTIR in Fig. 6, has stronger interaction with polar gas, such as CO_2 and O_2 than non-polar gas, e.g. CH_4 and N_2. In that case, the polar gas solubility can be enhanced and the gas permeability is increased. Although the interaction between CH_4 and amine-group can enhance the CH_4 permeability, as seen from the results, the functionalized TiO_2 nanoparticles have more effects on the CO_2 permeability than the other gases. The strong interaction between CO_2 molecules and amine groups on the TiO_2 surface is one of the important reasons for higher CO_2 permeability. CH_4 and N_2 permeation mechanism is adsorption and diffusion in inner surface matrix. Hence, the CO_2 permeation mechanism is surface diffusion, adsorption and diffusion through the polymer matrix. Another reason for increasing gas transport is that the voids created between polymer chains and TiO_2 nanoparticles increased with increasing TiO_2 nanoparticles loading ratio in the polymer matrix [11].

The strong interaction between CO_2 molecules and amine groups on the F- TiO_2 surface is an important reason for higher CO_2 permeability. CO_2 molecules may interact with the polar groups in the mixed matrix membrane. Functional amine groups on the surface of the inorganic nanofiller in F-TiO_2/PSf MMMs can also increase the gas permeability due to the interactions between polar gas and functionalized inorganic filler [9].

The separation performance of MMMs was investigated by ideal selectivity calculation of gas pairs. Selectivity results of O_2/N_2 and CO_2/CH_4 are shown in Fig. 11. As can be seen, this figure exhibits a general increase in MMMs selectivities relative to pure

polysulfone. When the F-TiO_2 loading was further increased from 2 to 10 wt%, the selectivity of CO_2/CH_4 and O_2/N_2 decreased. This tendency arises from the increase in free volume and voids which in turn decrease the size-selective nature of membrane. Also, the non-selective interfacial voids that are larger than the penetrating gas molecules may exist at higher loadings of F-TiO_2, due to the poor adhesion of F-TiO_2 surface and PSf matrix. An apparent reduction in ideal selectivities of gas pairs is observed in MMMs containing 10 wt% F-TiO_2 nanoparticles which can be related to unselective voids and micron-size aggregates formation in polymer matrix. Selectivity of gas pairs CO_2/CH_4 and O_2/N_2 reached 3.75 and 1.58 respectively at 10 wt% loading of F-TiO_2 in MMMs.
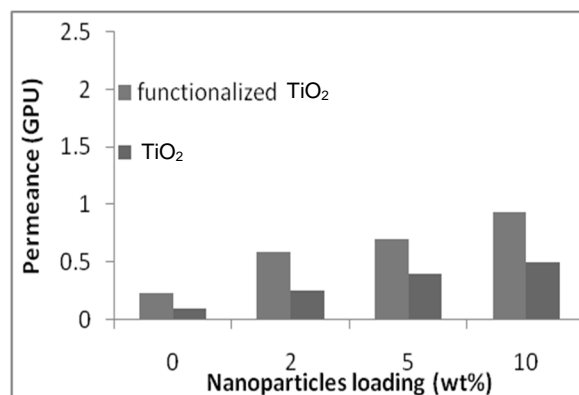

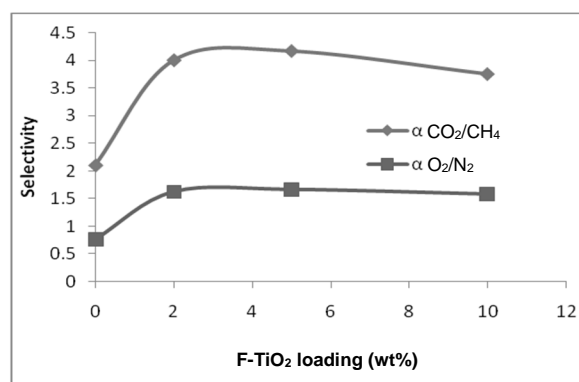**Figure 10.** Effect of Nanoparticles loading on CH_4 permeability.

Figure 11. Effect of F-TiO_2 loading on O_2/N_2 and CO_2/CH_4 selectivity.

4. Conclusions

A number of mixed matrix membranes were successfully prepared by addition of amine F-TiO₂ at different weight concentrations (0 to 10 wt%). Functionalization of TiO₂ nanoparticles with ethylenediamine (EDA) clearly impact on the MMMs gas permeation properties and morphology. The SEM images for surface area of MMM indicated that amine-functionalized-TiO₂ nanoparticles were well dispersed in the PSf membrane matrix at a loading of 5 wt% F- TiO₂. The effect of F-TiO₂ concentration on gas permeation was studied. The gas transport in the mixed matrix membranes through the interstice between F-TiO₂ and polymer chain is the major reason for the enhanced gas permeability achieved because of F-TiO₂ loading. The result showed that the F-TiO₂ can improve the membrane permeability for all gases. With increasing F-TiO₂ concentration, F-TiO₂/PSf membrane permeability for CO_2 increased from 2.32 to 3.49 GPU and selectivity of CO_2/CH_4 decreased from 4 to 3.75. It was found that as the weight ratio of F-TiO₂ increases in PSf composites, the permeability of CO_2 increased but the selectivity decreased slightly.

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