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Separation Techniques 2020: High performance of Ternary Mixed Matrix Membrane Containing Calix[4]arene and TiO2 Nanoparticles: Scientific Opinion- Mona Zamani Pedram - Toosi University of Technology

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Introduction:

Growing consumption of the fossil fuels during the past century causes many environmental problems.1-3 Global warming and climate changes resulted from the increment of the greenhouse gases, especially CO2, are highlighted as the most concerns and the main treat for ecosystem all around the world.4 Many efforts have been performed to decrease the destructive effects of the greenhouses gases in last 20 years including distillation and cryogenic technologies that remove the produced CO2 in industries.5 However, presence of the some disadvantages like environmental problems, high energy consumption, numerous complicated operation units as well as high investment cost make these methods undesirable for many countries.6-8 on the other hand, the membrane separation technologies which are identified as green environmental friendly technology are assumed as one of the best solution for this challenge.9-10 Among various materials for fabrication of the membranes, polymer membranes has been considered in many studies due to their suitable properties.11 In particular, matrimid 5218 has been interested in many studies for gas separation because of its unique properties.12 Matrimid is a common commercial polyimide polymer with relatively high gas permeability and selectivity, along with excellent mechanical properties, solubility in non-hazard organic solvents as well as commercial availability. However, good solubility of Matrimid in organic solvents makes it easy to swell in the environment of organic chemicals, thus deteriorating the separation performance of membranes.13 The presence of solvent plasticization causes the transport rates of all penetrants in a mixture to increase, which may result in significant selectivity losses because the increase for the slower permeating component is larger than for the faster permeating component.14 However, this category of materials faces many difficulties for using in membranes including plasticization, structure instability, and low selectivity as well as their limitation in comparison to the Robeson’s upper bound trade-off.15-16 Hence, the recent studies are focused on the properties enhancement of the polymeric membranes. Introducing fillers in the polymer matrix to mixed matrix membranes is considered as one of the best methods in modification of the membranes properties.17- TiO2 nanoparticles consider as on the most frequented applied particles in fabrication of the mixed matrix Membranes. Low cost and minimum incompatibility with organic phase in comparison to other inorganic particles make this particle interested in many studies.20-24 on the other hand, introducing of the organic fillers in the mixed matrix membranes have been recently investigated and exhibited promising results. Nadeali et al. established the constructive effects of calix[4]arene particles on improving selectivity of Pebax-1657 based mixed matrix membranes.4 according to this report, calix[4]arene could be highlighted as new generation of the organic fillers with extraordinary properties. Vase body shape, presence of the versatile functional groups, presence of the plenty binding sites, and many other advantages make this susceptible host desirable for fabrication of the gas separation membranes.25 Preparation of the two- and three-component membranes on the basis of the matrimid has been pursued in the current study. Noteworthy, calix[4]arene and TiO2 nanoparticles were used as organic and inorganic fillers, respectively, in the matrix of the polymeric membrane. The permeation of the fabricated membranes for CO2 and CH4 gases was evaluated at 35 °C and pressure range 2-10 bar. Moreover, the structure of the membranes was investigated by FTIR spectroscopy, SEM and AFM imaging, and XRD crystallography.

Materials and Methods:

matrimid (Mw = 5800 g.mol-1) was supplied from alfa-easer. N,N-Dimethyl formamide (DMF) dichloromethan were provided from Merck. For p-tertbutylcalix[4]arene (CA) synthesis, 4-tert-butylphenol, diphenyl ether, sodium hydroxide (NaOH) and formaldehyde were supplied from Merck. N2, CH4, and CO2 gases (purity of 99.99%) were also purchased from technical gas services Inc., Tehran, Iran. TiO2 nanoparticles with average particle size of 30 nm was supplied from sigma.

2.1. Synthesis of Calix[4]arene

A mixture containing p-tert-butyl phenol (15.00 g, 0.10 mol), 37% formaldehyde solution (50 ml, 0.66 mmol, 0.16 equivalents) and NaOH (0.60 g, 15.00 mmol, 0.30 equievalents) was poured into a three-necked flask equipped with magnetic stirrer and condenser. The mixture was stirred for 30 minutes under argon flow at room temperature. Then, flask was put in an oil bath and heated for 1 h at 120 °C to 130 °C under argon flow until a yellow resinous mass was produced. Next, the achieved resin was cooled down to 50 °C under inert gas flow and diphenyl ether (100 ml) was added to the flask as solvent. Afterwards, the flask put back in the oil bath and heated up to 120 °C under argon gas flow in order to complete dissolution of viscous resin and removal of water vapors. The reaction was followed by placing flask in thermal mantle and heated for 4 h at 240 °C. As time drags on, the flask was removed from the mantle and kept cool to reach the room temperature. In order to achieve CA white residues, ethyl acetate (400 ml) was added to the mixture and stirred for 30 minutes. Finally, the obtained white residue was filtered and washed with ethyl acetate (2 × 50 ml), acetic acid 1 N (1 × 70 ml) and acetone (2 × 50 ml). The filtrate residue was dried in an oven at 70 °C for 48 h to achieve white crystals in 66 % yield (10.5 g).26 NMR data was consistent with literature.27

1HNMR (200 MHz, CDCl3): δ= 1.19 (s, 36H, CH3), 3.43 (d, J=14.0 Hz, 4H, ArCH2Ar), 4.18 (d, J=13.4 Hz, 4H, ArCH2Ar), 6.98 (s, 8H, HAryl), 10.28 (s, 4H, OH). MS (EI.) (70eV): m/z (%) 649 (30) [M]+, 634 (5) [M- CH2 bridge]+, 593 (8) [M- t-Bu]+, 537 (25) [M-2 t-Bu]+, 480 (15) [M- 3 t-Bu]+,423 (9) [m- 4 t-Bu]+, 57 (100) [t-Bu]+.

2.2. Neat Membrane

In a pre-dried one neck round bottom flask equipped with a magnetic stirrer, a solution of matrimid in dichloromethane (4 % w/w) was prepared. This solution was agitated for 24 h at room temperature. Then, the polymer was casted on a glass sheet and kept at room temperature for 24 h .after wards, the membrane was separated from the glass and was placed the sheet in oven for 12 h at 90 °C.

2.3. Calix[4]arene containing membranes (Mat-Ca)

The required amount of the matrimid (Table 1) was dissolved in dicholoromethane (10 ml) by agitating at room temperature for 2 h in a one neck round-bottom flask. Then, the suspention was sonicated for 30 minutes for better distribution of the particles as we as inhabitation of their agglomeration. Afterwards, matrimid (0.53 g) was added to the mixture, gradually, which was followed by agitation of the solution for 24 h at the same conditions. Eventually, the solution was casted on a petri-dish and was remained intact for 48 h at room temperature and was placed in oven for 24 h at 60 °C to remove excess solvent.

2.4. TiO2-Calix[4]arene containing membranes (Mat-Ca)

In a one neck round bottom flask equipped with magnetic stirrer, calix[4]arene (0.5 % w/w, 0.06 g) was poured on the dichloromethane (10 ml) and the mixture was stirred for 6 h at room temperature. Then, calculated contents of TiO2 were added to the mixture and the mixture was agitated for more 6 h at the same condition. Then the flask was moved into a sonication bath and was sonicated for 30 minutes. Afterwards, marimid (0.53 g) was added to the mixture and the flask was placed on a magnetic stirrer to agitate for 24 h. Finally, the mixture was cast on a petri-dish dried for 24 h at room temperature. The membrane was separated from the dish and was placed in oven at 60 °C for 24 h to remove remained solvent from the polymer matrix.

Table1- Filler contents for membranes.

Sample	Calix[4]arene content (%wt)	TiO2 content (%wt)
Neat Membrane	0	0
CA-MA 0.5	0.5	0
CA-MA 1.0	1.0	0
CA-MA 1.5	1.5	0
CA-MA 2.0	2.0	0
T-CA-MA 0.25	0.5	0.25
T-CA-MA 0.5	0.5	0.5
T-CA-MA 0.75	0.5	0.75
T-CA-MA 1.0	0.5	1.0

2.5. p-tert-butyl Calix[4]arene Particles and Membranes Characterization

The characterization of the prepared membranes was investigated through following analyses. It should be indicated that remain enmeshed solvent and moisture in the membranes were removed by drying in an oven at 100 °C overnight before each test.

2.5.1. Brunauer-Emmett-Teller (BET)

Specific surface area and pore size distribution of calix[4]arene were measured from the adsorption/desorption data on the BEL Japan BELSORP mini-III. Before running test, they were dried in oven at 190 °C for 15 min following with cooling at the liquid nitrogen temperature (-196 °C). All the samples were degassed at 100 °C for 10 h before measurements.

2.5.2. Field Emission Scanning Electron Microscopy (FESEM)

Morphology of the neat and mixed matrix membranes, the size and distribution of nanoparticle as well as qualitative structure were investigated via FESEM apparatus MIRA-III TESCANE. Additionally, recording of membranes cross-sectional morphology images was performed by fracturing in liquid nitrogen which was followed by sputtering with gold before FESEM analysis.

2.5.3. Attenuated Total Reflection -Fourier Transform Infrared (ATR-FTIR).

The ATR-FTIR analysis was performed to investigate the grafting groups as well as the effect of calix[4]arene particles in membranes via Perkin-Elmer Spectrum Frontier in the range of 400 to 4000 cm-1.

2.5.4. Differential Scanning Calorimeter (DSC)

The glass transition temperature (Tg), melting points (Tm) and other membranes thermal properties were measured by differential scanning calorimeter (DSC). The analysis was carried out via NETZSCH DSC 200F3 instrument under nitrogen atmosphere at the temperature range of -100 to 350 °C and heating rate of 10 °C.min-1. 2.6. Gas permeation experiments

The permeability and selectivity of the prepared membranes were measured for gases including CO2, CH4 and N2 at five various pressures (2, 4, 6, 8, 10 bar) at temperature of 35 °C via a constant volume setup as was depicted in scheme 2. Gas permeation experiments have been carried out as follow: the membrane with an effective area of 11.34 cm2 was placed in a stainless steel permeation cell sealing with two silicone O-rings in order to prevent gas leakage.28 In this regards, to calculate the permeability and selectivity, the slope of pressure increase in terms of time (dp.dt-1) was obtained via constant volume setup and then the gas permeability coefficient was calculated by the following Eq. 6.

$$P=\frac{273.15\times10^{10}\times V\times l}{760\times A\times T\times\left(\frac{P_0\times76}{14.7}\right)}\left(\frac{dP}{dt}\right) \quad (6)$$

Where V, L, dp.dt-1, A, T, Po and P are constant volume of the permeate that is 110 cm3, the membrane thickness (cm), the pressure increment in terms of time (mmHg.s-1), the membrane effective area (cm2), the operating temperature (K), the feed pressure (Pisa) and the permeability coefficient (Barrer) (1Barrer = (10-10 cm3 (STP) cm)/(cm2 s cmHg)), respectively. Diffusion coefficients (D) of the gases through the membranes can be calculated via time lag method determined as follows:

$$D=L^2/6\theta \quad (7)$$

Where L is the membrane thickness and θ is the time lag. Additionally, Solubility coefficients (S) were measured by the following equation (Eq. 8):

$$S=P/D \quad (8)$$

Furthermore, the ideal selectivity was estimated by the permeability ratio of the gases using Eq. 1. The ideal CO2/CH4 and CO2/N2 selectivity were measured based on Eq. 9 and Eq. 10 as a scale to present the separation efficiency of prepared membranes.

$$\alpha_{CO_2/CH_4}=P_{CO_2}/P_{CH_4} \quad (9)$$

$$\alpha_{CO_2/N_2}=P_{CO_2}/P_{N_2} \quad (10)$$

Scheme 2. Applied volume constant set-up for gas permeation test.

3. Results and discussion

Evaluation of the membranes surface morphology was carried out by SEM imaging. In this regards, the neat membrane, CA-MA 0.5, and T-CA-MA 0.75 samples have been investigated. The result revealed that the neat membrane did contain any defection in its surface and showed a uniform appearance (Figure 1a). It should be mentioned that the chain packing effects between the chains of the polymer could be responsible for the observed result. On the other hand, it has been known that introducing a particle into the polymer matrix led to achieve a disturbed structure for the membranes due to the incompatibility of the organic polymer and inorganic particle. Contrary, the maximum consistency between particle and the polymer matrix was expected in this study due to using an organic particle as calix[4]arene in the matrix of the polymer. This assumption was confirmed by SEM imaging of the CA-MA 0.5 membrane. As it could be observed (Figure 1b) a flawless surface was achieved for this sample and minimum agglomeration for the calix[4]arene particles was yielded. The result for T-CA-MA 0.75 sample was quite different due to the presence of the TiO2 particles as inorganic particles. As a matter of fact, the incompatibility of the TiO2 nanoparticles particles and polymer matrix as inorganic and organic phases, respectively, was caused to observe defection as well as agglomeration in the polymer matrix (Figure 1c).

Figure 1- SEM images of the neat membrane (a), CA-MA 0.5 (b), and T-CA-MA 0.75 (c).

The investigations on the structure of the prepared membranes were carried out by ATR-FTIR spectroscopy. Evaluation of the neat membrane spectrum confirmed the purity of the applied matrimid polymer. Two observed absorbing bands around 3400 – 3600 cm-1 was assigned to the primary amines in the matrimid structure. Furthermore, the aromatic the absorbing bands around 3050-3100 cm-1 and 2900-2800 cm-1 could be related to the aromatic and aliphatic C-H groups, respectively. Regarding to the presence of two different carbonyl groups including C=O group of maleimide ring and benzopheone, there were observed two different absorbing bands in 1710 and 1786 cm-1 (Figure 2). On the other hand, it was expected that the recorded spectrum for CA-MA and T-CA-MA membranes exhibit any distinguishable difference in comparison to the neat matrimid membrane due to the low concentration of the calix[4]arene and TiO2 particles. The results for CA-MA 0.5 membranes revealed that the related finger print absorbing bands for aromatic rings around 1900 cm-1 was intensified due to the high number of the aromatic rings in the calix[4]arene structure (Figure 2). Furthermore, the observed spectrum for T-CA-MA 0.75 showed the same result in comparison to the CA-MA 0.5 sample except for the appeared absorbing band at 638 cm-1 that was assigned to the trace concentration of TiO2 nanoparticles.

Figure 2- FTIR spectra of fabricated membranes.

Regarding to the importance of the particle porosity characteristics including pore size, surface area and mean pore diameter on the gas-transport separation mechanism,29 those have been explored via BET measurements. According to the results of the BET theory, the surface area of the calix[4]arene was estimated to be about 2.47m2.g-1 (Figure 1). This result was in agreement with reported literatures.29 Additionally, the calix[4]arene diameter was found to be about 1.29 nm regarding the BJT theory. Considering the calix[4]arene size, this value has been pretended to be correct, too. Moreover, it could be assumed that the CA was behalf as type III pore particle due to the absorption-desorption graph (Figure 1).30 Therefore, a vase shape was confirmed for the CA which approved by comprising this result with previous investigations.31 Furthermore, a weak interaction between the particle and the gas has been conceived by evaluation of the absorption-desorption graph (Figure 1). Therefore, it could be supposed that calix[4]arene exhibited a promising affinity to gases with partial charges due to the presence of the partial charges on calix[4]arene body structure.

Figure 3- Resulted N2 adsorption- desorption graph from BET analysis.

The surface morphology of the membranes was evaluated by AFM imaging and XRD crystallography. According to the AFM images, the neat matrimid membrane wxhibited the most uniform surface. In fact, the highest height difference in this sample was about 15 nm that was derived from the fast vaporization of the dichloromethane as solvent in the casting step of the membrane preparation (Figure 4b). On the other hand, the height difference for CA-MA 0.5 and T-CA-MA 0.75 samples was determined to be about 50 nm and 70 nm, respectively. The observed result for CA-MA 0.5 sample was assigned to the presence of calix[4]arene particles that was crystalized during the drying step of the membrane fabrication. Additionally, the observed height for T-CA-MA 0.75 membrane was about 70 nm (Figure 4c) that was related to the presence of the TiO2 nanoparticles with the particle size of around 30 nm. It Should be noted that the interaction between calix[4]arene particles and TiO2 nanoparticles was led to the more crystalline morphology in T-CA-MA 0.75 sample in comparison to the two other membranes.

Figure 4- AFM images of the neat membrane (a); CA-MA 0.5 , and T-CA-MA 0.75 (c). XRD crystallography was the other method for studying of the membranes morphology. The result revealed those two peaks around 8 and 15 θ was observed for neat matrimid membrane (Figure 5a) that was in agreement with previous reports 32. These peaks could be assigned to the dipole-dipole interactions between carbonyl groups of the semi-crystalline segments of the matrimid chains. On the other hand, it was expected that the exhibited peaks vanished or removed by addition of the nanoparticles. This assumption was confirmed in the XRD diagram of the CA-MA 0.5 membrane. As it could be seen, the yielded peak at 8 θ was vanished thoroughly after introducing of the calix[4]arene particle. Conclusively, it could be understood that the non-covalent interactions between the calix[4]arene and carbonyl groups of the matrimid have been formed. Noteworthy, there was any significant difference for XRD diagram of the T-CA-MA membrane due to the trace content of the TiO2 nanoparticles. Furthermore, the crystallinity content of the membranes could be diagnosed by the XRD test, too. The resulted crystallinity for the neat membrane was about 24, according to the test report. This value was increased to 31 by addition of the calix[4]arene particles in CA-MA 0.5 sample. This result could be related to the formation of the non-covalent bonds between calix[4]arene and backbone of the matrimid. However, the crystallinity value was reduced to 28 in the T-CA-MA 0.75 sample after addition of the TiO2 nanoparticles. Accordingly, the crystallinity of the membrane was affected by introducing of the TiO2 nanoparticles as an inorganic particle.

Figure 5-XRD curves of the fabricated membranes.

The gas permeation properties of the fabricated membranes for CO2 and CH4 gases was evaluated at 35 °C and operative pressure of 2 – 10 bar. Evaluation of the permeation properties of the neat membrane showed that this membrane was more permeable to CO2 in comparison to CH4 gas. Among to the most affected parameters on the gas permeation including solubility and diffusivity, it was expected that the diffusivity have played the main rule in the observed result. In fact, the glassy structure of the neat membrane and its packed chains effected on the solubility of the gases and reduced it. On the other hand, the CO2 gas was more diffuse than CH4 due to tits lower kinetic diameter which is known to be 3.30 Å for CO2 gas and 3.80 Å for CH4. The achieved result was repeated for CA-MA membranes and these membranes were more permeable to CO2 in comparison to CH4 gas, too. As it could be seen, addition of the 0.5 % wt of calix[4]arene particle was led to increasing of the CO2 permeation in comparison to the neat membrane (Figure 6). High chain-packing and decreasing of the membrane free volume was known responsible for this result that was derived from non-covalent interactions between particle and polymer matrix. However, introducing of the more calix[4]arene particle reduced the CO2 permeation and decreased the selectivity. Agglomeration of the calix[4]arene particles that was known to be responsible for the observed result. Additionally, it should be mentioned that increment of the pressure did not have a significant effect on the prepared glassy membranes. According to the results, the CA-MA membrane containing 0.5 %wt of calix[4]arene was determined as the membrane with the optimum content of the particle (Figure 6).

Figure 6- permeation and selectivity of the fabricated membranes containing calix[4]arene.

The optimized content of the TiO2 nanoparticle in the ternary membrane was distinguished by introducing of the various contents of TiO2 nanoparticles in the matrix of the membrane. The results revealed that the permeation of the both gases was increased by increasing of the TiO2 nanoparticle contents. As a matter of fact, addition of a inorganic particle into the matrix of a polymeric membrane effected on the consistency of the ingredients and raised their incompatibility. The free volume was affected by this phenomenon that was led to increment of the membrane porosity. Although the ternary membrane containing 0.75 %wt of TiO2 exhibited the best result among other ternary membranes, as a consequence, the selectivity of the ternary membranes containing calix[4]arene and TiO2 nanoparticles was lower than the neat membrane and calix[4]arene containing membranes (Figure 7).

Figure 7- permeation and selectivity of T-CA-MA membranes.

Eventually, the comparison between the prepared membranes with previous literature, the achieved results was compared with Robeson’s upper bound limits. The results revealed that the all of the prepared membranes including neat membrane, CA-MA and ternary membranes were lower than the limit in the Robson plot (Figure 8).

Figure 8- comparison between achieved results and Robeson’s upper bound limits/

However, it was observed that the two component membrane containing 0.5 %wt of calix[4]arene and ternary membrane containing 0.5 %wt of calix[4]arene and 0.75 %wt of TiO2 nanoparticle showed higher selectivity than other prepared samples. This result was known to be directly related to the presence of the calix[4]arene particle. As a matter of fact, the non-covalent interactions between the calix[4]arene and the chain of the polymer facilitated the diffusivity of the polar gases. In this case, CO2 was more polar than the CH4. Moreover, the lower kinetic size of the CO2 was assumed to be helpful in facilitating the transmittance of this gas through the basket of calix[4]arene (Figure 9).

Figure 9- Probable interactions of CO2 with calix[4]arene.

Conclusion

Matrimid based two- and three- component membranes containing TiO2 and calix[4]arene nanoparticles were fabricated for effective separation of the greenhouse gases like CO2 and CH4. Investigation on the structure of the prepared membranes revealed that the compatibility of the organic polymer matrix with an organic filler, like calix[4]arene, was led to the improving of the chain packing and decreasing of the membrane porosity. Conversely, introducing of an inorganic nanoparticle like TiO2 decreased the selectivity of the membrane due to increasing of the porosity. Accordingly, the best result was achieved by two component membrane containing 0.5 %wt of calix[4]arene that improved CO2/CH4 selectivity about 87 % in comparison to the neat membrane.

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