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Polysulfone membranes for CO_2/CH_4 separation: State of the art

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ABSTRACT

The world market for CO_2/CH_4 separation using membrane technology is getting bigger and polysulfone (PSf) is one of the most widely investigated polymer membrane materials. However, the existing PSf membranes performances are insufficient to fully exploit these opportunities. Therefore, modification that would produce membrane that fit the needs of target separation performances is a main issue. Firstly, various manufacturing processes to achieve best CO_2/CH_4 separation performance are discussed, including important post-treatments. The formulation of polymer solution and effects of manufacturing parameters on the resulting membranes are presented. Other modifications, which involved PSf structure modification, PSf-based copolymer, mixed matrix membrane and facilitated transport membrane, are also discussed. Performances of those modified membranes are compared with the Robeson's upper bound and some modifications give satisfying results. Finally, commercial application of PSf membranes for CO_2/CH_4 separation is discussed.

Keywords* - *CO_2 separation, polysulfone membrane

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1. Introduction

One of the most widely investigated glassy polymer membrane materials for CO_2/CH_4 separation is PSf. Polysulfone pure- and mixed-gas permeation properties have been extensively explored for gas separation due to its low price, chemical stability, and mechanical strength [1]. Compared to CA, PSf has lower CO_2 permeability and CO_2/CH_4 selectivity [2] but higher plasticization pressure [3]. Plasticization pressure becomes important in practice due to its effect on membrane selectivity. Membrane with higher plasticization pressure can maintain its selectivity better than membrane with lower plasticization pressure on high CO_2 feed concentration or on high operation pressure.

Various types of PSf-based membrane for CO_2/CH_4 separation have been developed but there are two limitations faced by the available membrane. Acquiring higher selectivity with at least similar productivity is the first challenge and the second challenge is maintaining membrane performance in the presence of complex and aggressive feed [4]. Many researches have been done to overcome those challenges by changing the membrane manufacturing process, formulation, and conduct material modification. In this work the variability of PSf-based membrane for CO_2/CH_4 separation will be explored. The most important objective is to provide comprehensive information about PSf-based membrane for CO_2/CH_4 separation.

2. Manufacturing processes

In general, there are three types of PSf membrane that can be used for CO_2/CH_4 separation, dense, asymmetric, and composite. Dense and asymmetric membrane consists of PSf only while composite membrane consists of PSf and other polymer in different layer. Manufacturing processes of these types of membranes are different and versatile. For dense and asymmetric membrane there are three major process; dry, wet, and dry/wet.

Dry process is so named because the membranes are formed without immersion in precipitation bath. In this method, the polymer solution consists of binary mixture between a polymer and a solvent or a mixture of polymers, solvents and nonsolvents. The polymer solution is then cast on a suitable support and the solvent is allowed to evaporate [2]. The PSf membrane obtained by dry process is a dense membrane. The gas permeation rate of this membrane is usually low due to the thickness of the selective layer [5].

In wet process, the polymer solution composition is the same with dry process. Prior to coagulation in a precipitation bath, a brief optional evaporation is often used to concentrate the outermost region of the membrane. The evaporation step does not induce the phase separation of the membrane. The phase separation phenomena occur in the coagulation bath due to the diffusional exchange of solvent and nonsolvent. The diffusional exchange causes the solution to be unstable thermodynamically and demixing occurs. In some cases, demixing occurs instantaneously and a porous membrane is obtained but in other cases, demixing occurs only after a certain period of time and produce membrane with asymmetric structure. Delay demixing can occur when nonsolvent with low mutual affinity is used. Even thought this process can produce PSf asymmetric membrane, generally the PSf membrane has too many defects to be used in gas separation without further treatment [5]. The most popular treatment is coating layer application. The coating material must have high flux so it will not give an additional resistance to gas transport, such as silicone rubber, the most popular coating material.

To produce PSf membrane with ultra thin defect free toplayer and negligible sublayer resistance, Pinnau and Koros proposed a new technique, dry/wet process. In this process, there are two solvents are used, a more volatile solvent and a less volatile solvent, which have different affinity to the nonsolvent. The cast film is then subjected to convective evaporation and free standing evaporation prior to immersion in the precipitation bath. Convective evaporation step is believed to be the important step to produce defect free membrane. The schematic diagram of dry, wet, and dry/wet process is given in Fig.1. For processes that included immersion, selection of nonsolvent is important. Water is frequently used but when water is used, solvent exchange step is necessary. Solvent exchange is conducted to reduce the surface tension of water in membrane pores. High surface tension can cause pores wall collapse when water is removed and create a thick non-selective layer. Flat sheet composite membranes usually simply made by coating the second polymer onto the surface of the substrate polymer [6, 7, 8] and deposited the polymer for certain time while HF composite membranes made by dip-coating the substrate polymer [9, 10, 11] or co extrude spinning process [12, 13].

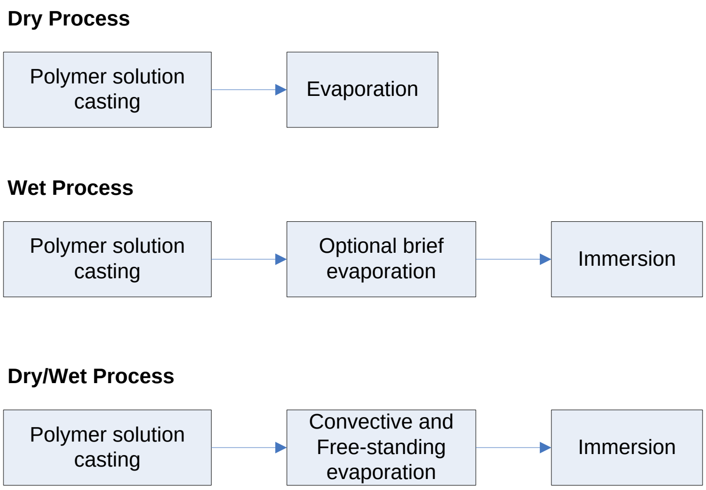

Figure 1 Schematic diagram of dry, wet, and dry/wet process

The asymmetric membrane manufacturing processes that have been discussed above are categorized as the standard procedures. To obtain defect free PSf membrane, it can also be made from dense PSf membranes by supercritical CO_2 process [14]. This process involves chloroform as a solvent. Chloroform was added to one side of the dense film then the film was immediately transferred into a high-pressure vessel and supercritical CO_2 was introduced and expanded. This process allows a very-controlled thickness of both the porous and dense layer. Factors affected those thickness are chloroform/Psf mass ratio, $SCCO_2$ density, and depressurization rate of $SCCO_2$. Due to difficulties to make defect free and food performance membrane, many studies about additional treatments in manufacturing processes have been conducted. Those treatments can be divided into two groups; first group is treatment during the manufacturing process of the membrane and the second group is treatments after the membrane is formed (post-treatments). To avoid defects formation during the manufacturing process of membranes, Shojaie et al. [15] proposed the usage of electric field. During the membrane manufacture, an optimum electric field, 2.2 kV/cm a.c., was maintained constant. The treated membranes show the average number density of defect decrease. In contrast, the total defect area is increase.

Gas separation membrane can be given several post-treatments to be modified physically or chemically and improve their separation characteristic [16]. Ilconich et al. [17] have studied the effect of ion beam irradiation on the structure and properties of asymmetric PSf membrane. The treated membranes possessed lower permeance and selectivity than those made conventionally. The energy used in this study was too high so it penetrates to the sublayer structure of the membrane so it caused a collapse of the porous sublayer structure and forms a thick non-selective resistance layer. Another study involve molecular bromine to form charge-transfer complex with unpair electrons along the PSf backbone. The molecular bromines in the treated membranes alter the free volume in such way so they achieve 100% selectivity increase with only 36% reduction in CO_2 permeability. The stability of those membranes was inconsistent so this treatment has not proved to be able to produce industrial membranes yet. Choi et al. [18] used ozone to oxidize and change the chemical structure of PSf membranes. The membranes were exposed to ozone containing oxygen for a certain time and those treated membranes show a significant increase of CO_2/CH_4 selectivity with CO_2 permeability decrease. Another study conducts surface fluorination of PSf asymmetric membranes. Those membranes only need to be exposed to the trace concentration of fluorine gas for several minutes to increase the CO_2/CH_4 selectivity and decrease the CO_2 permeability [19, 20].

Table 1 Performance of PSf membranes made based on Pinnau and Koros formulation
[a] Forced convective residence time THF as a volatile

Membrane type	**P/l CO2 (GPU)**	**P/l CH4 (GPU)**	**Selectivity**	**Shear rate (/s)**	**FCRT[a] (s)**	**Coating**	**Reference**
Flat sheet	11.41	0.36	32.63	367	20	v	21
Flat sheet	13.91	0.42	33				22
Hollow Fiber	89	2.27	39.5	9710	0.71		23
Hollow Fiber	32.4	0.5	65.5	9710	0.71	v	24
Hollow Fiber	54	1.39	39.1	8838	0.475		25

Table 2 Intrinsic permeation properties of dense PSf [22]

Permeability coefficient x 10^{10} [cm3(STP)cm/s cm cmHg]		**Intrinsic selectivity**
CO2	CH4	
4.5	0.16	28.1

3. Membrane formulations and manufacturing parameters

Membrane formulation is a very crucial step to make a defect free and low resistance membrane for CO_2/CH_4 separation. There are many aspects involve in the membrane formulation such as polymer concentration, influence of solvent ratio, effect of shear rate, influence of gelation media and conditions, effect of solvent evaporation condition, and additives. Many researches were done to find the optimum PSf membrane formulation. A formulation that has been used widely to make ultra thin defect free PSf membranes [21, 22, 23, 24, 25, 26] was given by Pesek and Koros [27]. Performances of those membranes are given in Table 1. The optimized polymer solution in dry/wet process consists of 22% PSf, 31.8% solvent, 31,8% DMAc as a less volatile solvent, and 14,4% ethanol as a nonsolvent.

The selectivity and permeability of the membranes in Table 1 are higher than the intrinsic selectivity of PSf as given in Table 2, so the defect free PSf membranes can be obtained by dry/wet process and Pinnau and Koros formulation. Beside defect free, this process and formulation, when combined with proper manufacturing parameters produce membrane which performance exceeded Robeson’s upper bound as shown in Fig.2. To get a comprehensive understanding about how those parameters can affect the membrane performance, explanations are given below.

3.1 Polymer concentration

Optimum polymer concentration of polymer solution has to be determined in order to achieve defect free and thin selective layer for CO_2/CH_4 separation process. Membrane casted from a dilute polymer solution produces a thin and porous selective layer that promotes high value of permeance but low selectivity. In contrast, higher polymer concentration in polymer solution leads to a denser and thicker selective layer that promotes higher selectivity but lower permeance [28, 29].

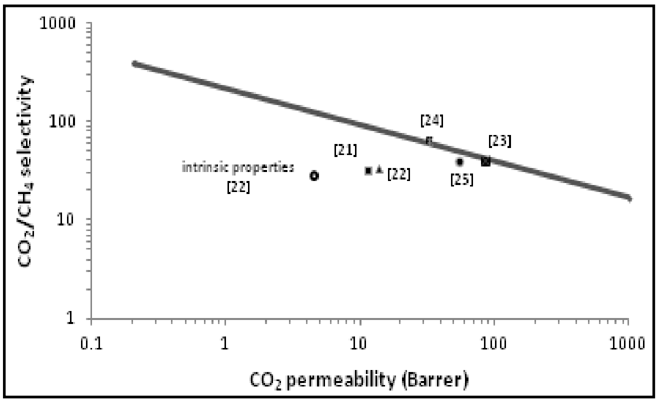

Figure 2 Performance of dry/wet process membrane

Table 3 Water miscible solvent for hydrophobic asymmetric membrane [27]

Solvents	**Boiling point (°C)**
Acetone	56.5
Tetrahydrofuran	65.4
Acetonitrile	81.6
1,4-Dioxane	101.3
Dimethylformamide	153
Dimethylacetamide	165.2
Dimethylsulfoxide	189
N-Methylpyrrolidinone	202
γ-Butyrolactone	204.5
2-Pyrrolidinone	245

Interaction of solvent-polymer and nonsolvent-polymer can increase with increasing polymer concentration. Increase in solvent-polymer interaction reduces the coagulation value and increase in nonsolvent-polymer interaction reduces the dissolving power of the solvent. Those effects will promote delay demixing. In addition to those effects, increasing polymer concentration also increase the interaction of solvent and nonsolvent that retard diffusional exchange between solvent and nonsolvent, thus promote delay demixing too.

3.2 Influence of solvent ratio

In dry/wet membrane preparation process, a more volatile solvent introduced to the polymer solution to adjust the solvent evaporation and polymer coagulation well. Most common water miscible solvents used in hydrophobic asymmetric membrane are shown ini Table 3. Selection of a more volatile solvent is difficult due to some limitations.

More volatile solvent must have a good miscibility with water.

Whereas good water miscible solvent usually have a high degree of polarity and hydrogen bonding that suppress the solvent volatility. More volatile solvent is then removed during the evaporation process and in the outermost surface of the membrane generates a high polymer concentration. The more co-solvent evaporated, the thicker the concentrated polymer region that lead to the thicker selective layer of the membrane [28] and leads to a reduction in gas permeation rate. Furthermore, solvent ratio (ratio of more volatile solvent to less volatile solvent) can alter kinetics of phase inversion process depend on the degree of interaction between polymer and the solvents.

3.3 Effect of shear rate

Shear rate is defined as the ratio of velocity of the casting knife (or dope extrusion rate in the case of HF membrane) to membrane thickness. Increasing shear rate enhances molecular orientation in selective layer and offers a chance to increasing membrane selectivity [21, 24]. According to research by Sharpe et al. there is an optimum shear rate to produce defect free ultra thin PSf membrane. When the applied shear rate is too low, the membrane will have a thick selective layer while too high shear rate will produce thin and defective selective layer [23]. Literatures review on the effect of shear rate on membranes performance is shown in Table 4.

Table 4 Effect of shear rate on membranes performance

Membrane type	Shear rate (/s)	DER (cm3/min)	CO2 pressure normalized flux (cm3(STP)/s cm2 cmHg)	CO2/CH4 selectivity	Reference
PSF FS	220		8.91	15.98	21
	275		11.7	24.99	
	367		6	31.9	
PSf HF		1	17.6	39.1	24
		2.5	32.4	65.6	
PSF HF		0.8333	16	23.4	23
		1.5	19.3	25.5	
		2.5	89	39.5	
		3.33	61.9	12	
PSF FS	254		15.68	64.04	37
	381		18.02	64.2	

3.4 Influence of gelation medium and conditions

Gelation medium and conditions has a big influence on membrane structure and its gas transport properties. It is known that choice of gelation medium and condition can affect the speed of coagulation process. Mulder et al. were made PSf membrane by wet process and the results show that fast coagulation resulted in asymmetric membrane with thin porous selective layer while slow coagulation produced asymmetric membrane with dense and thick selective layer [30,31].

In order to produce an ultrathin defect free asymmetric FS membrane, Pinnau and Koros [32] studied the effect of different organic gelation media in dry/wet process. Methanol, ethanol, and 2-propanol were used as the gelation media. The study showed that methanol and ethanol quenched membrane had higher selectivity and flux than 2-propanol quenched membrane. The results indicate that the phase separation and vitrification processes occurring during the wet process should be as rapid as possible. Another study was held by Yamasaki et al [29] using dual bath method. The first gelation media is 2-propanol and the second gelation media is water. The selective layer thickness determined by SEM is increase with the immersion time increase in the first bath thus changing the immersion time in the first bath can control the growth of the selective layer. Kim et al. [33] also studied the effect of dual bath gelation media on the morphology of the membrane. The first bath is polyethylene glycol (PEG) and the second bath is water. The results show that there is an optimum immersion time in PEG which lead to the formation of defect free selective layer. Radovanovic et al. [34] added solvent to the gelation bath. As a result, the flux of nonsolvent across the phase interface is decreases with an increase of solvent concentration in the gelation bath because of the higher mass transfer resistance.

In the making of HF membrane, the influence of gelation media is more complicated than in the FS membrane because there are two different gelation media that can be used; the external and internal coagulant. Wang et al. [35] used water as the external coagulant. The internal coagulant used include water, ethanol, 2-propanol, the mixture of water/ethanol and water/2-propanol. The results show that membrane made with ethanol or 2-propanol as the internal coagulant show low permeability and selectivity. Ethanol and 2-propanol is known as weak nonsolvent for PSf so the internal coagulation rate and coagulant diffusion are very slow. This tends to increase the substructure resistance and thus reduce the permeability and selectivity.

3.5 Effect of solvent evaporation condition

In dry/wet process, convective evaporation is a crucial step to obtain ultrathin defect free asymmetric membrane. Some parameters in convective evaporation step, such as duration and temperature can influence the gas transport properties of a membrane. Typically, with the increase of convective evaporation duration or temperature, membrane skin thickness is also increase [36] and it leads to a lower CO_2 permeance [25, 37]. According to Pesek and Koros [38], 10 to 15 s evaporation time are typically allowed to form ultrathin defect free membrane while only 0.5 to 1 s is needed for HF. In the making of hollow fiber membrane, the duration of solvent evaporation can also be expressed as air-gap length. The effect of evaporation duration in HF membrane is more complicated than FS (flat sheet) membrane. Nonsolvent from the lumen side penetrated deeper into the fiber and as the evaporation time increase, the nonsolvent can erode the skin layer of the membrane, causing thinner skin layer and a slight decrease in selectivity. Literatures review on the effect of solvent evaporation duration on membranes performance is shown in Table 5. Another research by Tsai et al. [39] shows that the air gap length and ambient humidity have dramatic effect on the membrane morphology. Macrovoids in the membrane can disappear, reappear and redisapper with increasing air-gap length.

3.6 Additives

The addition of additive into the polymer solution is known to changing solvent capacity [40, 41], phase inversion kinetics and thermodynamic properties [42]. The most widely used additive is polymers such as PEG and polyvinyl pyrolidone (PVP). Another additive can be nonsolvent, inorganic salts, mineral filler, etc. Zheng et al. studied effects of PEG introduction on kinetics of membrane formation [41]. From the experiment, it was found that PEG addition could enhance solution demixing thermodynamically and hindrance solution demixing rheologically. Another study gave characterization of PSf membrane with PEG as additive. It was seen that when molecular weight of PEG increases from 400 to 20000 Da, the mean pore size of the prepared membrane decreases, while the porosity and pore density increase [43].

Table 5 Effect of solvent evaporation duration on membranes performance

Membrane type	FCRT (s)	Air gap length (cm)	CO2 pressure normalized flux (cm3(STP)/s cm2 cmHg)	CO2/CH4 selectivity	selective layer thickness (A)	Reference
PSf HF	0.214	9	19.3			25
	0.357	15	12.6	30.6	726	
	0.475	20	11.9	30.9	845	
PSF FS	5		87.2	22.31	138	21
	10		55.53	25.28	639	
	15		6	31.9	929	
	20		11.41	32.63	800	
	30		4.44	33.2	1724	
	40		10.76	33.69	2286	
	50		6.71	34.54	2723	
	60		6.6	32.87	3595	
PSf HF	0.237	5	82.2	36.8	848	23
	0.426	9	58.2	40.1	1070	
	0.71	15	89	39.5	794	
	0.947	20	84.4	26.3	590	
PSF FS	15		15.68	64.04		37
	18		12.17	67.33		

Kang et al. studied the effect of nonsolvent addition on membrane morphology [44]. The nonsolvent additive was formic acid, water, or ethanol. The addition of nonsolvent to the polymer solution can bring the initial composition of the polymer solution nearer to the precipitation point. When a nonsolvent additive is added to polymer solution, it can decrease the dissolving power of the solvent and thus increase polymer-polymer interaction. By additive addition, the solvent concentration in polymer solution is decrease and the polymer chains have a smaller included volume because of a more tightly coiled conformation. Nonsolvent additive also influences the diffusion coefficient, which is a crucial parameter in controlling membrane morphology. When the diffusion coefficient of the nonsolvent is high for a given gelation media, the membrane consists of a smooth, defect free surface and macrovoid-free cross section regardless of the kind of the nonsolvent additive employed. The diffusion coefficient increases with an increase in nonsolvent additive concentration.

Comparison of the effect of PEG 400, PVP, ethanol, and glycerol was studied by Aroon et al. [45]. Additions of additives bring the cloud point curves colder to the polymer-(solvent-additive) axis in the following order: PEG<ethanol<PVP<glycerol. The CO_2/CH_4 separation factor improves in the same order of the position of the cloud point.

4 Structure related transport properties

The structure of PSf is affected the transport properties oh the membrane. The objective of researches effort on structure/property of PSf membranes is to create membranes with higher selectivity and permeability. Some researches try to fulfill this objective by change the structure of the commercial bisphenol A polysulfone and made polysulfone copolymer meanwhile other researches blend the bisphenol A PSf and inorganic material to create mixed matrix material [4].

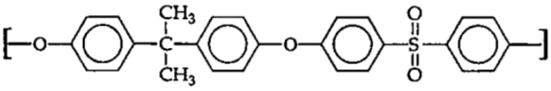

Figure 3 Primary chemical structure of bisphenol A PSf

4.1 Polysulfone structure modifications

The primary chemical structure of bisphenol A PSf is presented in Fig.3. Basically, all PSf modifications intend to change the free volume of the PSf chain and improve the gas transport properties. It was found thatthe CO_2 solubility coefficient and permeability increased with the increase in free volume [46]. Table 6 summarizes the results of those experiments. Effect of isopropylidene unit in bisphenol A PSf replacement was studied [48]. Aitken et al. [50] studied the effect of symmetry of phenylene linkages. In this study, the bisphenol A PSf was compared with the meta and para isomers of PSF, the meta and para isomers of TMPSF, and 3,4-PSf. The gas permeability coefficient trends for CO_2 are in a good agreement with the FFV and shows that the meta isomers are the less permeable but more selective materials due to their unsymmetrical structure. Aitken et al. [51] also studied the comparison of PSf, TMPSF, 4,4'-bisphenol (BIPSF), and corresponding polysulfones with methyl ring substitutions, tetramethylbiphenol polysulfone (TMBIPSF), and hexamethylbiphenol polysulfone (HMBIPSF). The results show that BIPSF and PSF have very similar transport characteristics due to their similar packing behavior. Tetramethyl substitution increases permeability while hexamethyl substitution does not. Pixton and Paul [52] have been measured CO_2 and CH_4 transport properties in adamantane containing PSf. In all cases, the gas permeabilities and selectivity is higher in the adamantane containing PSf. Effects of basic substituents on gas transport properties of PSf have been studied [53] and the result shows that gas permeability in the aryl-substituted PSf were lower than the unmodified PSf. Ghosal et al. [54] studied the effect of aryl nitration on gas transport properties of PSf.The gas permeability on aryl nitration PSf is decreased but the selectivity shows a significant improvement. Zuniga et al. [55] created new PSf copolymers from bis(4-fluorophenyl)sulfone and found that the newly-created

Table 6. Summary of permeability, selectivity, density, and FFV of the polymer modified membranes Permeability and selectivity measurement was done at 10 atm except for ^{a} 4 atm

Polymer	P CO_2 (Barrer)	CO_2/CH_4 selectivity	Density	FFV	Reference
PSF	5.6	22	1.24	0.156	47
TMPSF	21	22	1.51	0.171	
DMPSF	2.1	30	1.213	0.149	
DMPSF-Z	1.4	34	1.227	0.136	
HFPSF	12	22	1.427	0.168	48
PSF-F	4.5	24	1.282	0.151	
PSF-O	4.3	24	1.33	0.15	
TMPSF-F	15	26	1.184	0.163	49
TMHFPSF	72	24	1.286	0.196	
3,4-PSF	1.5	29	1.25	0.149	50
PSF-P	6.8	20	1.191	0.156	
PSF-M	2.8	25	1.201	0.151	
TMPSF-P	13.2	22	1.127	0.168	
TMPSF-M	7	25	1.141	0.158	
BIPSF	5.6	22	1.291	0.154	51
TMBIPSF	31.8	25	1.195	0.164	
HMBISPSF	25.5	27	1.144	0.178	
1,3-ADM PSF	7.2	22	1.238	0.153	52
2,2-ADM PSF	9.5	24	1.231	0.158	
PSF-NH2 (16%)	2.7	24	1.253	0.134	53
PSF-NH2 (38%)	3.2	25	1.273	0.118	
PSF-CH2-NH2 (51%)	1.95	18	1.253	0.125	
PSF-CH2-imide (51%)	2.12	26	1.279	0.122	
PSF-NO2(50%)	3.4	24	1.272	0.135	54
PSF-NO2 (98%)	2.3	29	1.306	0.121	
PSF-NO2 (192%)	1.5	30	1.353	0.113	
TM-NPSF	4.85^a	36.7^a	1.231		55
HF-NPSF	4.89^a	33.5^a	1.364		
TMHF-NPSF	6.6^a	30.4^a			
1,5-NPSF	1.6	44	1.328		56
2,6-NPSF	1.5	41	1.328		
2,7-NPSF	1.8	36	1.339		
BPSF	3.2	27	1.514	0.156	57
MPSF	2.2	29	1.213	0.151	
TMSPSF	15.1	16	1.126	0.167	

polymers have superior gas transport properties compared to unmodified PSf.

Aitkin and Paul [56] studied the effect of naphthalene unit and its isomers on gas tansport properties of PSf. It is shown that the naphthalene unit increases the selectivity at the expense of permeability. The naphthalene unit position does not affect the gas transport properties significantly. The gas transport properties of brominated PSf membrane (BPSf) was examined and compared with trimethylsilylated bisphenol A PSf (TMSPSf), MPSf, and PSf [57]. The strong polarity of bromine reduces the chain packing-inhibiting ability. The permeability rank correlates well with FFV and the selectivity increases in the order: TMSPS<PSf<BPSf<MPSf. Unfortunately, PSf modifications do not give satisfying results. The permeability-selectivity combination values are still far under the Robeson's upper bound as shown in Fig.4.

4.2 Copolymer membranes

Another research to change the structure of PSf is creating PSf-based copolymer. The copolymer material may provide excellent properties of each polymer in one membrane. Poly (ethylene oxide) is known as a polymer that has good affinity with CO_2 molecules [58], thereby resulting in high solubility-selectivity. However, pure PEO tends to create crystalline region which is less permeable region for CO_2. PSf-PEO random copolymer was proposed to overcome this problem and produce membrane with high CO_2 permeability as well as CO_2/CH_4 selectivity. In fact, the permeability of CO_2 in PSf-PEO membrane was reduced and the selectivity were not high due to the bad-phase structure separation of the copolymer.

4.3 Mixed matrix membranes

The mixed matrix is capable to combine the processability of polymers with the superior gas separation properties of rigid inorganic materials [59]. Polymer acts as the continuous phase or matrix and the inorganic material acts as the discrete phase. Schematic of a mixed matrix membrane is shown in Fig.5.

There are two kinds of inorganic material, porous and non-porous. Porous material inorganic enhance the gas separation properties by molecular sieving while non-porous inorganic material do that by conditioned the free volume of

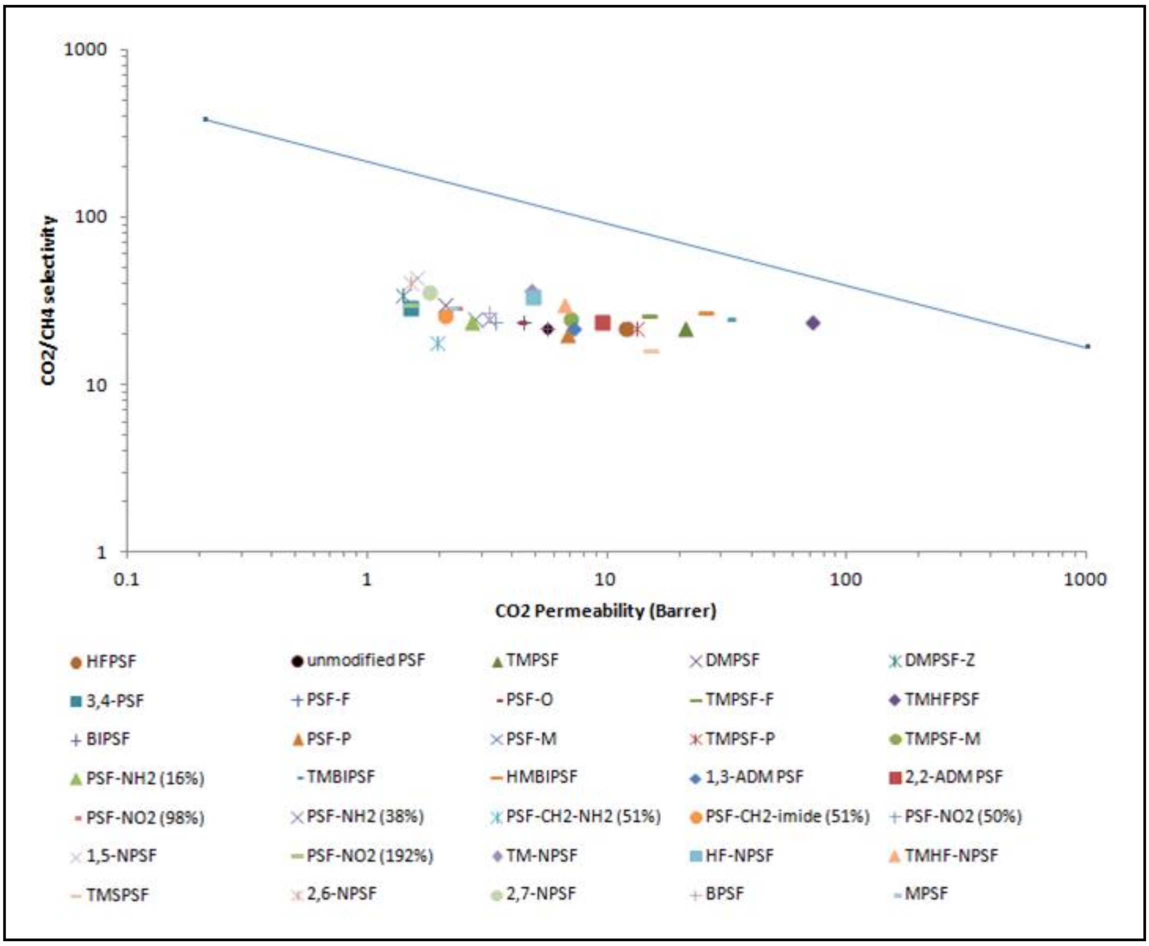

Figure 4 Performance of polysulfone-modified membranes

the matrix. The common inorganic materials used to produce MMM are zeolites [60, 61, 62, 63, 64], ordered mesoporous silica [65, 66], nonporous silica, carbon molecular sieves, and carbon nanotubes [67].

There are two major problems in the making of PSf MMM; the first one is inorganic material agglomeration and the second one is compatibility of the PSf and material inorganic. Both of those problems can reduce the selectivity of PSf MMM. To overcome the first problem, the composition of the inorganic material in PSf matrix should not be too much. Some action, such as inorganic molecular sizing [68], zeolite surface modification with silane [69], and particle functionalization [66, 70] can overcome the second problem.

Table 7 resumes the gas transport properties of MMM based on the type of inorganic material in the literature. The position of PSf-inorganic material permeability-selectivity combination values is presented in Fig.6 and only carbon black and silica-based inorganic material show interesting properties in terms of CO2 selectivity and/or permeability. In Wahab et al. experiment [72], the membrane structure made is asymmetric membrane; different with most of MMM experiment that made dense membrane structure as the continuous phase. Mass transfer resistance in asymmetric membranes is smaller than dense membrane so the CO_2 permeability can be higher. The optimum silica loading in this experiment is very low, 0.1%.wt. Particle agglomeration is unavoidable at higher silica loading and reduce the CO_2/CH_4 selectivity.

4.4 Facilitated transport membranes

Facilitated transport membranes comprise a carrier with a special affinity toward a CO_2 gas molecule and this interaction controls the rate of transport. Wang et al. reported an excellent CO_2/CH_4 selectivity through poly(N-vinyl-γ-sodium aminobutyrate-co-sodium-acrylate) (VSA-SA)/PSf composite membrane [75]. VSA-SA has a secondary amine and a carboxylate ion, which can reversibly react with CO_2 and thus can be expected to act as carriers for CO_2. In experiments with a mixed gas of 50 vol % CO_2 and 50 vol % CH_4, the selectivity was 46.8 and the CO_2 permeation rate was 9.2 x 10^{-6} cm^3 (STP)/cm^2s cmHg. Another research was held using Polyvinilamine (PVAm) as the selective layer [9]. The PVAm/PSf membrane was crosslinked by glutaraldehyde and sulfuric acid. As the result, the membrane posses higher CO_2/CH_4 selectivity and lower CO_2 permeability. This membrane has an ideal

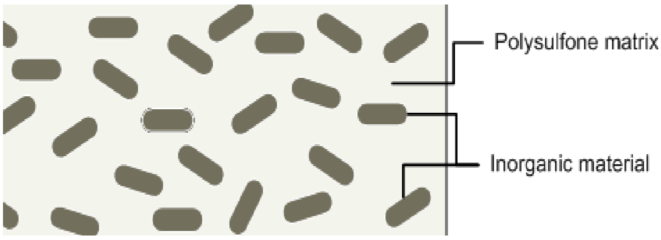

Figure 5 Schematic of a mixed matrix membrane

Table 7 MMM gas transport properties based on inorganic material type

Inorganic material	**wt-%**	**Permeability (barrer)**		**CO_2/CH_4 selectivity**	**Reference**
		CO2	**CH4**		
Zeolite ZSM-5	0	1.3624	0.2833	4.809	60
	10	1.513	0.3419	4.4253	
	20	1.5977	0.5505	2.9023	
Zeolite 13X	0	6.5	1.5	4.3	62
	10	6.1	0.26	23.5	
	20	6.1	0.32	19	
carbon nanotube	0	3.9	0.17	23.55	67
	5	5.12	0.27	18.82	
	10	5.19	0.28	18.41	
	15	4.52	0.28	16.09	
Silica MCM-41	0	4.5	0.17	23	70
	10	6.6	0.29	23	
	20	7.8	0.34	23	
	40	14.8	1	15	
carbon black[a]	0	86.12	2.1	40.98	71
	2	76.25	2.16	35.4	
	5	68.72	4.77	16.37	
	10	75.12	2.44	33.73	
fumed silica	0	78.11	2.52	31.05	72
	0.1	90.04	2.75	32.74	
	3	88.06	3.57	24.64	
	10	87.69	11.8	7.43	
Silica MCM-48	0	4.46	0.17	25.88	73
	10	8.45	0.33	25.47	
	20	18.21	0.77	23.58	

fumed silica[b]	0	6.3	0.22	29	74
	5	7.7	0.29	27	
	10	9.3	0.38	25	
	15	12.9	0.62	21	
	20	19.7	1.1	18	

[a] Pressure normalized flux [b] inorganic material in volume-%

separation factor of 206 and CO_2 permeation rate of 3.99 x 10^6 cm^3/cm^2s cmHg. Wang et al. [76] studied gas transport property of polyallylamine (PAAm)-poly(vinyl alcohol) (PVA)/PSf composite membrane. PAAm contains amino group as the fixed carrier and this membrane shows performance that can exceed the Robeson's upper bound (Fig.6). For CO_2/CH_4 separation, the selectivity reach 58 at 0.1 MPa feed gas pressure with 1.95 x 10^{-5} cm^3(STP)/cm^2s KPa permeance.

5 Commercial application

The world market for natural gas is estimated at approximately US$ 22 billion annually [4] and the market for membrane technology is getting bigger. Membrane technology can minimize the size of an amine system. Polysulfone membrane has been used commercially in CO_2/CH_4 separation applications, in example Air Products PRISM membranes. Hollow fiber PRISM membranes are capable of withstanding differential pressure up to 1000 psi. Highest CO_2 concentration in permeate, which is 95%, can be achieved from a feed containing 70% CO_2. The CO_2 purity in permeate flow is decrease as the decrease of CO_2 in the feed stream [77]. In July 2004, PRISM membrane technology was used in a CO_2 removal system engineered and built by Petraco. Capacity of the plant is 8 MMSCFD and designed to reduce CO_2 composition from 4.5% to less than 2%.

6. Conclusions

Abundant opportunities do indeed exist for PSf membrane for industrial CO_2/CH_4 separation; however, performance improvement is still needed for the existing PSf membrane. Membrane formulation and manufacturing parameters have significant impact on membrane performance. Suitable formulation and manufacturing parameters even can produce membrane with performances that exceed Robeson's upper bound.

PSf modification also plays important role in order to achieve better membrane performance. Mixed matrix and facilitated transport membrane show a promising future in CO_2/CH_4 separation despite of some technical barriers for industrial implementation. Overcome these barriers is a major goal to increase PSf membrane utilization in the field of CO_2/CH_4 separation.

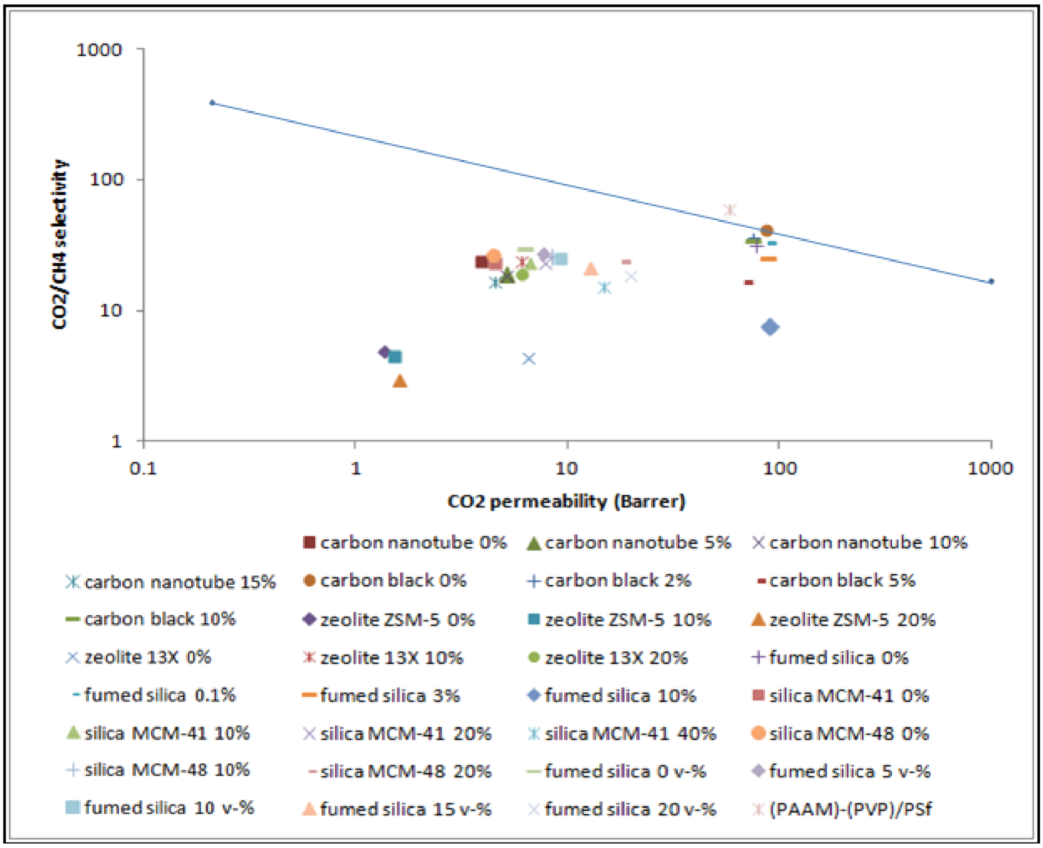

Figure 6 Performance of mixed matrix and facilitated transport membranes

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