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REVIEW

A Review on Advancements in Polysulfone-Based Membranes for Gas Separation Applications

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Gas separation has changed over the last few decades with membrane technology emerging as an important player. Polysulfone is considered an interesting material for gas separation membrane applications mainly due to its good thermal and chemical stability and excellent mechanical strength at a low cost. This review presents a comprehensive discussion on the advancements acheived in the development of polysulfone-based membranes for gas separation. It focuses on various strategies that have been reported to enhance the performance of these membrane materials, including filler incorporation, polymer blending and the addition or chemical modification of functional groups that confer specific adaptability to the polymers.

Keywords: Membrane, Polysulfone, Gas separation, Polymers, Composites.

INTRODUCTION

In recent years, the membrane separation process received worldwide acknowledgment and has been used in various applications such as wastewater treatment, desalination, gas separations of industrial gases, pharmaceuticals industries, *etc.* [1-5]. The membrane-based separation technology has many advantages including economical, treatment efficiency, low energy consumption, simple operation, cost-effective scale-up and flexibility for being combined with others, which makes it superior to other old-fashioned type processes such as absorption, adsorption or distillation [6-12]. Molecules and ionic species in the liquid or vapour phase are selectively transported across the membrane and the movement is by the pressure, temperature, or concentration gradient. Differential transport occurs when the movement of a substance through a membrane is selectively restricted. Since, the transportation process is a non-equilibrium process the separation through the membrane occurs due to the variation in the transport rate [13-17]. Any substance that forms a sufficiently thin and stable layer can be a membrane. This comprises metals, ceramics, glass, polymers and even structured molecular monolayers of liquids. All the polymeric materials may not be used for the formation of synthetic membranes. Only those with good mechanical strength, elevated glass transition temperature, film-forming ability, chemical stability and hydrophilic hydrophobic balance are preferred as the fabrication material [18-20].

Membranes can be categorized into isotropic and anisotropic groups based on structural characteristics [21]. Isotropic membranes come in three varieties *viz.* macro-porous, non-porous dense film and electrically charged membranes. They are composed of single materials and have homogeneous constitutions. The pore size spans from 0.1 to 5 µm for macroporous membranes and the solutes are segregated according to the pore and solute sizes [22,23]. Transport mechanisms in non-porous dense film membranes are governed by diffusion, influenced by gradients in electrical potential or concentration pressure. The diffusion rate and solvability govern the separation when penetrates flow through it. The outermost layers of electrically charged membranes, also known as ion-exchange membranes, are decorated with either positive or negative charges. They achieve partition by forcing ions with the same charge as the membrane aside. The rate at which the ions are transported relies on the charge density and the input ion concentration [24,25].

Anisotropic membranes are characterized by their variability in chemical and structural formulation, additionally; they can be categorized into phase-separation membranes and composite membranes [26,27]. At the same time, the classification into organic and inorganic membranes is according to the materials employed for membrane fabrication. Organic membranes are mainly prepared from polymers namely cellulose acetate, polysulfone, polyimide, polycarbonate, polydimethylsiloxane, *etc.* Inorganic membranes are primarily derived from metals metal oxides, alloys, *etc.* The inorganic membrane has a relatively high capital cost, fragile and offers limited permeability for highly selective membranes at moderate temperatures so polymeric membranes are more abundant in the market of membrane separation.The combination of ease in preparation and purification, along with operation at low temperatures, has resulted in their increased popularity within both commercial and academic communities [27]. Scientists have recently shifted their focus to membrane technology for gas separation from the mixtures because of the pronounced selectivity and distinct permeation of substances through membranes. Based on their permeability thin-film membranes specifically allow certain gases to pass through [27-32].

Membrane properties like thickness and pore size, the kind and characteristics of the gas and membrane-gas interactions influence the permeability. These membranes are paired with solvents that absorb the desired gas for enhanced capture. The technique functions by permitting the desired gas to flow across the membrane's pores and be absorbed by the solvent. The combined use of selective membranes with absorbent liquids leads to efficient and effective gas capture [33-35].

Gas separation principles: The separation of gases is mainly driven by the partial pressure gradient. Different techniques are being used to describe gas transport over membranes, based on the membrane and permeate gas properties.

Porous membrane: A variety of gas separation procedures have been suggested for use with porous membranes, and these methods include:

(a) Knudsen diffusion and Poiseuille flow: The gas permeation in porous membranes is facilitated by Poiseuille flow and Knudsen diffusion. Knudsen diffusion happens when the pores of the membrane are inferior in size to the mean free path (eqn. 1) of the gas molecules and will take place if the pore size of the membrane ranges from 0.5 to 10 nm [36-39].

$$\text{Mean free path}\left(\lambda = \frac{3\eta(\pi RT)^{0.5}}{2P\ 2M}\right)$$

where, η = viscosity of the gas, R = universal gas constant, T = temperature, M = molecular weight.

The ratio of Knudsen to Poiseuille depends on the pore radius and mean free path of the gas molecule and if the ratio (λ/r) < 1, the Poiseuille flow dominates and the flux of gas through the pores is given by:

$$G_{vis} = \frac{r(P_1 - P_2)}{16L\eta RT}$$

where r = pore radius, P_1 = gas partial pressure at the feed side, P_2 = gas partial pressure at the permeant side, L = length of the pore, η = gas viscosity.

(b) Molecular sieve: For a membrane to function as a molecular filter the pore size of membrane must be in between the gas molecules. For sieving to be more effective the size of pore should be maintained below 0.5 nm.

(c) Partial condensation: Partial condensation of the selective gas in pores and thereby transport of condensed molecules through pores may also attain the gas separation effectively.

(d) Selective adsorption: From a gas mixture, gas with maximum affinity adsorbs more on the pore lining followed by surface diffusion resulting in gas separation [39-41].

Dense membrane: The transport occurs *via* the solution diffusion process across a dense membrane. The crucial aspect of separation is the membrane's capacity to regulate different species' penetration. Using this approach, diffusion occurs after the permeants dissolve in the membrane material. The diffusion approach in solution-diffusion involves three key phases, *i.e.* (i) absorption or adsorption at the preliminary phase; (ii) solubility assisted diffusion across the membrane; and (iii) evaporation or desorption on the other side.

Differences in thermodynamic properties existing at the two phases of the membrane and the interactive forces existing between the membrane molecules and the gas molecules are the main reasons for the gas separation. The rate-determining parameter is the permeation coefficient since concentration gradient alone is considered a factor of chemical potential, then the permeability coefficient:

$$P = D \times S$$

where 'D' is the diffusion coefficient and 'S' is the solubility coefficient [42,43].

Polymer membranes: When gas separation is considered, the polymeric membranes work better than techniques like chemical absorption, pressure swing absorption or cryogenic distillation [44]. Polymeric membranes are additionally affordable, eco-friendly and energy-efficient. Nonetheless, there is no assurance regarding the membrane material, and sustaining the long-term regularity of flux is challenging. One problem with the most extremely permeable membranes is their lack of selectivity. The ideal characteristics for a membrane to be utilized in gas separation include significant permeability, great selectivity, exceptional thermal and chemical stability, strong mechanical strength and good processibility. These qualities can be obtained by employing mixed-matrix membranes (MMMs) or choosing polymer mixtures. Polysulfone, polyamide, polycarbonates and polyimide are some materials used as gas separation membranes [45-49].

Polysulfone: One significant group of polymeric materials used in the manufacturing of gas separation membranes is polysulfone (PSf). PSf is more resilient to temperature, chemical changes and frequently utilized to create ultrafiltration membranes and the matrix for composite membranes because of its T_g value of 190 ºC. Polysulfone (PSf, Fig. 1) is less hydrophilic in nature and it is the best option for the membrane production due of its exceptional resilience to both acidic and alkaline conditions, outstanding mechanical qualities and excellent film forming capabilities [50-52].

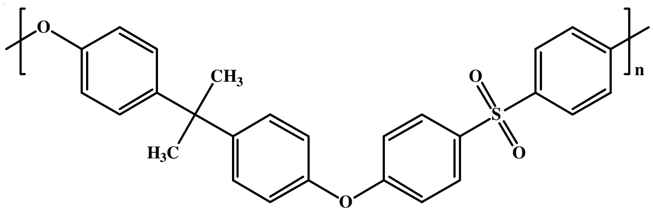

Fig. 1. Structure of polysulfone

There are three primary types of polysulfone gas separation membranes *viz.* asymmetric, dense and composite. The dense and asymmetric membranes are made entirely of PSf, whereas the composite membranes also include another substance. The methods used in the manufacture of these membranes differ greatly. Dense and asymmetric membranes can be fabricated using wet, dry or dry/wet techniques; the dry process does not include immersion in precipitation baths [17,53-55].

A polymer solution, consisting of a binary solvent-polymer mixture or mixtures containing solvents, non-solvents and polymers, is spread on a support and followed by solvent evaporation leading to the creation of a dense membrane, usually marked by lower permeation values. The wet process is comparable in solution composition to the dry process and involves initially concentrating the outermost layer of the membrane by evaporation [54]. Then, the submersion in a precipitation bath results in phase separation and demixing because of the diffusion exchange between the solvent-nonsolvent systems. Immediate demixing results in porous membrane whereas delayed demixing will lead to an asymmetric structure. Both methods usually produce polysulfone membranes with different defects. To overcome these defects the best way is to use a coating layer on the membrane thus improving their applicability in the gas separation process [56]. For manufacturing ultrathin anomaly-free surface layer of membrane, Pinnau & Koros [57] suggested an alternative strategy, a dry/wet process in which two solvents, which show much difference in the volatility are used, also they show diverse affinity towards the non-solvent. Then convective evaporation and freestanding evaporation are carried out for the cast film before immersion in a coagulation bath [54-56,58].

The selection of nonsolvent plays a vital role in membrane fabrication processes that include immersion in precipitation baths. Water is commonly used but, in that case, the solvent exchange step is crucial to ensure the reduction in surface tension in membrane pores [54]. Otherwise, owing to high surface tension at the membrane pores, the pores may collapse resulting in the non-selective layer. Flat sheet composite membranes are made by simply coating the second polymer onto the substrate and leaving it for deposition for a while, but in case of hollow fiber membranes dip coating is used. The supercritical CO_2 process can also be employed for the formation of defect-free polysulfone membranes. To achieve more permeable and selective membranes either during manufacturing time or post-treatment are adopted [54,58-60]. The modifications in materials used during manufacturing time to obtain defect-free gas separation membranes recently are as follows:

Aroon *et al.* [61] studied the fabrication and gas separation performance of asymmetric flat sheet membranes made up of polysulfone polymer. The efficiency was evaluated concerning the permeance of methane (CH_4) and carbon dioxide (CO_2), along with the ideal CO_2/CH_4 separation factor for the new membranes fabricated. The presence of additives shifted the binodal curve closer to the dope composition, having the order PEG400 > ethanol > PVP > glycerol. The addition of non-solvents and polymer additives generally enhanced both permeance and perm selectivity, because of the instantaneous demixing that formed a thin skin layer and suppressed finger-like macro-voids, which was confirmed by SEM analysis. Using THF/NMP solvent mixture instead of NMP alone yielded a highly selective membrane due to the rapid evaporation of THF, which induced rapid vitrification and effective orientation of macromolecules, leading to a reduction in defects. The influence of polymer concentration on gas separation properties and membrane morphology and the impact of casting solution composition and additive choices were also examined [61].

Novel porous hollow fiber membranes composed of polyvinylidene fluoride (PVDF) and polysulfone (PSf) were produced *via* a wet phase-inversion process. As the phase-inversion promoter, glycerol was employed. The significant increase in the precipitation rate of spinning dopes, associated with glycerol and resulting in unique membrane topologies, was determined by cloud point diagrams. The PVDF membranes included a very thin outer skin layer with minimal resistance to mass transfer and high permeability, whereas PSf membranes had a more open cross-section and smaller pore sizes. When compared to PVDF, PSf membranes were shown to be more hydrophobic and to have an anti-wetting property through the gas permeability experiments. The PSf membranes also exhibited a significantly reduced permeability. An ideal structure for the PVDF membrane was ultimately achieved. The optimized structure of the PVDF membrane achieved a CO_2 flux of 8.20×10^{-4} mol/m^2 s at an absorbent flow rate of 310 mL/min, where this value was higher than commercial asymmetric PVDF membranes. Therefore, based on the study of Ismail & Mansourizadeh [62], it can be suggested that these optimized PVDF HF membranes are better candidates for effective CO_2 absorption and separation compared to PSf in the gas-liquid membrane separators.

To study the plasticization effects of CO_2, a thin layer of polysulfone was spin-coated onto flat polytetrafluoroethylene (PTFE) supports (Sartorius, 0.2 µm pore size), with active layers less than 2 µm thick, at various temperatures. The plasticization occurred at lower pressures compared to dense membranes and an increase in plasticization potential when the active layer thickness decreased, demonstrated by permeability-pressure isotherm. Additionally, Scholes *et al.* [63] reported that the CO_2 plasticization potential decreased at higher temperatures. These findings confirm the prior research demonstrated that thin films have distinct CO_2 plasticization behaviours compared to dense membranes.

The effectiveness of zeolite ZSM-5 particles incorporated polyimide/polysulfone (PI/PSf) mixed matrix membranes (MMMs) in gas separation was investigated. The novel membranes were prepared by Dorosti *et al.* [64] with a solution casting approach and their transfer rates of O_2, CO_2, N_2 and CH_4 were evaluated. The impact of zeolite and polymer concentration on the induction of gas permeation and selectivity was also examined. The O_2 permeability of pure polyimide membrane elevated from 0.69 to 0.73 Barrer and 0.89 Barrer with 10% and 20% of zeolite (wt.%) loading, respectively. The 50/50 PSf/PI membrane showed the utmost selectivity, lowest permeability and the most uniform matrix. Additionally, MMMs showed better permeability with adequate selectivity parameters; however, membranes with 20 wt.% of zeolite showed void formation issues. The improved thermal reliability of the new membranes was attributed to the high thermal resistance of the additives and polyimide content and was explained by thermogravimetric analysis.

Kim & Park [65] prepared polysulfone–poly(ethylene oxide) random copolymers by polycondensation for the study of PEO content influence on gas transport properties. In these samples, PEO content is varied starting from 5 mol% to a maximum of up to 20 mol% in the PSf matrix. Surprisingly, the gas permeabilities did not improve by increasing PEO content (including CO_2), but rather saturated at a certain composition which was expected given the high affinity of POE chains for gas molecules. The reduced gas permeability was ascribed to non-phase separation between PSf and PEO segments, hence no clear phase of PEO regions. However, based on the microstructure analysis, the nature of intermixing between PSf and PEO segments is amorphous without any crystalline phase attributed to a single glass transition temperature. Consequently, the presence of PEO did not contribute to increased gas permeability, highlighting the importance of phase separation for improved gas transport properties.

Polysulfone was used as the material for the asymmetrical, defect-free membrane by the use of dual bath coagulation with wet phase inversion [66]. Distilled water was used as a second bath after the previous coagulation bath (water/alcohol combinations) produced the dense skinned layer. Investigations were conducted into the effects of a number of variables on the membrane performance, including the thickness of membrane, the amount of polymer in the casting solution, the kind of solvent used, the immersion period and the bath temperature. Thicker membranes with higher polymer concentration decrease the flux whereas observed increase in O_2 selectivity. Permeance was the parameter most affected by solvent, with DMF reaching the lowest values and those obtained for THF being higher. The non-solvent IPA content had a smaller influence on oxygen permeability. The propanol, ethanol and methanol increased the oxygen permeabilities in contrast. Further to this, higher temperature in the second coagulation bath resulted in the improved oxygen permeance but ultimately reduced selectivity as it was evidenced by faster demixing rates. The O_2 permeance significantly increased when a non-solvent and 3 wt.% PVP were added to the casting solution [66].

New asymmetric PSf-PI blended membranes with low PI content (5-20%) using the phase inversion technique were fabricated by Rafiq *et al.* [67]. The uniformity of the membranes, compatibility between polymers and single glass transition temperatures were confirmed by SEM, FTIR and DSC analysis. Tensile strength, Young's modulus and elongation at break elevated as the PI content increased. Permeation results showed that with a higher PI content, the permeance for both CO_2 and CH_4 increased when feed pressure ranged from 2 to 10 bar. The best CO_2/CH_4 specificity is reached by the membrane with 20% PI, which possesses excellent thermal and chemical stabilities besides meaningful gas separation properties [67].

Defect-free asymmetric polysulfone membranes were developed by Savoji *et al.* [68] for the separation of O_2 and N_2. The surface-modifying macromolecules (SMM) were incorporated into the casting solution and pre-solvent exposed cast films were soaked in isopropanol before being submerged in water. This method improved more in the performance of the membrane by increasing only the selective layer. These charged SMMs efficiently reduced defective pores in the skin layer and greatly enhanced O_2/N_2 selectivity. Extended immersion times in isopropanol produced a thicker, more uniform skin layer, resulting in decreased permeance but increased selectivity. Among the SMMs evaluated, cSMM-PPG and cSMM-PEG enhanced membrane selectivity by increasing the skin layer's thickness and reducing defect formation, whereas nSMM detrimentally affected membrane performance by promoting the formation of large, defective pores [68].

Details of the incorporation of nanosized fumed silica as reinforcing material in mixed matrix membranes (HF MMMs) for gas separation based on asymmetric polysulfone hollow fiber were reported by Wahab *et al.* [69]. Simultaneously, lower filler loading (0.1% w/w) results in the reduced CO_2 and CH_4 permeabilities of 90.04 and 2.75 GPU compared to neat polysulfone membranes; however, a more enhanced selectivity was determined for these composite systems on the other hand, a higher filler loading (10% w/w) induced particle aggregation leading to nanoscale point defects which permitted slow gases CH_4 and N_2 particles in through polymer phases hence reducing selectivity. The addition of fumed silica increased CO_2 permeability by 12-16% and T_g, resulting in higher thermal stability as well as an increase in matrix rigidity. The result of this study invariably suggests that effectiveness in gas separation increases at lower filler proportion *via* lesser agglomeration of particles.

Coterillo *et al.* [70] focused on the synthesis and analysis of ITQ-29 zeolite crystals with high Si/Ge ratios as well as various particle sizes suitable for mixed matrix membranes (MMMs). The molar ratio of Si/Ge and the seeding content in the synthesis gel were identified as crucial factors, yielding highly dispersed 2.5 mm sized particles with pure silica composition being amorphous or poorly crystalline. These zeolite particles were dispersed into a commercial polysulfone matrix at loadings of 4, 8 and 12 wt.%, showing significant H_2/CH_4 separation properties such as the highest H_2 permeability of only up to21.9 Barrer with the respective selectivity of approximately 118 being obtained for the membrane containing only time raised loading (*i.e.* polar effect dominance), which would enhance better functioning in advanced cracking conditions. The thermo-treatment conditions (temperature and time) as well solvent used was designed in a way to facilitate zeolite-polymer interactions and minimize particle agglomeration or formation of voids that would hinder gas permeation through the membrane. The use of dichloromethane (DCM) resulted in no solvent remaining so the higher complete mixing and dispersibility among MMMs interaction. The study showed that the pore-size selectivity of ITQ-29 zeolites was successfully translated directly into the polymer matrix leading to ideal perm selectivity ratios at ultralow relative loadings.

For gas separation purposes, Modarresi *et al.* [71] utilized low-frequency oxygen plasma to change the membrane surface properties of polysulfone membranes and analytical attention was given to the impact of treatment time duration plasma power used, *etc*. The plasma-treated membrane exhibited an increase in permeation for CO_2 and CH_4, up to 68.80 GPU of CO_2 or around 5.63 GPU for CH_4 accompanied with CO_2/CH_4 selectivity varying between 7.7 and 45.3 based on the specific treatment parameters. The introduction of oxygen containing functional groups to the membrane surface from ATR-FTIR spectra is attributed to an increase in hydrophilicity, as determined *via* a lowering water contact angle. Smooth surface morphology was confirmed by SEM observations when the plasma process was regulated, however, extended treatment led to rough surfaces as well as crack formations. These demonstrate the successful use of plasma treatment in enhancing gas separation performance *via* selective adjustments to membrane surface properties. Rafiq *et al.* [72] used the phase inversion technique to synthesize polysulfone/polyimide (PSf/PI) asymmetric membranes and incorporated silica nanoparticles. The characterization techniques like SEM, XRD, FTIR and TGA provided excellent thermal stability with distinct morphological features at different loading of silica but agglomeration was observed in case of higher stacking amount (20.1 wt %). Gas permeability analysis demonstrated that CO_2 permeance increased with silica content, reaching a peak of 73.7 ± 0.2 GPU at 5.2 wt.% silica and the greatest CO_2/CH_4 selectivity of 61.0 ± 0.3 at 15.2 wt.% silica after heat treatment. The obtained results showed that the PSf/PI-silica MMMs could not only be used as thermally stable but also highly permeable membranes for effective gas separations, especially at ideal silica loadings.

Polysulfone mixed matrix hollow fibers embedded with polymer-derived carbonized xerogels were assayed for gas separation analysis and calibration by Magueijo *et al.* [73]. The xerogels were further ground down and wet milled to attain submicron-size particles, which had pore properties that were measured by a surface area analyzer. The dry/wet forced convection spinning technique was utilized to fabricate mixed matrix hollow fiber membranes (MMFs) containing these particles. The stiffness of MMMs also increased for the branched MOF-xerogel composites. The membrane with mesoporous xerogels led to the promotion of Knudsen diffusion as a critical gas transport mechanism, thus increasing permeances for gases with larger molecular diameters, while simultaneously lowering fast/slow gas selectivity. In addition, all MMMs displayed enhanced CO_2/O_2 and CH_4/N_2 selectivity relative to those of the unfilled fibers, but polymers containing microporous xerogels showed increased CO_2 pressure-normalized flux without sacrificing CO_2/CH_4 selectivity.

Chenar *et al.* [74] established the solvent-structure relation and efficiency in gas segregation features of PSf membranes with silica nanoparticles, which were prepared *via* the sol-gel procedure using tetraethyl orthosilicate (TEOS) and incorporated in polysulfone matrix by thermal phase inversion technique. They employed a variety of solvents in their experiment, including tetrahydrofuran (THF), N-methyl pyrrolidone (NMP) and N-dimethyl acetamide (DMAc). With a few exceptions, the inclusion of silica nanoparticles reduced the gas permeabilities while improving the CO_2/N_2 and O_2/N_2 selectivity. The optimal solvent for uniformly distributing these nanoparticles and encouraging enhanced CO_2 permeability and selectivity was determined to be NMP. The polysulfone–silica (5 wt.%) membrane made with NMP has a CO_2/N_2 permeability of 7 Barrer and a CO_2/N_2 selectivity of 35. The reinforcement effect was caused by the efficient dispersion of silica nanoparticles in addition to their interaction within the polymer matrix.

The gas separation properties of a dual-layer polysulfone membrane were described by Ahmad *et al.* [75] in order to achieve high-pressure CO_2 extraction from natural gas. The membrane was developed using a dry/wet phase inversion technique and used polysulfone as the supporting polymer. Diethylene glycol dimethyl ether (DEG) was used as the casting solvent for the selective top layer, while glycerol was utilized as an additive to form the microporous support layer. This membrane showed high CO_2 permeability at low pressures possessed good resistance to plasticization at high pressures and avoided the use of additives commonly used in similar applications. The enhanced gas separation efficiency was attributed to the synergistic interaction between the two distinct layers, both derived from varied formulations of polysulfone, as well as the strategic selection of DEG as the casting solvent. The results revealed the dual-layered structure and DEG as a spinning task helped to improve CO_2 removal from natural gas in high-pressure conditions. The results showed that under high-pressure circumstances, the dual-layered structure with DEG as a casting solution improved CO_2 removal from natural gas.

To enhance CO_2 separation performance, a new mixed matrix membrane was developed in this study using the SAPO-44 zeolite as an addition to the polysulfone matrix by the use of the phase inversion approach. The optimal CO_2/N_2 and CO_2/CH_4 selectivity of membranes with < 5 wt.% loading was exhibited by well-dispersed zeolite particles, as validated by SEM and FTIR analysis. Higher zeolite contents (≥ 10 wt.%) led to significant particle agglomeration and formation of interfacial voids, reducing membrane performance. It appears that filler surface modification will be necessary to achieve defect-free MMMs and enhanced CH_4 separation capabilities since FTIR research revealed weak interaction between PSf and SAPO-44 at high loadings [76].

Mixed matrix membranes were successfully produced by mixing polysulfone polymer with amine-functionalized TiO_2 (F-TiO_2) at concentrations ranging from 0 to 10 wt.%. Kiadehi *et al.* [77] concluded that functionalizing TiO_2 nanoparticles with ethylenediamine (EDA) had a substantial effect on the morphology and gas transport properties of MMMs. The SEM images show that the nanoparticles achieve good dispersion within the PSf membrane matrix at 5 wt.% F-TiO_2. The relationship between the concentration of F-TiO_2 and gas permeation suggests that gas is entering the spaces created by the interstices between the polymer chains and F-TiO_2. Both the calculations and the experiments show that the addition of F-TiO_2 increased the permeability of membrane to all gases. The selectivity for CO_2/CH_4 decreased from 4 to 3.75 as the concentration of nanoparticles increased, while the permeability to CO_2 increased from 2.32 to 3.49 GPU.

Membranes for CO_2 separation from natural gas are limited in their use due to the trade-off between permeability and selectivity. Subsequently, Junaidi *et al.* [78] discussed the requirement for asymmetric polysulfone mixed matrix membranes (MMMs) using SAPO-34 zeolite for this purpose. Membranes with zeolite loadings varying from 5 to 30 wt.% were developed using phase inversion. At 10 wt.% SAPO-34 loading, optimal CO_2 permeance (314.02 GPU) was measured and CO_2/N_2 and CO_2/CH_4 selectivity reached 26.1 and 28.2, respectively. Excessive zeolite loadings resulted in particle agglomeration and interfacial voids, hence diminishing performance. This work emphasizes improving polymer/filler integration in membranes for better performance in CO_2 removal from natural gas.

Moradihamedani *et al.* [79] also prepared polysulfone-based membranes containing different quantities of TiO_2 nanoparticles and investigated their performance in gas separation. Morphological studies revealed the homogeneous dispersive property at low TiO_2 concentrations ($\leq$ 3 wt.%), morphological study by AFM exhibited an increasing surface roughness and TGA showed that thermal stability markedly improved than the pristine membranes. These membranes showed very high CO_2/CH_4 selectivity, as good as 36.5 at 3 bar and complete CO_2 separation was observed under atmospheric pressure conditions (1 bar). In contrast, aggregation of TiO_2 nanoparticles and the formation of macro-voids and defects were observed at higher loading ($\geq$ 5 wt.%), giving an increase in gas permeability but a reduction in selectivity. The superior gas separation performance was yielded at relatively low TiO_2 loadings in this research to reveal a balance between the permeability and selectivity of mixed-matrix membranes (MMMs).

Wang *et al.* [80] reported the CO_2 capture with commercially obtained flat-sheet polysulfone (PSf) membranes with an optimized inlet gas pressure of 0.4 MPa and 400 L/h residual gas flow volume and the inlet temperature was maintained at 50 ºC. Significant improvements in both selectivity for CO_2/N_2 separation as well as permeability were achieved due to plasticization effects brought about by water vapour on the PSf membrane. On the other hand, O_2 slightly reduced CO_2 separation and SO_2 had little effect. The involvement of gypsum particles exerted a notable decrease in the efficiency of CO_2 separation due to their physical clogging effect on membrane-active sites, increased resistance to mass transfer and adsorption of gases to a small extent. At higher feed gas pressure and CO_2 content, improves both CO_2/N_2 specificity and permeation rate. Conversely at higher residual flow rates an increase in selective separation ability with a lower fraction of enrichment per extraction. The separation performance presented almost no change in the feed gas temperature.

Adewole *et al.* [81] studied the effects of various solvent systems on the physico-chemical and permeability characteristics of polysulfone membranes as well as the resulting outcomes. In comparison to membranes constructed from standard systems like 1-methyl-2-pyrrolidone, N,N-dimethylacetamide, DMSO or DMF, diethylene glycol dimethyl ether (DEG) utilized membranes showed better gas permeability (29.08 Barrer) and CO_2/CH_4 selectivity values of 23.12. According to the findings, DEG was expected to perform better because of the favourable polymer solvent interactions. Thus, to develop better membranes, a thorough analysis of the polymer-solvent interaction is required.

A series of MMMs using carbon nanofibers (CNFs) from 0.01 to 1 wt.% in polysulfone composite membrane has also been prepared by Kiadehi *et al.* [82] for gas separation application. SEM, AFM and ATR-FTIR were used to confirm the characteristics of the membrane and the pure gas permeability and sorption tests through CNF-incorporated membranes revealed remarkable modifications in the membrane surface properties. Permeability tests demonstrated that CO_2 permeability exceeding 12.04 Barrer was obtained with increased CNFs content, while the membrane containing 1 wt.% of CNFs showed a peak in CO_2/CH_4 selectivity equal to 12.17 at provided pressure (4 bar). The SEM analysis confirmed that the CNFs were dispersed homogenously at different loadings, yielding increased gas permeability and selectivity with rising pressure feeding. Thus, suggested that CNF/PSf MMMs prepared with a suitable weight ratio can be good candidates for use in industrial gas separation applications showing an acceptable selectivity and high permeability of desired gases [82]. In another study [83], they reported that mixed matrix membranes were developed by adding functionalized carbon nanofibers (F-CNFs) to polysulfone to improve the distinction of gases such as CO_2 from CH_4 and N_2 from O_2. Using a solution casting technique, random F-CNF concentrations ranging from 0 to 1.5 wt.% were added to a PSf matrix, characterizing the membranes' shape and crystalline structure. According to an experimental investigation, the amine groups on the F-CNFs significantly interact with CO_2, increasing CO_2 permeability to 3.57 GPU and O_2 permeability to 1.58 GPU. The CO_2/CH_4 and O_2/N_2 selectivities were close to 7.7 and 3.5, respectively, as a result of the addition of 0.5 wt.% F-CNFs. On the other hand, N_2 selectivity reduced at higher loadings while increasing for the membrane loaded with 0.5 wt.% F-CNFs (from 3.3 to 3.5). The F-CNFs were evenly distributed across the PSf matrix at the 0.5 wt.% loading. An increase in the gas permeability was believed to occur at the filler-polymer interface, despite the fact that the specificity of membrane decreased with the addition of more than 0.5 wt.% of F-CNFs [83].

Asymmetric flat sheet PSf membranes were effectively developed using the innovative two-fold coagulation bath and dry-wet phase inversion technique. The temperature of the coagulation bath, the concentration of ethanol and the evaporation duration (ET) all affected the membrane shape. Thicker skin layers were produced by longer ET periods and membranes with ethanol contents greater than 20.4 wt.% were found to have dense skin layers free of defects. It was discovered that CBT had an impact on changes in pore size and distribution. When CBT is lower than 40 ºC, increased porosity and pore size are observed. For membranes prepared with EtOH concentrations of 14.4, 16.4, 18.4 and 20.4 wt.%, the O_2/N_2 selectivity at a pressure of 8 bars is approximately 14.77, 6.01, 3.27 and 4.11, respectively. The viscoelasticity, modulus and glass transition temperature of those membranes were altered by DC plasma treatment with various gases; O_2-plasma was more successful since it resulted in a larger modulus reduction. The plasma treatment greatly increased the gas permeability, but it also reduced the selectivity of CO_2/CH_4 and O_2/N_2 [84].

Development of PSf/PES blend membrane to improve mechanical and thermal stability, Mannan *et al.* [85] conducted a study where they said that PES decreases the CO_2 and CH_4 permeability but enhances selectivity, especially at elevated pressures when added to PSf. In ideal selectivity, the PSf/PES (20-80) membrane achieved the best improvement due to its smaller size and ease of CO_2 pass. These membranes exhibited higher stability and compatibility confirmed by uniform weight loss in TGA and FTIR tests. Moreover, the selectivity allowed by PES increased as a result of a denser internal structure making it more resistant to permeation. The PSf/PES blend membranes showed a good balance in the cost, selectivity and stabilities. Ahmad *et al.* [86] used modified SAPO-34 zeolite with1-ethyl 3-methyl imidazoliumbis(trifluoromethylsulfonylamide ([emim][TF2N]) triisopropylate and its incorporation within polysulfone (PSU) matrix to develop mixed matrix membrane. The ionic liquid modification did not change the crystal structure of zeolite but slightly decreased its specific surface areas and pore volumes. After extended exposure to ionic liquid, however, the zeolite CO_2 adsorption affinity drastically increased. This made the MMM, which consists of the modified SAPO-34 show an increase in gas segregation efficiency, especially in CO_2/CH_4 and CO_2/N_2 selectivity. Due to the uniform distribution of the modified zeolite particulate throughout the membrane as identified by SEM images, the membrane exhibited higher CO_2 permeability and significantly enhanced selectivity of CO_2 over other gases.

Chittrakarn *et al.* [87] mitigated the aging impact on the surface hydrophilicity and improve the gas separation effectiveness of PSf gas separation membranes. This work offers an effective strategy for developing PSf based mixed matrix membranes. Plasma treatment followed by short-term oxidation in ambient air and grafting from aqueous solutions of monomers like polyethylene glycol and acrylic acid *etc.* are the steps adopted for fabricating new membranes. Plasma-treated and grafted PSf membranes also possessed more hydrophilic surface properties than the original membrane, which nevertheless retained its satisfactory performance for a long duration over 120 days. Grafting efficiency depended on plasma exposure time, power and grafting duration was proved through various characterization techniques, including SEM, AFM as well as ATR-FTIR measurements. The surface modifications were also corroborated with the help of morphological analysis and functional group identification, while the gas permeation tests showed an enhancement in CO_2/CH_4 separation performance (from 54.06 to 60.05). Using the plasma-induced graft polymerization provides an efficient permanent hydrophilic modification for the PSf membrane without influencing its separation performance for gases.

Polycondensation of PSf containing ethylene glycol was used to synthesize a series of gas separation membranes. Jujie *et al.* [88] distinguished the permeability and selectivity for CO_2 and CH_4 in different temperatures from 25-55 ºC and pressure from 0.5-1.5 atm. The composition with 20 wt.% PEG exhibited gas separation efficiency with an ideal specificity for CO_2/CH_4 ratio of 43.0 and CO_2 permeability of 6.4 Barrer at 1.5 atm and 25 ºC. This selectivity value was much greater compared to a pristine PSf membrane, which had a value of 26.3. The results showed the efficiency of the PSf-PEG copolymeric membrane for CO_2 separation. Lu *et al.* [89] provided a facile method to blend ionic liquids (BMIMTFSI, BDIMTFSI, DCIMTFSI, DEMSTFSI, HDPhTFSI, *etc.*) with PSf and prepare a new type of membrane with porous surfaces. They suggested that the pore generation was due to the phase separation induced by the moisture present in the unused ionic liquids. This hypothesis was successfully verified with the FTIR and SEM results. Although all the ionic liquids improved the permeance of the membranes in comparison to the pure PSf membranes, only a few of them were able to enhance the selectivity. DEMSTFSI demonstrated the greatest CO_2 selectivity and permeance. The compatibility and gas separation performance with all the selected ionic liquids were found to be different. This can only be attributed to the difference in the molecular structures of the ionic liquids [89].

By integrating varying concentrations (0.5-5 wt.%) of zeolite-T particles into polysulfone matrices, Mohamad *et al.* [90] developed new mixed matrix membranes and characterized. The gas permeation experiments showed that pristine PSf membranes had CO_2 and CH_4 permeabilities of 12.33 and 4.69 GPU, respectively, with a CO_2/CH_4 selectivity of 2.63. when 3 wt.% zeolite-T was included in PSf matrix gave the maximum permeability of 82.3 GPU for CO_2 and in case of CH_4, it was 31.2 GPU, while a 4 wt.% loading achieved a maximum CO_2/CH_4 selectivity of 3.37, indicating an enhancement of 28.1%. Because of the optimal zeolite-T particle dispersion, the efficiency in gas separation improved, which elevated both permeability and selectivity. However, when the concentration of zeolite exceeded the optimal loading resulted in reduced performance due to interfacial voids and particle agglomeration. These results highlight the potential of zeolite-T integration to substantially augment the gas separation efficiency of PSf membranes.

Graphene oxide (GO) was incorporated into the doped solution prepared with polysulfone to synthesize hollow fiber mixed-matrix membranes (MMMs) and greatly enhanced gas permeability properties. The TEM and AFM analyses showed that the most feasible morphological type of GO nanosheet layer is retained and FE-SEM presented improved membrane architecture. The inclusion of GO increased the CO_2 permeability by 14% while promoting an enhancement in CO_2/N_2 and CO_2/CH_4 selectivity by 158% and 74%, respectively. Furthermore, these membranes were able to improve the mechanical and thermal properties and thus, demonstrated the potentiality of GO as a novel additive in MMMs for gas separation applications [91].

The effect of the incorporation of MWCNTs in Kapton-PSf-blend composite membranes for gaseous species separations was investigated by Soleymanipour *et al.* [92]. The analysis by FTIR and SEM illustrated that PSfs combine homogeneously with Kapton at the molecular level. It was found that increasing PSf content in the blends resulted in membranes with superior gas permeation capacity and optimal selectivity, mainly for CO_2/CH_4 separation. The addition of MWNTs additionally improved gas permeability and under this condition, the selectivity slightly decreased in all the membrane types. The membrane with the optimized concentration of Kapton-PSf (25/75 %) containing 8% MWNT presented elevated permeabilities for CH_4, CO_2, N_2 and O_2 gases which demonstrates them as promising gas separation materials.

Min *et al.* [93] studied the gas permeance of PSf HF membranes with a membrane module of 75 cm^2 surface area on ten gases (O_2, CO_2, CH_4 and H_2, *etc.*). The CO_2 and H_2 permeance reached up to 53.92 and 78.63 GPU, respectively; however, the breakthroughs for N_2, O_2, CH_4, argon, olefin and paraffin were in lower value as compared with low molecular weight gases. The specificity of CO_2/N_2 and CO_2/CH_4 were 44.92 and 35.95, respectively. Although an increase in CH_4 content with increasing stage cuts and CH_4 recovery efficiency decreased. On the other hand, CO_2 capture efficiency was enhanced with increasing stage cuts regardless of pressure fluctuations. Further tests validated the performance of the module, which was particularly well-suited to high-pressure duties such as in natural gas pretreatment units for acid gases.

The gas separation characteristics of mixed matrix membranes (MMMs) consisting of matrimid and PSf blend with the ZIF-8 nanoparticles were investigated for high-pressure natural gas separations. Shahid & Nijmeijer [94] observed significant improvements in CO_2 and CH_4 permeability over the pure polymer membranes with 136% enhancement in CO_2 permeability at a loading level of 30 wt.% ZIF-8 showing stable selectivity. The combination of polymer blend and ZIF-8 nanoparticles significantly enhanced the plasticization resistance, resulting in a failure point at around 25 bars *vs.* approximately 18 bars for pristine PI/PSf and about 8 bars for pure PI membranes. Mixed gas experiments also confirmed the plasticization inhibition, observed an increase in CO_2 permeability by 197% and promotion of CO_2/CH_4 selectivity exceeding 30% at high pressures. These results demonstrate that combining polymer blends with MOF is a feasible path for achieving maximum CO_2 permeabilities and CO_2/CH_4 selectivity while ensuring stability under high CO_2 partial pressures.

Titania nanotubes were used for the modification of PSf hollow fiber mixed matrix membranes, which were prepared using hydrothermal synthesis at different durations (10 h and 48 h). The syntheses were characterized employing TEM, XRD and BET analysis revealing that the TNT fibers possess a hollow double-walled cylindrical tube morphology when prepared at long reaction times that allowed extended growth of nanotube diameter with smaller effective pore sizes. The incorporation of TNT, particularly at a concentration of 0.4 wt.% TNT10, markedly improved gas permeation performance ($H_2/CO_2/O_2$), achieving an impressive increase of up to 150% in the permeance values for each penetrant. On the other side, TNT48 MMMs showed a lower flux, yet higher selectivity ascribed to their narrower internal tube diameters. The work of Zulhairun *et al.* [95] on TNTs provides a rather economical, efficient resource of filler for MMM production in which the nanotube morphology has a considerable effect on gas separation performance.

Using a dry/wet phase inversion process, ethanol was added to the polymer solution to develop flat sheet asymmetric mixed matrix membrane films with nano-sized silica/PSf and DMAc or THF solvent. At an initial concentration of nanosilica, the performance of the membrane deteriorated as a result of void formation and agglomeration. About 22 wt.% PSf, 31.8 wt.% DMAc, 31.8 wt.% THF, 14.4 wt.% ethanol and a 20 s evaporation period were found to be the optimal parameters, resulting in a CO_2/N_2 selectivity of 15.6 and CO_2 permeance of 14.2 GPU. The performance of the membrane has shown a significant impact from the optimization of the fabrication factors, namely the solvent ratio, evaporation time and nano-silica loading. Increasing nano-silica content increased CO_2 permeance by 181% but reduced CO_2/N_2 selectivity to a value of 49%, as aggregates within the top layer of the dense membrane due to polymer/nano-silica interphase inconsistency and particle agglomeration acted as locations for enhanced void formation. While this level of selectivity is 32% lower than values in the literature, its CO_2 permeance was over double for applications requiring high flows [96].

Six distinct varieties of PSf hollow fiber membranes have been prepared from a single polymeric dope solution, differing by the key aspects used in the spinning approach, to identify the best membrane with maximum efficiency for gas separation. In the study by Roslan *et al.* [97], it was reported that CO_2/CH_4 and O_2/N_2 gas pair selectivity for all membranes were significantly increased when coated with a polydimethylsiloxane (PDMS) layer. At a greater air gap and lower dope extrusion rate, the PDMS coating on these produced membranes best supported up to 36.36 CO_2/CH_4 and 6.65 O_2/N_2 selectivity, respectively. Although some previous studies demonstrated higher performance of poly(ether block amide) (Pebax) than PDMS in flat sheet membranes, Pebax did not show any enhancement in both gas permeance and selectivity in hollow fiber membranes wherein an issue was encountered to provide a defect-free coating layer on top. The reproducibility was a challenge due to the fiber stickiness at Pebax coating. More study is needed for the optimization of Pebax coating deposition and its drying in the context of hollow fiber membrane production. Thus, in general, PDMS was a better option for providing gas pair selectivity enhancement to the PSf-based membranes.

Polysulfones modified with benzyldimethylamine (DMA), benzyltrimethylammonium fluoride (TMAF) and benzyltrimethylammonium iodide (TMAI) were synthesized and tested as membrane materials for CO_2/N_2 and CO_2/CH_4 distinction. Zhu *et al.* [98] identified that DMA had no marked effect on the CO_2 selectivity. The composite PSf membrane containing TMAI had improved the CO_2/CH_4 selectivity from 4.4 to 5.2 and CO_2/CH_4 permeability from 21 to 45. However, even in the optimal case, the permeability of CO_2 decreased from 5.6 to 1.7 Barrer. In general, a difference in the effect of functional groups on diffusivities is observed, which is also in agreement with the free volume model.

Karimi *et al.* [99] investigated the characteristics of the PSf/PEG gas separation membranes at various PEG concentrations in the PSf matrix. To ascertain the overall permeability and selectivity, the gas separation property of PSf/PEG membranes was investigated using pure gases N_2, O_2, CH_4 and CO_2 as a feed stream. When compared to membranes doped with PEG, pure PSU membrane exhibited the best selectivity for CO_2/CH_4 and CO_2/N_2. A significant pattern was identified in the response of membrane to CO_2 plasticization during testing at different gas pressures. Initially, permeability to CO_2 reduced as pressure climbed until a particular point was reached, after which it increased for all PEG concentrations.

Nasiriani *et al.* [100] studied the role of the molecular weight of PEG on permeability and selectivity of PSf/PEGs composite membranes. PEG10000 retained the greatest CO_2 permeability of 7.64 Barrer (20 wt.% composite) among the PEG variants. The CO_2/N_2 selectivity of PSf/PEG composites increased with increasing PEG content and a maximum selectivity value was obtained as 32.12 for the composite containing 20 wt.% of PEG (PSf/PEG10000). The membranes had high CO_2 selectivity and stability across pressures from 2 to 10 bar. The results revealed that higher PEG molecular weight and content result in a dramatic enhancement of gas permeability and selectivity, especially concerning the CO_2/N_2 gas pair.

Wijiyanti *et al.* [101] investigated the implementation of zeolite-templated carbons (ZTCs) as a nanoporous filler in polysulfone based mixed-matrix hollow fiber membranes (MMMs) for gas separation applications. The ZTC was synthesized using a zeolite-Y template and sucrose with impregnation, while MMMs were prepared through a dry-wet spinning approach at a diverse loading of ZTC from 0.4 wt.% to 0.7 wt.%. Among the novel membranes, one exhibiting enhanced gas permeation capability is characterized by a ZTC loading of 0.4 wt.%, achieving permeability values of 5.9, 58.5, 5.0, 14.0 and 169.2 GPU for CH_4, CO_2, N_2, O_2 and H_2, respectively. Also, illustrated the significant betterments in the optimal selectivity of CO_2/CH_4, O_2/N_2, H_2/CH_4 and CO_2/N_2. Unfortunately, at ZTC loadings as high as 0.7 wt % showed decreased selectivity and increased permeability because of the formation of voids within the membrane structure.

The performance potential of polysulfone–polyethylene glycol/silica (PSf–PEG/silica) composite membranes for N_2, O_2, CH_4 and CO_2 gas separation properties was studied. The PSf/PEG10,000 with 20 wt.% of silica membrane displayed high gas separation performance and showed superior CO_2 permeability (13.36 Barrer) and good CO_2/N_2 (45.76) selectivity. The permeability of polar gases was significantly increased when the silica nano additives were loaded, due to the increased interactions with OH groups in the nanocomposite structure. The FT-IR, SEM, XRD and DSC study confirmed the proper distribution of silica within the polymer matrix resulting in greater amorphous regions, elevated glass transition temperature and reinforced thermal stability. This was confirmed by the mechanical rheometry measurements suggesting that the increase of silica content improved interfacial interactions and phase strength, which changed the material transition points from a liquid to solid behaviour. Finally, Salahshoori *et al.* [102] reported that the performance of nanocomposite membranes was even more excellent than pure PSf and PSf/PEG composites in comparison to Robeson's upper bound indicating great efficiency for gas separation.

Farrokhara & Dorosti [103] elucidated the effect of 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIM-BF_4$) ionic liquid on CO_2/CH_4 separation efficiency using symmetric PSf membranes. The approach involved the comprehensive study of both pure PSf and ionic liquid incorporated membranes using characterization techniques. By dissolving ionic liquid into the polymer matrix, membrane permeance increases from 4.3 to 601.9 Barrer and CO_2/CH_4 selectivity improves significantly from around 8.2 to 25. In the tests of mixed gas CH_4 presence caused a worse selectivity compared to pure gas tests. The porosity of membranes is increased by ionic liquid as per FESEM analysis. Thermogravimetric analysis shows that higher ionic liquid content decreases thermal stability; but, the membranes with 20 wt.%, 30 wt.% and 40 wt.% ionic liquid surpass the Robeson upper bound, demonstrating superior CO_2 selectivity and permeability, with 30 wt.% ionic liquid membrane identified as optimal.

Zeolitic imidazolate framework-8 (ZIF-8) infused mixed matrix membranes (MMMs) of PSf were fabricated by Khan *et al.* [104] and their effect on the natural gas separation process was identified. The PSf hollow fiber membranes with different ZIF-8 loadings up to 1.25% were prepared and characterized. The thermal stability, glass transition temperature and surface smoothness were improved with low ZIF-8 loadings. The PSf membranes with 0.5 wt.% ZIF-8 exhibited the best linear performance in both CO_2 permeability (36%) and 28% improvement in CO_2/CH_4 selectivity at 6 bar pressure, against pure PSf membrane. Yet, an increase in both ZIF-8 loading and pressure led to a decrease in the separation factor partly due to CO_2-induced plasticization. Higher compatibility contributed to the uniform dispersion of ZIF-8 at low concentrations, which was favourable for gas separation efficiency. However high pressure applications are still difficult because of the plasticization effect.

Iron pillaring was employed to modify Cloisite 15A (C-15A) montmorillonite clay, which was later included into PSf mixed matrix membranes (MMMs) developed by Natarajan *et al.* [105]. Fe-pillared Cloisite 15A (P-C15A) membrane with 1 wt.% loading shows optimum properties among the newly fabricated membranes with varying additive concentrations from 0.1 to 1.5 wt.%. The substantial increase in permeation efficiency of CO_2 and O_2, with increases of 240% and 274%, respectively was observed in gas permeation studies and only slight reductions in gas selectivity. The 1 wt.% clay-loaded MMMs exhibited a CO_2 permeability of 18.01 bar and selectivity of 4.95 for the CO_2/N_2 gas pair and 18.34 for the O_2/N_2 gas pair, in agreement with the Robeson upper bound and indicating high efficiency to use in gas separation applications. Sutrisna *et al.* [106] fabricated new mixed matrix membranes, which are constructed from PSf and cellulose acetate polymer blends filled with inorganic ZIF-8 and TiO_2 particle fillers. The mZIF8 membranes obtained displayed remarkably higher permeabilities of CO_2, N_2 and CH_4 gases. However, the selectivity suffered a bit from this as well since there was only a small difference in diameters between the membrane pore size and gas molecules.

Graphene oxide (GO) and carbon nanotubes were introduced directly to the PSf matrix as fillers for the fabrication of new MMMs. Jiang *et al.* [107] found significantly increased gas permeability with CNTs and GO addition, where CO_2 permeability rose from 553 bar to 975 bar whereas the N_2 permeability was enhanced from an initial value of about 536 bar up to 745 bar at 0.2 MPa. The maximum CO_2/N_2, ideal separation coefficient at 0.1 MPa was as much as 1.94, which is higher than for pure PSf membrane of roughly equal thickness. Increasing CNT content was found to substantially enhance CO_2 permeability whereas varying inlet pressures significantly affected the N_2 permeability. These results establish a theoretical foundation for the development of PSf/GO/CNT MMMs in the industrial separation process.

By utilizing porphyrin filler in PSf polymer to enhance CO_2 separation Shafiq *et al.* [108] established new mixed matrix membranes. These membranes showed uniform filler dispersion, exceptional thermal stability with glass transition temperatures ranging from 480 to 610 ºC and increased CO_2 affinity due to the presence of π-π interactions and Lewis basic sites in the porphyrin filler. Gas transport properties were achieved at and above Robeson's line due to the introduction of porphyrin filler. Significant improvements in permeation rates (97% for CO_2, 82% for CH_4 and 81% for N_2) were reported by these mixed matrix membranes along with enhanced binary gas selectivity of 85% for both the mixtures containing CO_2/CH_4 and CO_2/N_2. Moreover, high temperatures decreased the activation energy of gas transport which is a strong indication for good long-term stability in the polymer matrix. The findings revealed the potential of MMMs containing porphyrins in achieving promising CO_2 separation performance from natural gas streams and hold significant promise for industrial utilization for a wide range of applications.

It is essential to remember that mixed matrix membranes usually improve the performance of polymers in gas separation by elevating either permeability, selectivity, or both. In order to create ZIF-95/PSf MMMs, Shafiq *et al.* [109] disseminated the zeolitic imidazole framework 95 (MOF ZIF-95) in the PSf polymer matrix. The PSf matrix included the ZIF-95 with loading percentages of 8%, 16%, 24% and 32% by weight. The permeability values for the gases He, H_2, O_2, CO_2, N_2 and CH_4 rose as the ZIF-95 loading percentage increased. The selectivity was also impaired by high loading. The improved loading membrane has a significantly increase in H_2/CH_4, O_2/N_2 and H_2/CO_2 in-selectivity by 16%, 15% and 8% as well as permeability in H_2, O_2 and CO_2 by 80.2%, 78.0% and 67.2%. The molecular sieving effect of ZIF-95 is mostly due to its improved performance for smaller gas molecules, while molecules with larger kinetic diameters encountered a diffusional barrier.

The current review is focused on the development of ultrathin separation layers for polysulfone membranes, which found effective application in the gas separation process and was fabricated by wet-phase inversion that may be achieved *via* solution modification through casting solutions. The thinnest separation layers showed the highest perm selectivity, while only a slight increase in permeabilities and diffusion coefficients occurred compared to those for thick samples. The effects of the solvent choice on membrane characteristics and material-related factors are revealed by the SEM images, aqueous and gas permeation measurements. Morphology was maintained while changing the structural stability and separation layer thickness, by employing ethanol instead of distilled water in the precipitation bath. These results indicate that chain packing governs gas permeability and diffusion coefficients in thin films, which renders sieving effects stronger within them so perm selectivity can be elevated for smaller species [110].

Polysulfone membranes were fabricated for gas separation using several solvents, namely tetrahydrofuran (THF), N,N-dimethylacetamide (DMAc), dichloromethane (DCM) and N-methyl-2-pyrrolidone (NMP). The concentration of THF in the casting solution was varied from 0% to 35% to enhance gas separation performance. The SEM confirmed that the NMP laid membrane had the heavier layer and lighter PSf support layers were laid from the combination of NMP/THF. The PSf membranes prepared from NMP show higher gas permeability and with NMP/THF mixture have exhibited CO_2/N_2 selectivity higher than other membranes and lower permeability. The PSf/NMP membrane showed the highest permeances of CO_2 (0.0728 GPU) and N_2 (0.0186 GPU), but low selectivity between CO_2 and N_2 due to a pin-hole defect on its surface. Abdulabbas *et al.* [111] reported that the highest CO_2/N_2 selectivity of 8.69 was recorded for PSf membrane fabricated by blending NMP and THF, giving evidence about the possibility that other combinations from solvents could increase gas separation performance [111].

The PSf membrane morphology has a pronounced effect on the gas separation mechanism and efficiency, which is mainly based on two influential configurations: finger-like or sponge-like pore structure. Yousef *et al.* [112] aimed to obtain an insight into the role of these structures on gas transport properties in PSf membranes prepared by phase inversion at two different thicknesses *i.e.* 100 μm for sponge-like and 200 μm finger-like morphologies respectively. All the key features including pore architecture, morphology, porosity percentage and surface functional groups were determined along with the crystallinity and mechanical strength of the as-developed adsorbent. Gas permeation tests were performed for CO_2, N_2, H_2 and CH_4 at up to 60 ºC under fractionally diverse pressures. This finger-like PSf membrane has a smaller pore size, higher porosity, better mechanical strength and thermal stability as well as pressure capacity than the sponge-like one. Moreover, compared to the pure polyurethane membrane it also exhibited superior gas permeability and selectivity, which was particularly high in the case of H_2/CH_4, H_2/N_2 and H_2/CO_2 making this a potential candidate for separation applications.

The compromise between selectivity and permeability in polymeric membranes has prompted ongoing efforts to fabricate mixed matrix membranes (MMMs) to boost CO_2 capture efficiency. Thus, Suhail *et al.* [113] developed mesoporous MCM-41 silica treated with pyrazole, which was used as a nano-filler in MMMs to develop effective gas separation membranes. The performance of the membrane was significantly improved by the addition of MCM-41 nano-filler at different loadings (10, 20 and 30% wt.%). The highest loading was reported to be able to achieve up to a 79% increase in permeability and significant improvements for CO_2/CH_4 and CO_2/N_2 selectivity compared to pure PSf. The characterization revealed that pyrazole functionalization fortified the polymer-particle interaction and had a superior effect on thermal stability while improving the glass transition temperature and activation energy of gas permeation. In regards to both permeability and selectivity, the MCM-41 MMMs containing pyrazole-derived ionic liquid (IL) were better than those prepared with pure PSf membranes, especially at highest loading which exhibited promising for practical applications in CO_2 separation industries. The enhanced performance is due to the porous structure and presence of functional groups which show preferential interaction with CO_2 of modified mesoporous silica [113].

A new membrane based on the PSf polymer matrix with polyphenylene sulfide (PPs) filler has been developed for gas separation application especially H_2/CH_4 and CO_2/CH_4 mixtures. Different PPs loadings (1, 5 and 10% w/w) were also studied, exhibiting that a higher concentration of inclusions produced better gas permeability. The CO_2 permeability improved by as much as 376.19% and the H_2 increased by 191.25%, while CH_4 did not exceed the pre-addition of PPs value. Moreover, these membranes were further coated with polydimethylsiloxane (PDMS) to enhance gas selectivity and the resultant PDMS-coated membrane demonstrated a 255.06% improvement in CO_2/CH_4 and by 179.44% for H_2/CH_4 separation performance relative to uncoated. Both structures as well the homogeneous distribution of PPs have been confirmed by Junaidi *et al.* [114] using several techniques such as FTIR, XRD or SEM. These results demonstrate the promise of sulfide-based organic materials for greatly improving gas separation in membranes.

Mohamed *et al.* [115] employed PSf membranes supported by non-woven carbon fabric (CF) using phase inversion in the preparation of sponge pore structure and finger pore structures adjusting the thickness of PSf during SP/FP fabrication. In this work, the fundamental properties of these PSf/CF membranes and their gas transport behaviour in terms of permeability and selectivity were investigated. The morphological analysis revealed that both membranes had a strong adhesive structure of an asymmetric polymeric matrix layer over a thick porous sublayer. Compared to the sponge pore structure, the finger pore-structured dense layer exhibited smaller pore sizes and higher porosity; the roughness was increased whereas thermal stability and rigidity were improved. Nonetheless, gas permeation results demonstrated that sponge pore-structured PSf/CF membranes gave superior overall gas permeability compared with. In addition, sponge pore membranes provided substantially better gas separation selectivity of 2.3 for H_2/CH_4 and 3.5 for H_2/CO_2 and H_2/N_2 as well as the enhancement in gas selectivity up to 27%. Therefore, these results indicate that the CF-supported PSf membranes containing sponge pore structures are very attractive for hydrogen purification with reduced emissions and substantially improved durability at a significantly lower cost compared to chemical techniques commonly used.

Imtiaz *et al.* [116] fabricated polysulfone braid-reinforced hollow fiber (PSf-BRHF) membranes with polyethylene terephthalate (PET) as a braiding through dip coating and drying technique to overcome the low mechanical strength of self-supported HFM. Because of this, different coating layers with varying PSf concentrations (15 wt.%, 18 wt.% and 21wt.%) were investigated. The characterization including SEM, TGA and DSC gas separation and mechanical strength confirmed that higher polymer concentrations as well at the increased number of coating layers lead to denser structures containing thick separation layers. The gas separation performance of the 21 wt.% PSf membrane, tested up to 400 ºC, was superior to the others when it came to CO_2/CH_4 selectivity as high as 1.83. BRHF exhibited a tensile strength of 68.2 MPa, significantly greater than that of the traditional self-supported PSf hollow fiber membranes. Research indicates that BRHF membranes provide significant potential for natural gas purification, with optimal performance dependent upon the polymer concentration or the number of coating layers applied.

The mixed matrix membranes (MMMs) were developed by incorporating $MgNiO_2$ nanoparticles into a PSf matrix, leading to the generation of nanoscale finger-like voids and enhanced gas diffusion, selective permeation and membrane stability [117]. The membrane with a loading of 100 mg of $MgNiO_2$ confirmed a major enhancement in permeability and selectivity as permeance values of 56.9 H_2, 16.3 CH_4 and 15 GPU CO_2 and selectivity values of 3.5 for H_2/CH_4 and 3.8 for H_2/CO_2. Increased permeability and selectivity attributed to the reduction in mass transfer resistance by enhanced finger-like voids. The PSf/$MgNiO_2$ MMMs, especially those having low nanoparticle contents, showed promising potential for gas separation applications. Moreover, the results of this work recommend that MMMs can solve the balance between permeability and selectivity and pave the way for sustainable, energy-efficient gas separations in industrial applications.

Conclusions and future prospects

Polysulfone (PSf) materials have shown remarkable gas-separation performance based on a balance of thermal stability, mechanical strength and selective permeability characteristics. They are seen as the answer because of their superior performance characteristics in feed gas purifying which includes gases such as carbon dioxide, nitrogen and methane; ideal for use across various industries. The future trends in polymer engineering such as the emerging mixed matrix membranes and functionalized fillers would likely boost the efficiency and selectivity of polysulfone-based membranes. Additional research is needed to optimize modification procedures further and search by more cost-efficient or greener processes. In general, it is concluded that polysulfone retains a material that plays an important role in achieving efficient gas separation technology and also assists in the welfare of energy and environmental conservation.

The increasing demand for energy-efficient and sustainable gas separation methods suggests that the future of polysulfones and related polymer composites is bright. Continued research and development in this field is likely to propel future innovations for membrane materials and assist the industry in meeting new criteria as needs across various industries shift. Significant advances are probably going to involve the enhancement of permeability and selectivity by the incorporation of efficiently modified fillers into mixed matrix membranes (MMMs). Membranes are expected to exhibit improved gas selectivity and anti-plasticization properties after undergoing selective manufacture and targeted functionalization to alter their surface. This, in turn, would improve their capacity to carry out complete separation.

Furthermore, by developing new polysulfone derivatives and block copolymers, it may be possible to tailor gas separation characteristics to satisfy certain industrial demands. The ability of PSf-based membranes to interact with hybrid separation systems and flexible fabrication techniques has the potential to greatly improve their performance, according to several technological breakthroughs. The focus on sustainability is anticipated to grow, with efforts towards developing biodegradable alternatives and recyclable membranes. The energy sector, in particular the CO_2 capture and hydrogen purification industries, will benefit from polysulfone membranes as a result of application-specific advancements in technology. Ultimately, the computational methods will offer a vital resource to enhance decision making in the sensible design of materials and separations. In general, polysulfone-based polymers are expected to continue playing a significant role in the advancement of gas separation technologies, tackling present and upcoming obstacles.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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