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Polyurethane Membranes for Gas Separation

7.1 Introduction

Gas separation is one of the main processes in gas treatment plants in order to purify the gas streams or to recover useful gases. [1-4]. Sipek *et al*. [5] reviewed polymeric membranes as effective materials for separation of gases and vapors. A variety of glassy and rubbery polymers have been explored as membrane materials for separations of gaseous streams. Recently, Bernardo *et al*. [6] has also explored industrial applications and process intensification options for membrane gas separations. Membrane separation systems, being simpler in operation and maintenance, reliable, compact, efficient, are being widely used as an alternative to other cumbersome techniques such as absorption, adsorption or cryogenic distillation. Polymeric membranes for gas separation are widely used in diverse areas like carbon dioxide recovery, helium gas removal in natural gas purification, hydrogen recovery in ammonia plant purge streams, oxygen and nitrogen separations, CO_2 recovery from biogas, oxygen upgrading from air, etc. [7-9].

Polyurethanes (PU) are a versatile category of polymers possessing good physical and tensile strength, chemical resistance, bio-compatibility and mechanical properties. These properties make polyurethanes promising candidates for membrane separation. To underline the importance of polyurethane membranes for separation processes, a large number of reviews have been generated exploring the synthesis [10-12], versatility [13], and applications of polyurethanes as rigid foams [14], in scaffolds [15,16], in pharmacy [17], in composites [18], for separation applications in the form of foam sorbents [19], in medicine for bio-stability and carcinogenicity [20], for drug delivery [21], for cancer therapy [22], in spine surgery [23], for water purification [24], among others [25-27]. Polyurethanes consist of hard (glassy) and soft (elastomeric) segments [28]. The hard segments act as physical crosslinks as well as fillers and are in an amorphous glassy or crystalline state. On the other hand, the soft segments are rubbery which provide the polyurethanes both flexibility as well as elasticity. Polyurethanes are generally synthesized by the

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reaction of polyfunctional isocyanates with polyols. By variation in reagents' molecular chain length, chemical nature and functionalities, a wide range of linear or cross-linked polyurethanes with different physiochemical properties can be obtained. Accordingly, polyurethane can vary in terms of chain length, free volume, density of polar groups, etc. Thus, various polyurethane grades though have the same chemical urethane group, however, behave differently depending on the reactants selected.

The soft segments in polyurethanes are generally made of polyether. By chain extending a terminal diisocyanate with a low molecular weight diol or diamine, the hard segment is usually prepared. Occasionally, polyurethanes undergo phase separation because of the hard and soft segment incompatibility. The intermolecular hydrogen bonding interactions between hard segments is the major reason for domain formation. A number of characterization techniques like dynamic mechanical analysis [29-31], thermal analysis [32-37], infrared spectroscopy [35-40] and scattering techniques [41] have been used for the study of polyurethanes morphology and hydrogen bonding. Phase separation into hard and soft segment domains is possible due to their type and process parameters used [31,42,43]. Howarth *et al.* [44] has also reviewed the various synthesis techniques of polyurethanes and suggested some modifications for the future. Overall, with different chemical characteristics and microstructures, polyurethanes are of high potential in gas separation [45]. Polyurethanes can behave as thermoplastic and thermosetting materials depending upon the chemical and morphological fabrication. Recently, George *et al.* [46] reviewed the polymer membranes for their acid gas separation applications including polyurethanes. For instance, Figure 7.1 also summarizes the permeability of various membranes for hydrogen sulfide, H_2S. As can be seen that there is still a large degree of advancement needed to generate high permeability PU membranes to match existing membrane systems.

In this review, various literature studies specifically reporting the developments in the synthesis and structure-property correlations of polyurethane membranes for specific applications as gas separation materials have been reviewed.

7.2 Theory of Membrane Gas Separation

In membrane separation performance, the essential characterizing features are the permeability coefficient, P_X, and the selectivity $\alpha_{A/B} = P_A/P_B$, where P_A is the more permeable gas's permeability while P_B is that of the lesser permeable gas [47]. The solution-diffusion phenomenon describes the gas transport
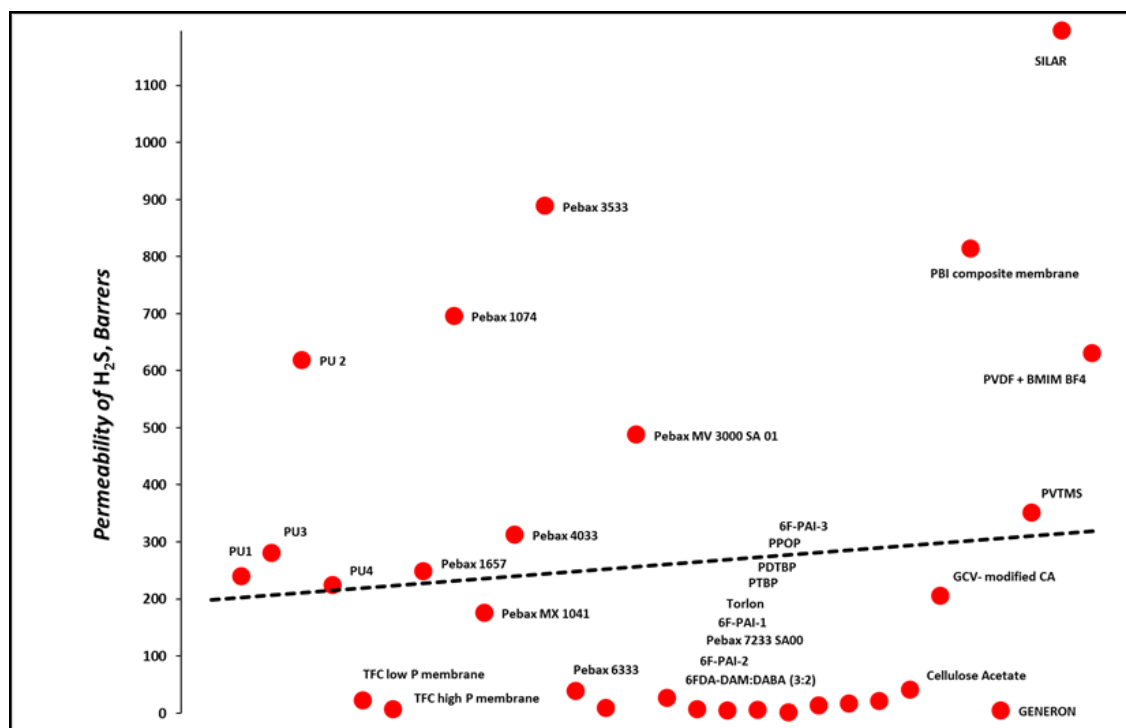
Figure 7.1 H_2S permeability of various membranes. Reproduced from Reference 46 with permission from Elsevier.

behavior of polymeric membranes. P_X is the contributed result of solubility and diffusivity through the membranes. Both solubility and diffusivity are polymer and penetrant dependent. Apart from polymer structure, a number of other parameters are responsible for its gas transport properties. The open volume available between polymer chains through which gas penetrant can pass through is an important parameter. Altering the polymer structure changes the T_g and the free volume which in turn can significantly influence the solubility and diffusivity. As the polymer chain packing efficiency increases, the free volume decreases thereby decreasing the permeability. The increasing penetrant size of gas molecules decreases the diffusion coefficient. Solubility is related to the condensability of the penetrant. The gas and vapor transport is strongly influenced by prevailing pressure and temperature conditions. According to the dual-mode sorption in glassy polymers and Henry's law in rubbery polymers, solubility increases with increase in pressure, while the changes in temperature have a reverse effect [48]. Many research studies have reported the gas permeation behavior through polyurethane membranes and established relationships between diffusion coefficient and the free volume using William-Landel-Ferry theory [49-51]. Schneider *et al.* [52] also observed that the changed glass transition temperature of polyurethanes due to

variation in soft segment contents does not impact the gas and vapor permeation behavior [52].

7.3 Ideal Membrane Characteristics

As mentioned earlier, in polymeric membranes, the permeability can be evaluated based on diffusivity and solubility of the permeant into the polymer. Diffusivity is a kinetic term which is a function of the permeant molecules mobility inside the polymer. It depends on the free volume and mobile chain length of the polymer as well as the molecular diameter of the permeant. Solubility shows the affinity between the polymer and the permeant and is a thermodynamic term. Gas transport through membranes is strongly influenced by the polymer's state, i.e., glassy or rubbery. Generally, the gas sorption process in rubbery polymers, being in equilibrium state, $(T>T_g)$ is simpler than that of glassy polymers $(T<T_g)$ [53-55].

The selectivity, permeability and life-time are the evaluating parameters for polymeric membrane efficiency [56]. The extent of the recovery of the separation process is directly impacted by the selectivity and indirectly by the feed gas flow requirements and the total membrane area. The permeability directly affects the amount of membrane requirement, while the membrane durability affects the maintenance costs. For making membrane-based separations economical than other conservative processes, the polymeric membrane materials should have both high permeability and selectivity [57,58]. The efficiency and performance of the membrane systems also relies on the membrane configurations and modules, irrespective of the inherent properties of the polymeric material. An integration of all these features is important for generating a commercially viable product. High gas fluxes are characteristics of thin layers because of which packing of large membrane areas per unit volume can be achieved. The higher the degree of crosslinking in the membranes, the lower will be the permeability as the gas diffusion coefficients are much lower [59].

7.4 Influence of Polyurethane Structure on Permeability and Selectivity

7.4.1 Influence of Hard and Soft Segments

The majority of the permeability data so far for gas separation via polyurethane membranes are below Robeson's upper bound limit for gas pairs (CO_2/CH_4) and (O_2/N_2) [60]. There exists a tradeoff between the permeability and selectivity and a large number of studies have been carried out to over-

come permeability-selectivity tradeoff relationship [61-63]. In polyurethanes, the gas permeation mainly occurs through the soft segments, while the hard segment act as physical crosslinks or impermeable filler in rubbery soft segment phase. An increase in the gas separation performance of polyurethane membranes has been a challenging task. Attempts have been made to enhance the permeability and selectivity of the membranes by optimizing the hard segment content [51]. Few of this include, studying the dependence on hard and soft segments in polyurethane membranes for gas permeability behavior [64], dependence on polymerization methods [65], using metal chelated polyurethane membranes [66-68], etc. Attempts to enhance the performance have also been made through the addition of amine and carboxyl functionalities [69] including the use of PDMS [70-72], epoxidation of hydroxyl terminated polybutadiene [73], polycarbonate–polyurethane membrane [74], etc.

Another attempt to advance the gas permeability and selectivity also included the usage of polymer blends [75-77]. In homogeneous blends, the interaction between the polymers influences the diffusion process, while in the case of heterogeneous blends, degree of heterogeneity influences the permeability significantly [78]. Different studies have reported on structure-morphology-property relationship of the thermoplastic polyurethanes by studying the synthesis, hard segment effect, hydrogen bonding effect, and properties [64,69,79-82]. Mohammadi *et al.* [83] studied the effects of temperature, pressure and stage cut on the gas transport properties through poly(ester urethane urea) for pure gases (CO_2, N_2, CH_4) as well as ternary gas mixtures of CO_2, CH_4, and H_2S. H_2S/CH_4 and CO_2/CH_4 selectivities of 43 and 16 and average permeabilities of 95 and 45 for H_2S and CO_2 were reported.

Wolinska-Grabczyk *et al.* [84] studied poly(acrylonitrile-*co*-butadiene)-based polyurethanes with varied extent of nitrile groups for CO_2 membrane gas separations. It was observed that with higher extent of polar nitrile group polymers, the permeability decreased, while the permselectivity increased. The polymer had less severe trade-off between the gas transport properties and exhibited much higher permeabilites. The polymer structure was analyzed and a relationship was established between the permeability and glass transition temperature.

Talakesh *et al.* [85] studied the polyether based polyurethanes with different hard and soft segments which were prepared by thermal phase inversion method. The soft segments were PEG (2000g/mol), PTMG (2000g/mol) and PTMG/PEG mixture, etc. It was reported that the chain mobility got restricted as the phase separation of hard and soft segments decreased. This led to a hike in the T_g values of the soft segment. By altering the physical conditions,

the gas transport properties were studied using constant pressure method. With increase in the ether group content of the polymer structure, gas permeability decreased for pure gases, while CO_2/N_2 ideal selectivity increased. A drop in CO_2 permeability from nearly 130 Barrer in polyurethane containing PTMG in soft segment to 20 barrer in the PU containing PEG in soft segment was observed. An increase from 28 to 90 in CO_2/N_2 selectivity was reported. It was observed that highest selectivity for the polyurethane membranes with 75:25 wt% ratio of PEG:PTMG. Poreba *et al.* [86] also studied nanocomposites based on polycarbonate-based polyurethane with bentonite for thermal, mechanical and gas transport properties. Hexamethylene diisocyanate and butane-1,4-diol were used for hard segment formation. High degree of phase separation was observed for polyurethane based polymer and its nanocomposites. The gas permeation properties exhibited dependence on hard segment content, though not much significant change was observed after varying the polymer structures.

Khosravi *et al.* [87] studied the effect of polyurethane membrane with different polyol, diisocyanate, and chain extender on gas permeability. More phase interaction was observed by the changing of polyol type. The hydrogen bonding, which caused the packing density of the hard segments, was increased by the phase separation of hard and soft segments. This was achieved by changing the diisocyanate groups from cyclic aliphatic to linear aliphatic ones. The phase separation of hard and soft segments was increased on changing the chain extender from a diol one to a diamine. It was observed that more condensable gases permeate more in rubbery polymers and the solubility governs the selectivity of polyurethane. As the microphase separation increased, the permeability and rubbery behavior increased along with their selectivity. Due to the higher rubbery property, polypropylene glycol based polymers exhibited maximum permeability. The high C_3H_8/CH_4 selectivity of 5.47 and permeability of 200 Barrer was reported. Wang *et al.* [88] considered a series of polyurethane films consisting of hydroxyl terminated polybutadiene/acrylonitrile as soft segment, and consisting of TDI and butanediol as hard segments. It was observed that a direct relationship existed between the gas permeability and free-volume. This relation was based on the free-volume parameters and gas diffusivity. The free-volume played a significant part in determining the gas permeability. Marques *et al.* [89] also studied the free volume in polyurethane membranes using positron annihilation spectroscopy. Further, the authors studied the gas permeability and temperature–dependent free volume correlation in polyurethane membranes. Scholten *et al.* [90] also reported electrospun fibers based on polyurethane for removing

volatile organic compounds from air. Polyurethanes had 4,4-methylene-bis(phenylisocyanate) (MDI) and aliphatic isophorone diisocyanate as hard segments, whereas butanediol and tetramethylene glycol were used to form the soft segments (Figure 7.2). The sorption performance and capacity of the generated polyurethane fibers was observed to be similar to activated carbon, thus, indicating advanced performance due to balance of hard and soft segments.
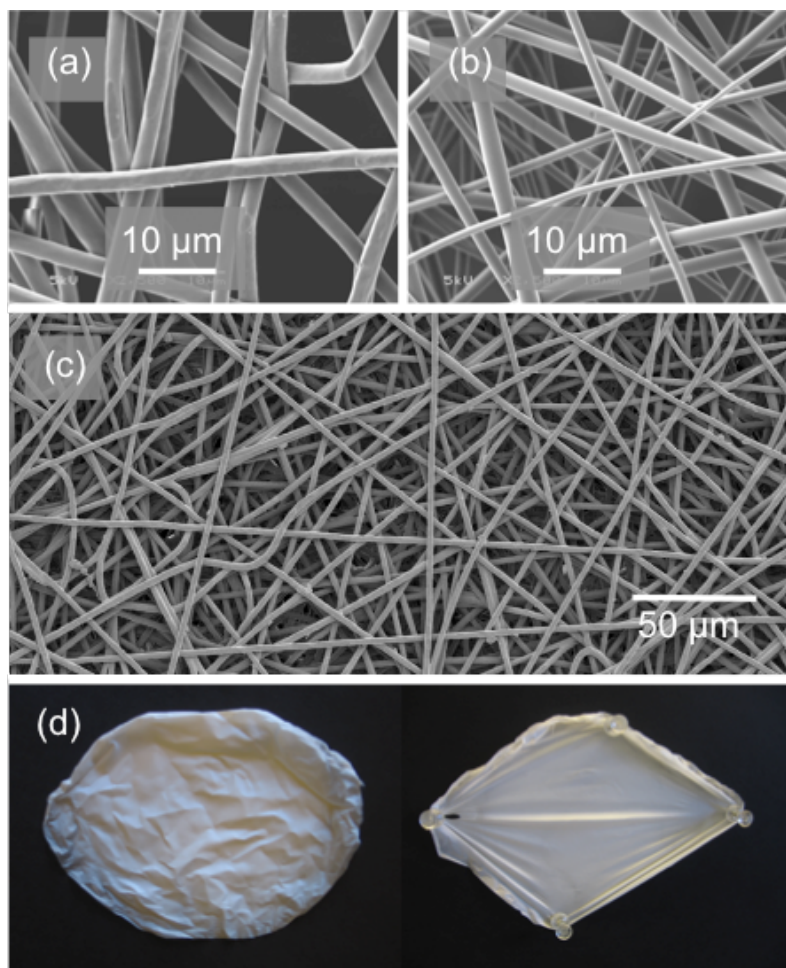

Figure 7.2 SEM images of (a) MDI-based and (b) isophorone-based non-woven fiber mats; (c) SEM image indicating the uniformity of MDI-based PU fiber diameter and mat density; (d) stretched   fiber mat exhibiting lack of tearing or breaking. Reproduced from Reference 90 with permission from American Chemical Society.

Sadeghi *et al*. [91] studied the effect on the hard and soft segment microphase separation with the changes in diisocyanate from aromatic to linear aliphatic, and CO_2/N_2 selectivity of 45 and permeability of 186 Barrer were reported. Ruaan *et al*. [92] studied the microstructure behavior of hydroxyl

terminated polybutadiene (HTPB) based polyurethane membranes. With increase in hard segment content, the oxygen and nitrogen permeability was observed to decrease. The authors suggested that the low O_2/N_2 selectivity was because of hydrogen bonding. It was indicated that the key to success for selectivity improvement is to avoid the hydrogen bond formation between the hard segments. Queiroz *et al*. [71] also studied the structural characteristics and gas permeation properties of PDMS/poly (propylene oxide) urethane urea bi-soft segment membranes. The authors reported increased CO_2, O_2, N_2 permeabilities with increase in PDMS membrane content. Lower degree of crosslinking and lower hydrogen bonding contribution between the hard segments exhibited higher permeability. Semsarzadeh *et al*. [93] investigated the effect of hard segments on the gas permeabilities for polyether based urethanes. As the hard segment content was increased, there was a decrease in the permeabilities of the gases. Gas permselectivity of the membranes with same hard segment content increased with increase in soft segment. These studies underlined the importance of optimization of hard and soft segment contents for optimum permeability and selectivity.

Galland *et al*. [94] studied the soft segment molecular weight as a major factor controlling the diffusion. It was reported the gas permeability depended on the chemical composition due to the nature of chain packing and degree of phase segregation. Huang *et al*. [95] recently studied thermoplastic polyurethane (TPU) films synthesized using layer-multiplying co-extrusion. The authors studied the morphological effect of confinement, along with gas barrier and mechanical properties. The soft TPU having the hard segment of 52% exhibited phase separation, whereas the rigid polymer having 100% hard-segment TPU exhibited amorphous structure. A multilayer structure with elasticity ratio of 100 and the viscosity ratio of 10 was genertaed. A significant reduction in oxygen permeability was observed when stretched at 75% which was due to the micro-confinement occurring during orientation. Park *et al*. [70] studied urethane urea membranes based on polysiloxane/polyether mixed soft segment for gas separation properties. The authors reported that small addition of PDMS into polyurethane matrices based on polyether increased the N_2, O_2, CO_2 permeabilities and N_2 selectivity. Also, the small addition of polyethers like PPO, PEO, PTMO and PEO-PPO-PEO inside the PDMS based polyurethane urea matrices decreased the gas permeabilities, but had no effect on the gas selectivities. In other studies, the authors studied segmented PU and PUU membranes with different soft segments for the separation of toluene and nitrogen. The poly(tetramethylene oxide) (PTMO)/PDMS mixed soft segment based polyurethane membranes exhibited good perfor-

mance for toluene separation. The authors reported toluene/N_2 selectivity of about 70-140 and permeability as high as 17,500 Barrer. Increased gas permeability was observed with an increase of polysiloxane molecular weight [70,96,97]. Wolinska-Grabczyk *et al*. [98] studied segmented polyurethanes for gas properties with variation in the soft segments. PU membranes exhibited lower permeability when synthesized with more polar or shorter macrodiol segments. The authors observed that the diffusivity and solubility of oxygen and nitrogen were in correlation with glass transition temperature of macro-diol segments. Gomes *et al*. [72] generated poly(ether siloxane urethane urea) with varying content of polysiloxane. Gas permeation properties for O_2, N_2, CO_2, CH_4, n-C_4H_{10} were analyzed. Soft segments of polysiloxane and permeation properties were observed to have strong correlation. Gnanasekaran *et al*. [99] studied the structure-transport and microstructure of mixed soft-segmented poly(urethane-imide) membranes. Polycaprolactone diol, polypropylene glycol, and bis(3-aminopropyl)-terminated polydimethylsiloxane were used as soft segments for membrane synthesis. The membranes exhibited the potential application for n-C_4H_{10}/CH_4 separation because of higher selectivity for a mixture of gases as compared to single gases. Li *et al*. [100] studied a series of polyurethane ureas synthesized using various polyether diols. The polyethers were terathane (R) 2000, terathane (R) 2900, PEG 2000, PPG 2700, and a mixture of PEG 2000 and terathane (R) 2000. The fractional free volume increased with increase in soft segment content and the increase in polyether molecular weight, which increased the gas permeability.

McBride *et al*. [51] studied linear polyurethane membranes and the relation between the aromatic content present in diisocyanates and gas diffusion. The authors observed that the motion of the soft segment chains could be controlled, as hard domains at temperatures below the T_g acted as crosslinks. As the aromatic content increased, the motion of the soft segments was further restricted because of the increased crosslinking effectiveness. On the other hand, on increasing the length of soft segment, it increased the soft segment mobility. With increase in hard segment content, the activation energy increased which further reduced the permeability of the gas. Matsunaga *et al*. [101] studied the influence of chemical structure of thermoplastic polyurethane elastomers on CO_2 and O_2 gas permeation. Both the soft segment as well hard segments' chemical structure affected the gas permeabilities. The authors reported that there was an increase in gas permeabilities with soft segment chain lengths for membranes containing poly(oxytetramethylene)glycol. The diffusion process predominated for dissolution-diffusion gas permeation process.

7.4.2 Effect of Urethane/Urea Content

Teo *et al.* [102] studied the effect of chain extenders and PEG molecular weight on urethane moiety association. Polymeric membranes prepared from PEG with molecular weight of 600 exhibited promising performance for permeation of gas pairs like CO_2/CH_4, He/CH_4, H_2/N_2 and O_2/N_2. Sadeghi *et al.* [103] reported that the content of urea influenced the gas transport characteristics of PU membranes. Polytetramethyleneglycol (PTMG) and isophorone diisocyanate (IPDI) prepolymers were used for the synthesis. Butanediol (BDO) and butanediamine (BDA) were used as chain extenders to synthesize PUU with urethane/urea linkage. With increase in the urea linkages, the hard and soft segment micro-phase separation increased. Increasing urethane content in the polymers decreased the permeability, while with increasing urea content the gas selectivity decreased. The CO_2 permeability was reported to be 128 Barrer and CO_2/N_2 selectivity of 27. Molecular dynamics studies were carried out by Amani *et al.* [104] for understanding the effect of urethane and urea contents on gas separation properties of poly(urethane–urea) membranes. The membranes were synthesized from PTMG, IPDI and designed ratios of 1,4-butanediamine to 1,4-butanediol as chain extenders. For nanostructure characterizations of the membranes, the fractional free volume, X-ray diffraction patterns, glass transition temperature, density, and radial distribution function (RDF) were calculated. The gas permeations studied were done for O_2, N_2, CO_2, CH_4, and H_2S. Phase separation of hard and soft segments increased with increasing urea contents in the membranes and, thus, the *d*-spacing and fractional free volume. The gas permeability of the membranes proportionally increased with increasing urea linkages in the polymer. These studies underlined the importance of attaining balance of urethane and urea contents for effective gas permeation performance.

7.4.3 Effect of Temperature and Pressure

With temperature variations, the permeability and diffusivity change which allows the determination of activation energy. From this, the temperature dependence of the selectivity can be calculated. In case of large difference in permeation activation energies, the selectivity is also higher for those gas pairs [105,106]. For polyurethane membranes, the temperature variation effects on the transport properties have been studied by many researchers [107,108]. For polyurethane and polyurethane blends [77,109], the observed permeability order is $CO_2 > H_2 > O_2 > CH_4 > N_2$. Kinetic diameter [105], critical

temperature and the solubility for the gas molecules have been reported to be responsible for this order. Lee *et al.* [75] studied the effect of synthesis temperature and molecular structure variation on the polymer network and gas transport properties. In specific, the gas permeability dependence of synthesis temperature, composition, aromatic content of diisocyanate, molecular weight of the polyol was analyzed. The increase in synthesis temperature and aromatic content decreased the permeability coefficient. There was an increase in tensile strength of the membrane due to the decreasing synthesis temperature and crosslinking density. The authors also studied further the effect of crosslinked state and annealing for gas transport in interpenetrating polymer network membranes.

The reduction in gas permeability due to the increase in pressure has been predicted by dual-sorption model [110], however, this has not been always observed [111,112]. In most of the glassy polymers [105,113-117], there is a decrease in permeability with pressure, when the permeating gas has high critical temperatures, like CO_2. In case of permeant gases like N_2 and O_2 with lower critical temperature, there is no influence of pressure variation on permeabilities, both for rubbery and glassy polymers [105,112,116,118-120]. However, there are some exceptions as well, which reported decrease in permeability of O_2, N_2, CH_4 with increasing pressures like poly(urethane urea) [121], polyimides [115], polyvinyl pyridine ethyl cellulose blend [114]. Madhavan *et al.* [119] studied a series of poly (dimethylsiloxane –urethane) membranes for gas transport properties. Pressure dependence on gas permeation was studied for oxygen, nitrogen and carbon dioxide gases. CO_2 permeability exhibited dependency on pressure, while O_2 and N_2 permeabilities didn't. The reported value of the O_2/N_2 permselectivity was 2.3 and CO_2/N_2 was 8.5. Thus, mixed effects of pressure have been observed on the gas transport properties of various polymers, depending on the type of permeant gas.

7.4.4 Effect of Molecular Chain Extension

Carboxyl or hydroxyl groups as organic functional groups in polyurethane membranes have direct influence on the gas transport properties of the membranes, molecular crystallinity, density and glass transition temperature. The separation coefficient for oxygen-nitrogen separation increases with increased content of functional groups, and is strongly subjective to the character of the functional group. The carboxyl group-containing poly(butylene glycol adipate) (PBA)-type polyurethane membrane was observed to exhibit

higher density, glass transition temperature, crystallinity, higher gas permeability, separation coefficient [69].

Knight and Lyman [122] studied block copolyether membranes for the effect of chemical structure and fabrication variables on gas permeation. The authors observed that for copolyether-urethane-urea, a linear relation existed between the gas permeability and propylene glycol segment molecular weight. Copolymers of polypropylene segment were more permeable than those with polyethylene segment due to the crystallizing ability of polyethylene glycol. Chain packing nature of different chain extenders affected the permeability, higher the packing, the lower was the gas permeability. The addition of salts like LiBr or urea and variations in casting solvent did not impact gas permeability. Semsarzadeh *et al*. [123] studied polyether-based polyurethanes for the effects of chain extender length on the gas permeabilities. Toluene diisocyanate with 1000 and 2000 g/mol molecular weight and polytetramethylene glycol were used for polyurethane synthesis. Different chain extenders (1,6-hexane diol, 1,4-butane diol, ethylene glycol and 1,10-decane diol) were used. The permeability and diffusivity studies were performed for N_2, O_2, CH_4, CO_2. The glass transition temperature of the polymers decreased on increasing the chain extender's length. The phase separation was more probable with increased chain extender's length. With increasing the length of the chain extenders, the permeability and diffusivity of gases increased. Selectivity of CO_2/N_2 gets changed by chain extender length, while selectivity of CO_2/CH_4 and O_2/N_2 did not show any remarkable change. Damian *et al*. [124] studied the various hybrid membrane networks based on isocyanate chemistry. The permeability coefficients and the morphology depended upon the soft segment's polarity and chain length along with the composition of the networks.

7.4.5 Effect of Polymer Blending

Polymer blending is an attractive approach for enhancing the performance of polymeric membranes as it is both time and cost effective method for tuning the properties. In recent years, a variety of polymer blends have been explored for gas separation membranes. Mannaan *et al*. [125] recently reviewed polymer blend membranes for permeability, selectivity and phase behavior. For the enhancement of the transport properties, the morphology of the phase separated polymer blends was reported to play a major role. The fundamentals of polymer blends in transport processes (like gas barrier and separation) has also been discussed by Robeson *et al*. [126]. Kim *et al*. [127] studied the

blend membranes of polyurethane with polyetherimides and poly (amide-imide) for CO_2 separations. As the blend ratio was increased, there was a decrease in gas permeability. The selectivity of CO_2/N_2 was improved with reduction in polyurethane content. The volume fraction of the dispersion component is an important factor to be taken care of for gas separation properties [127]. Patricio studied the gas transport behavior of gases such as H_2, N_2, O_2, CH_4, and CO_2 using polyurethane and PU/PMMA blend membranes [77]. In correlation with the decrease in average free volume size, the blends with higher wt% PU demonstrated lower permeabilities when compared with the PU membranes. For H_2/N_2 gas pair, the selectivity increased with increase in PMMA content in blends, while for other gas pairs, no marked changes were observed. The H_2 selectivity improvement could be associated with increased rigidity of amorphous phases. Ghalei *et al*. [128] studied PU/PVAc blend membranes for permeation of O_2, N_2, CO_2 and CH_4. The membranes had higher CO_2 permeability as compared to other gases, and higher CO_2/N_2 and CO_2/CH_4 selectivity. De Sales *et al*. [109] studied the polyurethane and PMMA blend membranes for temperature and pressure dependence of gas permeabilities for CO_2, H_2, O_2, CH_4, N_2 gases. With the addition of 30 wt % PMMA, the gas permeabilities decreased approximately 55%. It was observed that CO_2 had lowest permeation activation energy value (28 kJ/mol) with variation in temperature. For low temperatures, the gas pair selectivity increased, and the selectivity was higher for gas pairs having permeation activation energy value difference of about 15 kJ/mol. For pressure variation study, it was concluded that the permeabilities for CO_2 and H_2 gases through PU and the blend membrane increased by 35% at elevated pressure. CO_2 permeability increased by around 35% at higher pressure for the polyurethane and the blend membranes. Also, the O_2/N_2 selectivity increased with pressure, while the permeability to nitrogen decreased in the case of the 30% PMMA blend. Similar to earlier study, Semsarzadeh *et al*. [129] also studied the PU-PVAc blend membranes synthesized in the presence of various pluronic copolymer contents. Blends with 5 wt% PVAc exhibited higher CO_2 permeability in comparison to the PU membrane. Domain size of the dispersed PVAc was controlled by the addition of pluronic and had a positive effect on the permeability. Saedi *et al*. [130] investigated the blend membranes of polyethersulfone/polyurethane for CO_2 and CH_4 separations. The relative affinity of CO_2, CH_4 and H_2O for PES and PU were obtained using density functional theory calculations. Gas sorption by PU, viscosity of solution and PES membrane's mechanical properties were also analyzed. The fractional free volume and *d*-spacing of casting solution decreased the membrane porosity, glass transition temperature, thermal

properties, gas sorption and plasticization. This was attributed to decreased Langmuir capacity and increased PES membrane strength at yield and elongation at yield. This resulted in the decrease of CO_2 permeability, a boost in CO_2/CH_4 selectivity and plasticization pressure of the PES membrane due to the presence of polyurethane. Also, the feed temperature affected the membrane behavior against pressure and the mixed gas composition.

7.4.6 Effect of Modifiers and Fillers

Another functional way to improve the gas transport behaviors of membranes can be improved by incorporating fillers. These fillers can be salts, metals, metal oxides, ions, inorganic silica, layered silicate, zeolites, carbon nanotube, graphene, etc. As the polymeric membranes are mixed with inorganic fillers, these membranes are thus termed as mixed matrix membranes. Incorporation of nanoporous filler particles is important breakthrough for boosting the gas separation capabilities of polymeric membranes. Out of a large variety of filler, metal organic frameworks (MOF) have become popular as a new group of nanoporous materials for enhanced membrane characteristics. Remarkable developments in gas permeability and selectivity have been reported for membranes based on MOFs. Erucar *et al*. [131] reviewed the recent developments in membranes incorporated with MOFs. The authors studied the experimental and computational methods to generate the polymer and MOF selection criteria for efficient gas separation membranes. Following sections summarize studies reporting the incorporation of polyurethane with a variety of reinforcements for generating effective gas separation performance of the membranes,

Zeolites

Zeolite incorporated nanocomposite membranes combine the advantages of both the polymer and the zeolite, thus, overcoming the individual shortcomings of the two materials [132]. Tirouni *et al*. [133] investigated polyurethane/zeolite mixed matrix membranes for the separation of C_2H_6 and C_3H_8 from CH_4. The hard and soft segment phase separation increased with the addition of butanediamine chain extender. With increase in urea groups of the polymer structure, both permeability and selectivity were observed to increase. Gas permeation data of polyurethane-zeolite 4Å membranes exhibited an increase in methane permeability and decrease in C_2H_6/CH_4 and C_3H_8/CH_4 selectivity, as the amount of Zeolite 4Å was increased up to 10 wt%. Polyure-

thane–zeolite (ZSM-5) membranes also exhibited significant improvements in selectivity and permeability of all hydrocarbons. With 20 wt% filled PU–ZSM 5 membranes, the propane permeability increased from 64.8 to 117.2 Barrer and C_3H_8/CH_4 selectivity increased from 2.6 to 3.64. Ciobanu *et al*. [134] studied the use of zeolite SAPO-5 nanocrystals for the synthesis of polyurethane composite membranes. Zeolite content was ranged from 10 to 70%. The zeolite nanocrystals were observed to act as a cross-linker for the polyurethane matrix.

Silica

A number of PU-silica based composite membranes have been reported in the literatiure. Khudyakov *et al*. [135] reviewed the status of UV-curable polyurethane nanocomposites incorporating nanosilica and organically-modified clay. A large number of studies have been reported related to the structure and characteristics of polyurethane nanocomposites formed through dark reactions as well as by UV-curing of urethane acrylate oligomers. Polyurethane nanocomposites with low loadings (less than 5%) of fillers have been reported to have dramatic property improvements [135,136].

In another study, Petrovic *et al*. [137] studied the polymerization of polypropylene glycol/hexamethylenediisocyanate/1,4-butanediol to gain insights about the gas transport properties. Tetraethoxysilane was used to prepare silica nanoparticles through sol-gel method, while the nanocomposites were synthesized by solution mixing technique. Various characterization techniques were used to confirm the desired nano-scale distribution of silica nanoparticles. Gas permeation studies of the membranes revealed the enhancement in CO/N selectivities with increasing amount of silica nanoparticles. It was also observed that the nanocomposites exhibited nearly two fold increment in the selectivity when compared with pristine polyurethanes membranes. However, the CO permeability exhibited a reduction of nearly 35% for the composite membranes while comparing against pure PU ones. Higuchi model may be used to predict the gas transport properties in polyurethane-silica membranes [138]. In this study, properties such as dielectric permeability of nanocomposite membranes were studied. Studies on the ether-based PU and ester-based PU exhibited that the amalgamation of silica nanoparticles helped the improvement of CO_2/CH_4 selectivity. By taking an account of the nanoparticles interfacial layer leading to the formation of void volumes, a model was introduced to help predicting the nanocomposite membrane performance [139].

Polycaprolactone-based polyurethane membranes were studied for the effect of the addition of silica nanoparticles [140]. The membranes were prepared using conventional methods such as solution mixing and casting. Polycaprolactone/hexamethylene diisocyanate/1,4-butanediol based polymer was produced by polymerization involving a two-step methodology. Membrane performance was predicted using modified Higuchi model to obtain a fair agreement in theoretical and experimental values. In another study, hybrid polyurethane/silica based composite membranes were prepared using tetraethoxysilane, cetyltrimethyl ammonium bromide and polyvinyl alcohol [141]. Spectroscopic techniques were used to verify the presence of silica in the polymer network and SEM for the nanoscale distribution of silica particles. It was observed that with increase in the silica content, the diffusivity of gases and CO_2 gas permeability were reduced. With silica content >10 wt%, an enhancement of CO_2/CH_4 selectivity was observed.

In another study, the transport performance of carbon dioxide and methane gases was investigated in polyesterurethane mixed matrix membranes (MMMs), in separate tests, containing different fumed silica nanoparticles [142]. Non-modified and commercially-modified silica (with octylsilane and polydimethylsiloxane) were used as fillers. The structural features were studied by various microscopic, spectroscopic and calorimetric techniques to confirm the interfaces induced in PU microphase when silica was present. Surface treatment of silica filler with long hydrophobic chains condensed the accumulation of nanoparticles and enhanced dispersion in MMMs. Regardless of silica type, both separation factor and CO_2 permeation were increased with the presence of silica nanoparticles, which was attributed to the interrupted chain packing and improved dynamic free volume. The results revealed that among silica nanoparticles, the unmodified particles with OH groups on the surface exhibited better performance for CO_2/CH_4 separation. A new model of gas permeation through PU/silica membranes was proposed considering the presence of filler aggregation in the matrix as well as free volume at the interface layer [142].

Another study revealed the gas transport of two types of polyurethane membranes which are synthesized from PCL225 and PPG polyether [143]. It was observed that by using silica content up to 2.5%, the permeability increased. However, the permeability exhibited a downward effect on increasing the silica content father. It was observed that the selectivity of propane over methane increased with the increase in the amount of silica particles. The studied membranes were the ones with 12.5% silica and the permeation tests were conducted at 2 bar pressure.

With the addition of nanofillers, the flexural properties of the polymer matrix are required to be retained. Ideally, the hybrid polymer materials are expected to exhibit enhancement in properties such as mechanical strength and polymer flexibility. Enhanced material properties are possible with more homogeneous distributions of the inorganic components leading to the formation of high performance functional membranes [144]. In another study, polyurethane (PU) based mixed matrix membranes were generated with polytetramethylene glycol and polyvinyl alcohol along with silica nanoparticles [145]. The dispersion in the nanocomposite membranes was confirmed using microscopic, spectroscopic techniques. Gas permeation studies for pure CH_4, O_2, CO_2, N_2 and He gases were performed through the composites with varying amounts of silica particles. It was observed that upon increasing the silica content, the permeability of the CO_2 gas was enhanced, while the transport properties of other gases decreased. The permeability of CO_2 increased from 68.4 to 96.7 Barrer, where the membrane contained 10 wt% of nanoparticles.

Layered Silicates

Osman *et al*. [146] studied the gas permeation properties of modified montmorillonite based nanocomposites with polyurethane adhesives. The nanocomposites were generated to act as barrier against oxygen and water vapor. Thus, their application in gas industries can be envisaged as membranes which allow permeation of hydrocarbons, but do not allow any other gases like O_2, CO_2 and water vapor to pass through. A correlation between the gas permeation and volume fraction was established. With the incorporation of small volume fractions of nanoparticles, the permeation rate of O_2 and water vapor was decreased (Figure 7.3 for oxygen permeation). A 30% reduction was observed with 3 vol% of filler, when bis(2-hydroxyethyl) hydrogenated tallow ammonium or alkylbenzyldimethylammonium ions were used for clay modification. The clay modified with dimethyl dihydrogenated tallow ammonium ions increased the O_2 permeation rate with increase in inorganic fraction. The above variation was attributed to the phase separation between the pure hydrocarbon modification and polar polyurethane. This underlined the need of generating compatibility between the filler and polymer phases in order to achieve optimum performance. Increase in oxygen permeation for dimethyl dihydrogenated tallow ammonium ions modified clay composites could still be used for O_2, water vapor separation as the membranes were impermeable to water vapor, whereas highly permeable to O_2 molecules. In a similar study, Mittal [147] also reported the gas permeation performance of

polyurethane-clay nanocomposites and underlined the impact of synthesis procedure as well as filler-matrix compatibility. As shown in Figure 7.4, the composite with Tixogel VZ, the clay surface modified with a benzyl(hydrogenated tallow alkyl)dimethyl ammonium ions, exhibited a decrease in oxygen permeation. On the other hand, the composite with Tixogel VP, the clay surface modified with bis(hydrogenated tallow alkyl)dimethyl ammonium ions, exhibited an increase in oxygen permeation as a function of filler fraction. Similar to the previous study, the water vapor permeation in both the composites was reduced as a function of filler fraction. Thus, the chemical
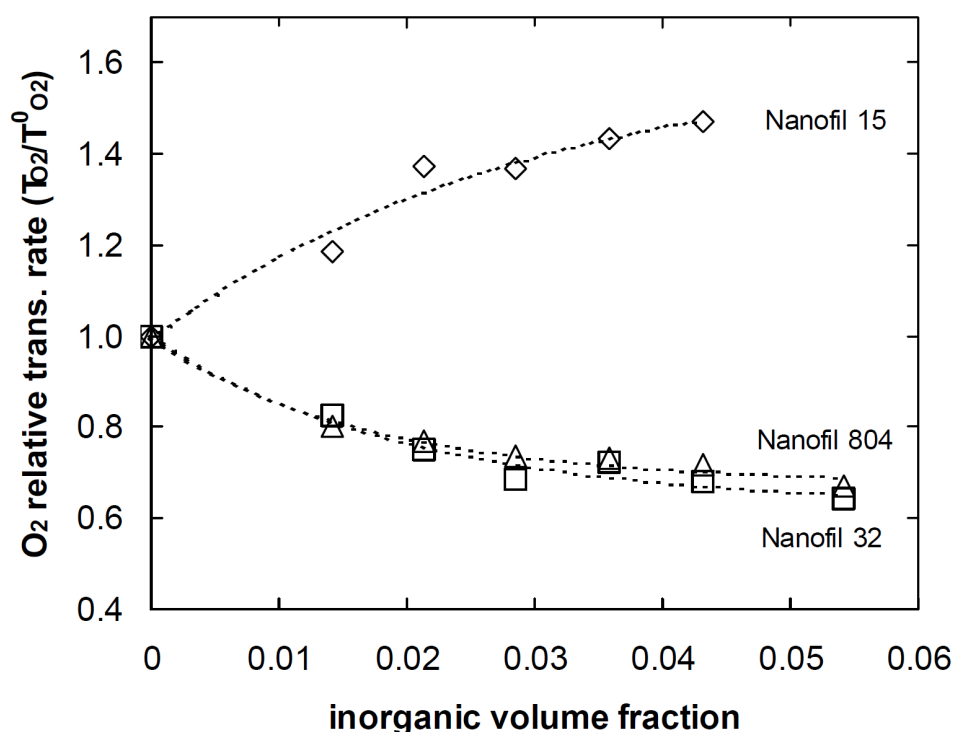

Figure 7.3 Dependence of the oxygen transmission rate through the PU-nanocomposites on the inorganic volume fraction. The dotted lines are guides for the eye. Reproduced from Reference 146 with permission from American Chemical Society.

nature of the surface coating of the fillers resulted in specific interactions with the polymer matrix, which consequently affected the nanocomposite properties. The authors also compared the oxygen permeation through polyurethane-clay nanocomposites with molecular dynamics predictions in order to gain more insights about the average aspect ratio of the filler platelets in the composites [148]. In polyurethane composites, the clay platelets were observed to be present with an average aspect ratio of 100. In addition, the good

agreement with the experimental and predicted values was retained till 3 vol% filler fraction. Afterwards, the experimental values were observed to level off.
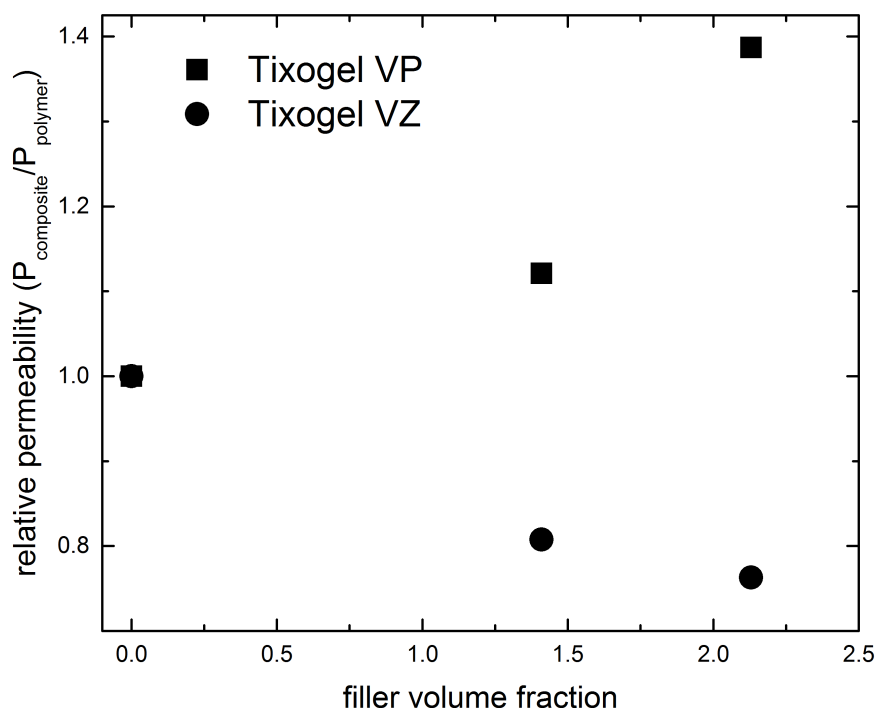

Figure 7.4 Oxygen permeation through the PU and PU nanocomposites as a function of filler volume fraction. Reproduced from reference 147 with permission from Wiley.

Also, as shown in Figure 7.5, the authors generated the relation between the reduction of oxygen permeation through the nanocomposites with filler fraction for both aligned and misaligned filler parties. The aligned filler particles were observed o be significantly effective in tuning the gas transport behavior of the nanocomposites. These studies indicated the successful development of polyurethane-clay nanocomposites with tuned reduction in water vapor permeation as well as increased or decreased O_2 permeation, based on the chosen filler system. Such systems can result in high selectivity membranes for the separation of hydrocarbons from other contaminant gases.

Dense polyurethane-based membranes containing hydrophilic clay were synthesized by Barboza *et al.* [149] and the permeability of carbon dioxide (CO_2) through the membranes was studied. Ethylene diamine was used as the chain extender, which led to the urea linkage network. The nanofiller fraction was optimized as 0.5 and 1% relative to the amount of poly(ethylene glycol).

The CO_2 permeability was observed to improve with the amount of PEG, whereas it was noticed to decrease with the amount of clay as the higher clay content contributed to the tortuous pathways for gas diffusion. A novel nano-composite was reported by Shamini and Yusoh, which consisted of Na^+ mont-morillonite which was further modified using transition metal ions such as copper (II) chloride and iron (III) chloride [150]. The presence of metal ions reportedly contributed to better dispersion of nano-filler and also reduced clay agglomeration. The gas transport properties exhibited remarkable de-crease. Polyurethane film containing 1% filler modified with iron chloride ex-hibited the permeability to decrease four fold. Iron and copper exhibited dif-ferent patterns for the reduction in permeability.
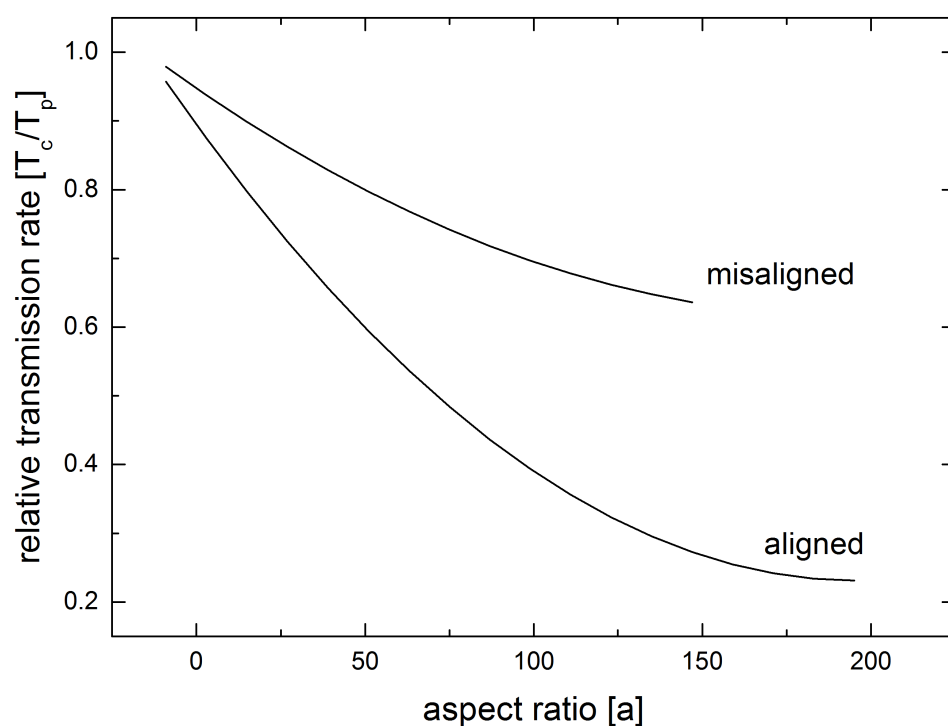

Figure 7.5 Numerical prediction of the effect of filler platelet misalignment on the gas permeation performance at 3 vol% loading. Reproduced from reference 148 with permission from Wiley.

It has to be mentioned that the reduction in permeability of different gases in the composite membranes does not indicate the reduction in the membrane performance, it only signifies the probable enhancement in the selectivity by blocking the passage of certain penetrants and possibly enhancing the perme-ation of others. In addition, the use of fillers also enhances the mechanical and

thermal properties, along with enhancing environmental stability. Most of these developed composite membranes, thus, have strong potential of application in various industries to separate gas mixtures.

Metals, Metal Oxide and Metal Ions

Ameri *et al*. [151] used alumina (Al_2O_3) at different concentrations to prepare polyurethane nanocomposites through a bulk two-step polymerization. Different chain extenders were used to complete the urethane polymer network. Alumina ensured improved O_2/N_2, CO_2/CH_4, and CO_2/N_2 selectivity, but with reduced permeability values. In another study, cobalt chelated plasma treated membranes were generated and the effect of subsequent formamide formation in the membrane matrix on the permeability properties was evaluated [152]. The chelation was obtained by treatment with cobalt(II)/formamide solution. With ethylenediamine plasma treatment, selectivity increased from 2.6 to 3.1 GPU whereas the CoCl •6HO/formamide treatment improved the value to 4.4 GPU. The enhanced O/N selectivity was attributed to the improvement in oxygen affinity achieved through chelation and size sieving effect. Chen *et al*. [153] incorporated TiO_2 nanoparticles at varying concentrations to the polymer to prepare thermo-sensitive polyurethane (TSPU). Membrane formation temperature was optimized in the study to tune the transport behaviors of the nanocomposites. It was observed that the permeability coefficients altered with different membrane formation temperatures. Increasing nano-TiO_2 concentration also favorably helped the transport phenomenon. Conventionally seen tortuous diffusion pathway based low permeation mechanism failed to explain the counter-intuitive phenomenon observed in the study. The authors suggested that the soft segment of the thermo-sensitive polyurethane packed around the TiO_2 nanoparticles, as if these were in the bulk polymer, thus, leading to the observed results.

In another study, PU membranes were synthesized through thermal phase inversion method [154] Polyol:diisocyanate:chain extender was blended at 1:2:1 molar ratio and the interactions at intramolecular level were analyzed. TiO_2 was varied up to 30 wt% and transport behaviors were studied for N_2, O2, CH_4 and CO_2 gases at varying temperatures. It was observed that an increased TiO_2 content led to a proportional rise in selectivity and a proportional fall in permeability values. Membranes of ionic polyurethane were also reported using N-methyldiethanolamine as chain extender, which was later complexed with cupric ions [155]. Different polymerization approaches such as single and double step were employed for the composite preparation. It

was observed that the incorporation of CuCl enhanced hard segment aggregation, whereas incorporation of crosslinker hindered the cluster formation by the hard segment. The soft segment aggregation helped to increase the permeability.

Carbon Nanoparticles

The formation of polyurethane nanocomposites have proven the ability to exhibit advanced performance as compared to pure polymer. In one such study, poly(ether urethane) membranes containing multi-walled carbon nanotubes (MWCNTs) were studied for improvements in mechanical strength and permeation capabilities [156]. The MWCNTs were grafted with various functional groups to obtain three types of membranes with fillers such as MWCNT-COOH, MWCNT-OH, MWCNT-IPDI. Fourier-transform infrared spectroscopy was used to confirm the successful grafting of functional groups on to the surface of the MWCNTs. Techniques like SEM, mechanical testing and thermal analysis confirmed the superior properties of MWCNT-IPDI based membranes (Figure 7.6). Despite the development towards the generation of strong, dura-
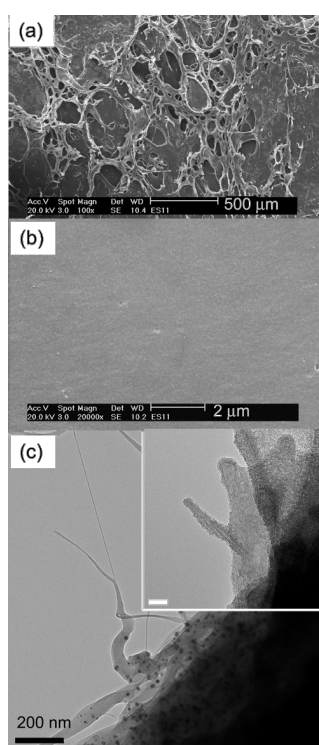

Figure 7.6 SEM and TEM images of PU nanocomposite membrane obtained by the electro spinning technique. Reproduced from Reference 156 with the permission from American Chemical Society.

ble, and cost-efficient carbon nanoparticles based polymer membranes, there is a need for the evolution of membrane materials with high gas transport properties [157,158].

Graphene

A large number of studies has reported the generation of polyurethane nano-composites by incorporating graphene/graphene oxide/modified or function-alized graphene [158-173]. Most of the studies have confirmed these nano-composites to have significantly superior thermal and mechanical properties. However, only a few studies report the gas permeation data for PU-graphene nanocomposites. Kim *et al.* [174] reported 90% decrease in nitrogen permeation with 3 wt% isocyanate treated graphene oxide filled thermoplastic polyurethanes. Figure 7.7 shows the mechanism of dispersion of functionalized
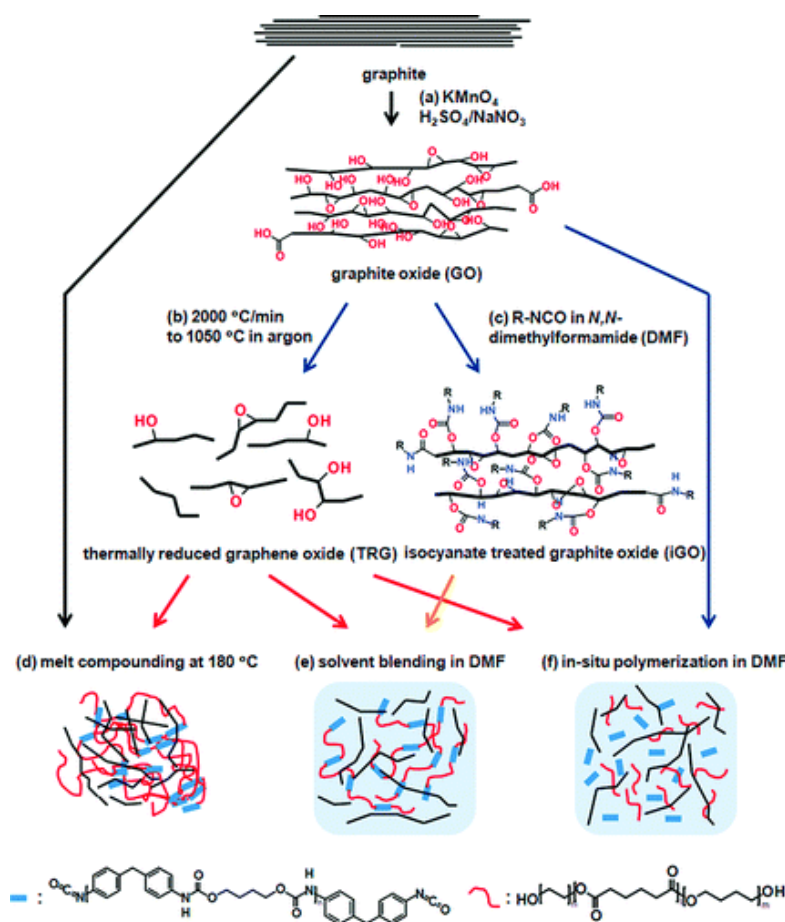

Figure 7.7 Scheme showing the mechanism of functionalized graphene dispersed in polyurethane. Reproduced from Reference 174 with the permission from American Chemical Society.

graphene in polyurethane. In another study, Thermoplastic composite films of polyurethane containing hexadecyl-functionalized low-defect graphene nano-ribbons were studied by Xiang *et al.* [175] for improved gas barrier properties. A decrease in nitrogen gas diffusivity by 3 orders of magnitude was observed with only 0.5 wt% of filler. The films were reported to have potential applications in food packaging and light weight gas storage containers. Figure 7.8 also shows the nitrogen pressure drop across the PU membranes and PU composite membranes. The composite with 0.5 wt% filler exhibited strong resistance against nitrogen for a longer period of time, indicating its barrier towards nitrogen permeation. Kaveh *et al.* [176] reported excellent gas barrier properties with an 80% decrease in permeability of Helium for 1 % graphene oxide incorporated thermoplastic polyurethane films. Thus, until now, the graphene nanocomposites have been largely developed to generate potential candidates for gas barrier properties, however, optimization of the graphene based composites for enhanced permeation is still needed. However, as mentioned earlier, decrease permeability of a certain permeant still opens the potential for these membranes to be selective towards the separation of certain gas mixtures.

7.5 Other Natural Gas Specific Applications

Polyether-polyurethane interactions as well as water vapor and methane separation selectivity were studied by Di Landro *et al.* [177]. Water absorption was shown to be higher for urethane rich polymers. Water vapor permeability was 10^3-10^4 times more than methane as well as other permeant gases. This makes these materials a potential membrane material for natural gas dehydration [9,177]. High H_2S/CH_4 selectivities of poly(ether urethane) and poly(ether urethane urea) membranes were reported by Chatterjee *et al.* [178]. The authors reported polymer PU4 as a favorable membrane material for H_2S separation from CO_2 and CH_4 mixtures. H_2S/CH_4 selectivity was reported to be greater than 100 at 20 °C in the pressure range from 4-13.6 atm. Other studies have also reported high permeability, permselectivity, durability for acid gas separtiob from natural gas and carbon dioxide removal from synthesis gas for polyether-urethane or polyether-urea block copolymers [179,180].

Ponangi *et al.* [181] studied for the split-up of volatile organic compounds from nitrogen either in dry or in humidified form using PU membranes. The membranes were examined for the vapor phase separation of a variety of gases such as benzene, hexane, p-xylene, and benzene/toluene/xylene mixtures
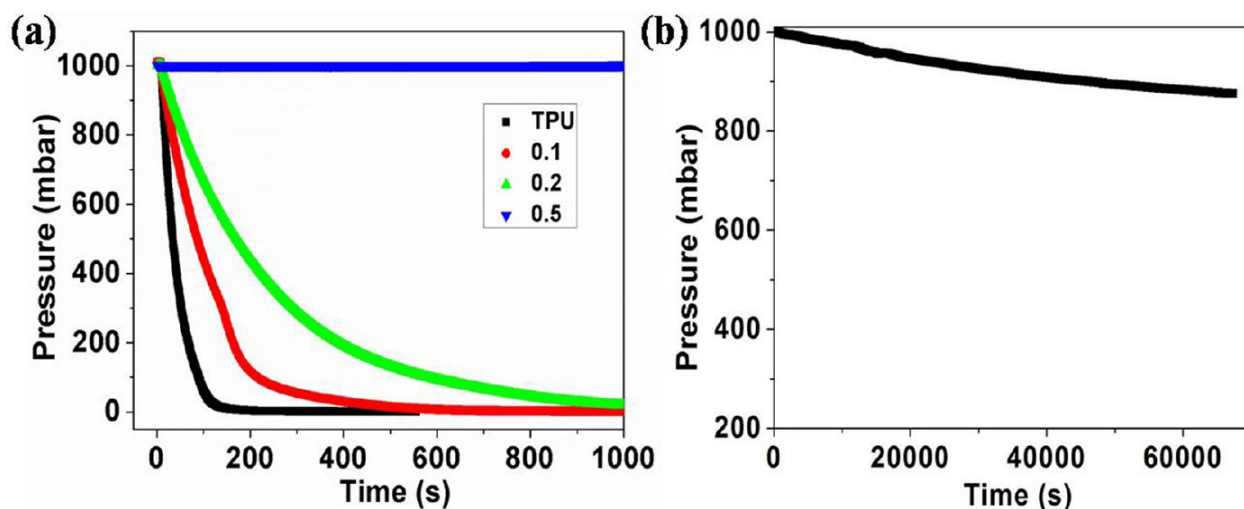
Figure 7.8 (a) Nitrogen pressure drop through PU and PU composite films; (b) nitrogen pressure drop through the composite wit 0.5 wt% filler over a longer period of time. Reproduced from Reference 175 with permission from American Chemical Society.

from nitrogen. The selectivities of organic/dry N_2 ranged from 30-210 and pressure normalized permeabilities of around $1.25x$ 10^{-3} cm³ (STP)/(cm² s cmHg). The nitrogen permeability was increased with swelling of the polyether membranes, but the organic/N_2 selectivity was lowered. Water permeability was observed to be low and did not depend on the organic feed component. The authors also further studied the free volume in polyurethane membranes for organic vapor diffusion [182].

7.6 Conclusion

In this review, various advancements for enhancing the applications of polyurethane membranes for gas separation have been explored. Polyurethanes represent useful class of materials with properties such as mechanical strength, dimensional stability, thermal resistance, resistance towards chemicals and tunable gas transport behavior. Various modifications in the molecular microstructure of polyurethanes have been achieved in order to enhance the permeability as well as selectivity of various gases through these materials. These modifications include optimization of soft and hard segments, tuning of polarity, blending with other polymers, adjusting urea urethane interactions, incorporation of fillers, use of a wide variety of chain extenders and cross-linkers, etc. It is evident that the tunability of gas permeability as well as selectivity in polyurethane membranes would further enhance the industrial application of these materials for gas separation processes.

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