REVIEW ARTICLE

Latest development on the membrane formation for gas separation

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Abstract

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The first scientific observation related to gas separation was encountered by J.K Mitchell in 1831. However, the most remarkable and influential contribution to membrane gas separation technology was the systematic study by Thomas Graham in 1860. However only in 1979, membrane based gas separation technology was available and recognized as one of the most recent and advanced unit operations for gas separation processes. Membrane is fabricated by various methods and the parameters involved to a certain extent are very complicated. The phase inversion technique that is normally employed to produce membranes are dry/wet, wet, dry and thermal induced phase separation. Other techniques used to produce membrane are also reviewed. This paper reports the latest development in membrane formation for gas separation. The route to produce defect-free and ultrathin-skinned asymmetric membrane is also presented that represents the cutting edge technology in membrane gas separation process.

Key words : membrane formation, gas separation, phase inversion, asymmetric membrane, defect-free

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Membrane separation processes has become one of the emerging technologies, which have undergone a rapid growth during the past few decades. A membrane is defined as a selective barrier between two fluid phases (Sirkar and Ho, 1992, Mark and Menges, 1985 and Pandey and Chauhan, 2001). Gas separation became a major industrial application of membrane technology only during the past 15 years, but the study of gas separation actually began long before that period (Baker, 2000). Gas separation processes require a membrane with high permeability and selectivity that is the asymmetric membrane (Lin *et al.*, 1996). Asymmetric membranes that are suitable for gas separation should have thin and dense skin layers supported by thick porous sublayers (Wang *et al.*, 1996, Pinnau *et al.*, 1990 and Peinemann and Lauenburg, 1988). Membrane structures can be classified according to the cross section microstructure as shown in Figure 1.

There are six major membrane processes, which are widely used, in industrial application. They are microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation and pervaporation. Gas separation is known as a developing process and most gas separation membranes are of the solution-diffusion mechanism type. The key membrane performance variables are selectivity, permeability and durability. For solution-diffusion membranes, permeability is defined as the product of the solubility and diffusivity. Traditionally, there has been a trade-off between selectivity and permeability; high selectivity membranes tend to exhibits less permeability and vice versa.

Gas membranes are now widely used in variety of application, as shown in Table 1. They

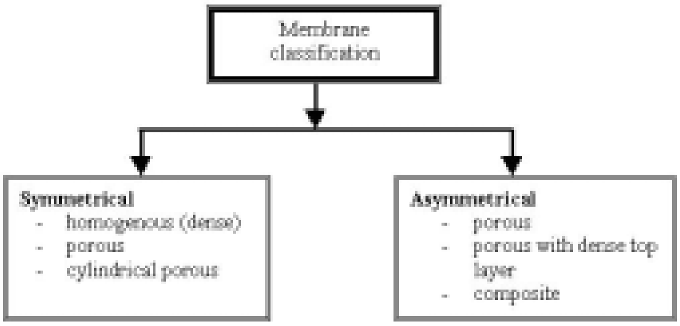

Figure 1. Membrane classifications

Table 1. Gas separation membrane application

Common gas separation	Application
O_2/N_2	Oxygen enrichment, inert gas generation
H_2/Hydrocarbons	Refinery hydrogen recovery
H_2/N_2	Ammonia Purge gas
H_2/CO	Syngas ratio adjustment
CO_2/ Hydrocarbons	Acid gas treatment, landfill gas upgrading
H_2O/ Hydrocarbons	Natural gas dehydration
H_2S/ Hydrocarbons	Sour gas treating
He/ Hydrocarbons	Helium separation
He/N_2	Helium recovery
Hydrocarbons/Air	Hydrocarbons recovery, pollution control
H_2O/Air	Air dehumidification

offer low capital cost, low energy con-sumption, ease of operation, cost effectiveness even at low gas volumes and good weight and space efficiency. Membrane processes for gas separation applications were commercially introduced in the early 1970's (Lokhandwala *et al.*, 1995).

1. The mechanism of membrane formation by phase inversion separation

Membrane gas separation by polymer membrane is a proven technology and has been found in a wide range of industrial applications. Membranes can be prepared by phase inversion techniques and can be categorized into four different techniques as shown in Figure 2.

In the air casting technique process, the polymer is dissolved in a mixture of a volatile solvent and less volatile nonsolvent. During the evaporation of the solvent, the solubility of the polymer decreases and then phase separation take place (Van, 1996).

In the precipitation from the vapor phase process, phase separation of the polymer solution is induced by penetration of nonsolvent vapor in the solution. Thermal induced phase separation (TIPS) technique is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying. In the immersion precipitation case, a polymer is cast as a thin film on a support or extruded through a die, and is subsequently immersed in a nonsolvent bath. Precipitation can occur because of the good solvent in the polymer solution is exchanged with nonsolvent in the coagulation bath. The differences between the four techniques originate from differences in the desolvation mechanisms (Van *et al.*, 1996).

Among these techniques, immersion precipitation is widely used to produce commercial gas separation membranes and other membrane based separation (Van *et al.*, 1996). Immersion precipitation technique can be further divided into three categories namely wet, dry and dry/wet phase inversion technique as shown in Figure 3.

2. Improving the separation characteristics

One of the major problems confronting the use of membrane-based gas separation processes in a wide range of applications is the lack of membranes with high flux and high selectivity. During fabrication, membrane formation process plays an important role and certain factors need proper attention in order to produce a good gas separation membrane. Currently, gas separation membranes technologies are challenged to maintain their favorable economics while improving their gas selectivity, flux and durability. The improved membranes would be attractive in large

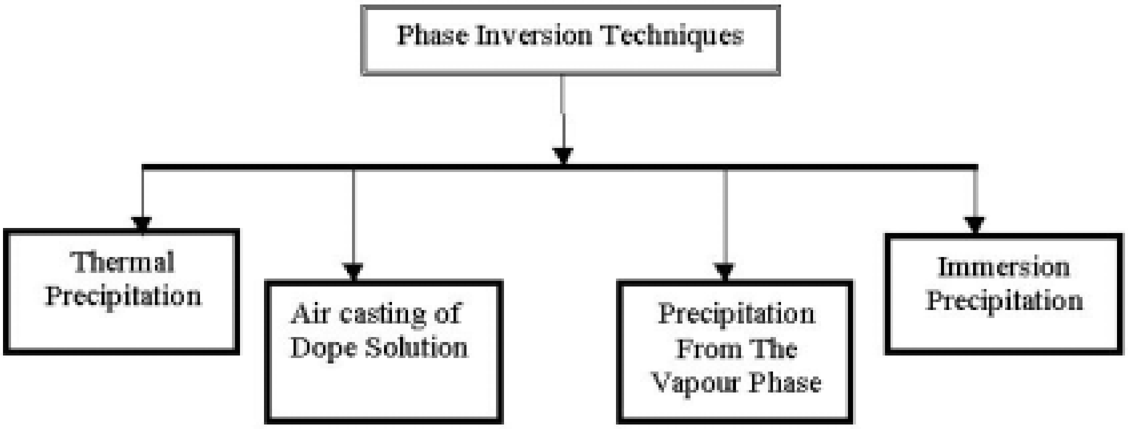

Figure 2. Phase inversion techniques

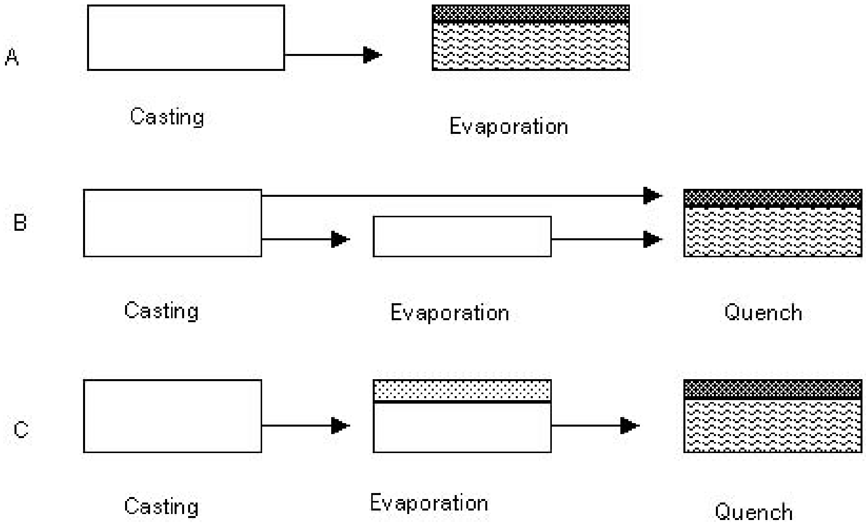

Figure 3. Schematic representations of immersion precipitation phase inversion processes: (A) dry, (B) wet, (C) dry/wet

potential markets such as CO_2/CH_4, hydrocarbon/H_2 and olefin/paraffin separations (Koenhen *et al.*, 1997 and Kawakami *et al.*, 1996). One potential route is through the use of inorganic membranes, which have demonstrated improvement in permeation property, and durability. However, the formation of inorganic materials is presently estimated at 1-3 orders of magnitude greater than polymeric materials (Kawakami *et al.*, 1996).

As a result, polymeric based materials such as mixed-matrix materials, and cross-linkable polymers might address the needs for improvement in selectivity and durability in next generation membranes (Kawakami *et al.*, 1996). All the attractive alternatives for advanced membranes require the ability to form essentially defect-free selective skins in order to achieve the full benefit from the intrinsically improved membrane materials are discussed in this paper.

3. Development of new polymer- zeolite-mixed matrix membranes

Membranes used for gas separation at the moment are of solution-diffusion type polymeric membranes. One way of improving the separation characteristics of solution-diffusion type polymeric membranes is to incorporate specific adsorbent such as zeolites into the polymeric matrix. A mixed-matrix material with inorganic zeolites or carbon molecular sieves with cause excellent gas separation properties embedded into the matrix of a prospective polymer (Carruthers, 2001).

In addition, those mixed matrix materials have the potential to provide membranes with higher permselectivity and equivalent productivity compared to existing membrane materials. It had been proven by Mahajan *et al.*, that successful mixed matrix materials can be formed using relatively low glass transition (T_g) polymers that have a favorable interaction with the sieves. One of the immediate challenges facing membrane material design is achieving higher permselectivity with equal or greater productivity compared to existing materials. Molecular sieving membrane materials, such as zeolites, are capable of overcoming this challenge, but not in an economical way (Mahajan *et al*, 2002).

Synthetic zeolite incorporation is reported to enhance the separation characteristics of rubbery polymers. The majority of the work on zeolite filled polymeric membranes utilises synthetic zeolites, such as zeolite A, X, Y and silicalite. However, there have not been many studies reporting the use of natural zeolites.

The effect of incorporating filler into the polymeric matrix of silicone rubber membranes on their gas separation properties was investigated in case of a natural zeolite, clinoptilolite. It is also expected that this study will help to determine the role of zeolite during gas transport through the membrane and for better understanding of the transport mechanism.

Recent studies have shown that zeolites may be useful in enhancing the permeability and selectivity of polymeric materials when the correct zeolite–polymer pair is selected. Tantekin-Ersolmaz *et al.* reported that the permeabilities of the silicalite–PDMS mixed-matrix membranes increase with the increasing of silicate crystallites particle size. This behavior may originate from difficulties in permeation due to the enhanced area and number of the zeolite–polymer interfaces in the cases of employing relatively smaller particle sizes (Tantekin-Ersolmaz *et al.*, 2000).

According to Paul and Kemp, the incorporation of zeolite 5A into silicone rubber did not improve the separation properties of the polymer (Paul and Kemp, 1973). This observation, though, cannot be generalized and quite a few contradictory results have been reported, indicating the existence of favorable effects of employing zeolites as fillers in the mixed matrix membranes. Some studies revealed that silicalite has significant potential for increasing the permeability and selectivity of various polymers for the separation of O_2 from N_2, CO_2 from H_2 and CO_2 from CH_4 (Kulprathipanja *et al.*, 1988 and Jia *et al.*, 1991 and 1992).

The zeolites 13X and 4A have also been shown to be useful for enhancing the performances of zeolite filled polymeric membranes for the separation of H_2 from N_2, CO_2 from N_2 and CO_2 from O_2 (Süer *et al.*, 1994 and Gürkan *et al.*, 1989). It is known that the permeability of gas through a zeolite filled polymeric membrane depends on the intrinsic properties of the zeolite and the polymer, the interaction between the two and the percentage of zeolite loading in the mixed-matrix membrane (Zimmerman *et al.*, 1997). However, the possible effect of the zeolite particle size on the permeation characteristics of the zeolite filled polymeric membranes has not been investigated.

The incorporation of zeolites into rubbery polymers has been shown experimentally to enhance both the permeability and selectivity in pervaporative separation of organic compounds out of water (Dotremont *et al.*, 1989, Boom *et al.*, 1998, Chandak *et al.*, 1997 and Netke *et al.*, 1995). Since then, there is a great interest in zeolite-filled polymeric membranes for gas separation (Yong *et al.*, 2001). The mixed-matrix membrane is a combination between polymer and zeolite. Previous studies indicated that the mixed matrix membrane give a good advantage in gas separation.

The advantages using polymer membranes are good processability, inexpensive production and low operating cost and modular design. Zeolite membrane advantages are in their separation performance and their chemical and thermal stability as shown in Figure 4 (A) and (B). The ad-

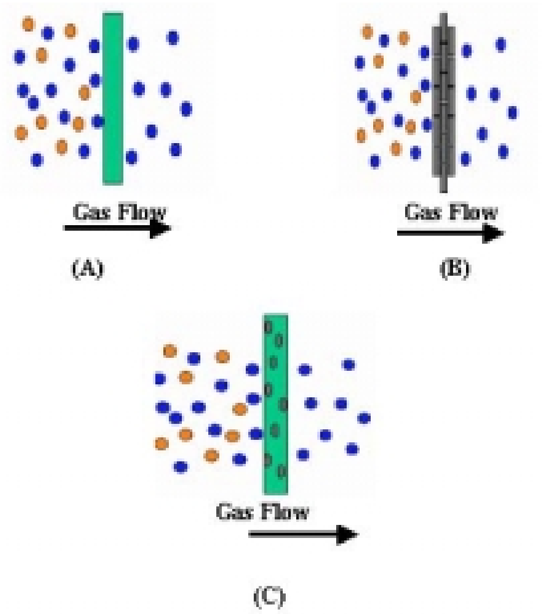

Figure 4. Schematic representations of (A) polymer membrane, (B) zeolite membrane (C) mixed-matrix membrane

Figure 5. Fabrication of mixed matrix membrane

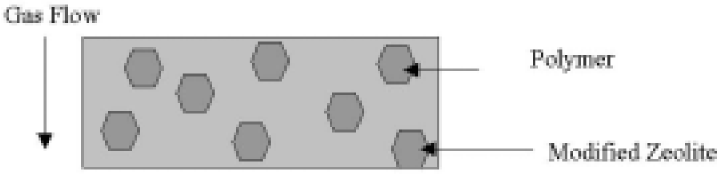

Figure 6. Homogeneous blend of polymer and zeolite membrane

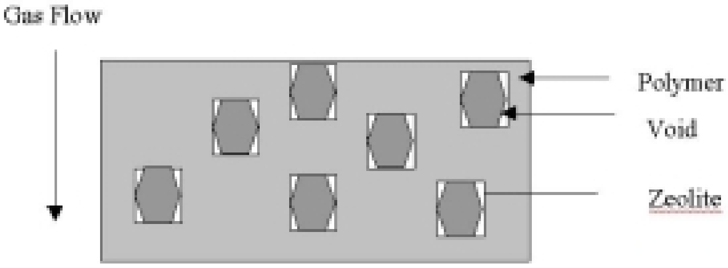

Figure 7. Incomplete blend of polymer and zeolite

vantages of mixed-matrix membrane are in gas separation performance in the processability and low cost operation as shown in Figure 4 (C).

Zeolite-filled rubbery polymer membranes were first investigated by Jia *et al.* (Jia *et al.*, 1991). They studied the permeation properties of various gases through poly- dimethylsiloxane (PDMS) membranes filled with silicalite-1, from which the permeabilities of He, H_2, O_2 and CO_2 were observed to increase, while those of N_2, CH_4 and C_4H_{10} were observed to decrease. They concluded that silicalite plays the role of a molecular sieving, although its pore size was larger than the kinetic diameters of gases. This means that the shape-selective effect is not only inherent in the equilibrium adsorption of gas molecules into zeolites but also in the kinetic adsorption and diffusion. Duval *et al.* studied the effect of zeolites incorporated into PDMS, ethylene-propylene rubber (EPDM), polychloroprene (PCP) and nitrile butadiene rubber (NBR) (Duval *et al.*, 1993). The results showed that silicalite-1, zeolites 13X and KY improved the gas separation properties of membranes, which was attributed to both CO_2 sorption enhancement and molecular sieving effects embodied by zeolites. However, zeolites 3A, 4A and 5A were totally ineffective in improving the permselectivity of the rubbery polymers. This behavior was attributed to the slow diffusion of the absorbed molecules from zeolite to polymer phase.

Subsequently, zeolite-filled glassy polymer membranes were investigated. Süer *et al.* studied the permeation rates of N_2, O_2, Ar, CO_2 and H_2 of polyethersulfone (PES) membranes filled with zeolites 13X and 4A (Süer *et al.*, 1994). They concluded that both permeabilities and selectivities increased at high zeolite loading (42-50 wt.%). Permeabilities decreased first and then increased with increasing zeolite loading. For PES-13X membranes, permeability showed a recovery above 8 wt.% zeolite loading. However, the permeability recovery of PES-4A membranes were observed to be above 25 wt.% zeolite loading. This result was interpreted by the fact that zeolite 13X crystals seemed to be more discrete, whereas zeolite 4A crystals were partly aggregated forming wider cavities. Pechar *et al.*, had successfully fabricated mixed matrix membranes of 6FDA-6FpDA-DABA, a glassy polyimide, and modified zeolites (ZSM-2) and used He, N_2, O_2 and CO_2 as a test gases. The ZSM-2 zeolites were fictionalized with amine groups by reacting them with aminopropyltri methoxysilane in toluene (Pechar *et al.*, 2002).

Duval *et al.* focused on the formation of interfacial voids due to the poor adhesion of the glassy polymer and the zeolite surface (Duval *et al.*, 1994). When silicalite-1 was added into glassy polymers such as cellulose acetate (CA), polysulfone (PSF), polyetherimide (PEI) and polyimide (PI), permeabilities increased but selectivities decreased or have maintained. This result is attributed to void formation. In order to make zeolites more compatible with polymers, they modified the external surface of zeolites with silane, or evaporated the solvent used to prepare the polymer solution above the T_g of the polymers during membrane fabrication. However, permeation properties of membranes were hardly improved. Gür approaches this problem with another method (Gür , 1994). A melt extrusion process fabricated zeolite 13X filled PSF membranes, and then CO_2, O_2, N_2 and CH_4 permeabilities of the membranes were measured. However, a pronounced effect of the filler was not observed. He concluded that the pore size of zeolite 13X was larger than the kinetic diameters of any gas molecules tested. Hence, separation due to size exclusion did not take place. The results mentioned above could not show any clear explanation on why zeolite-filled glassy polymer membranes could not improve the permselectivity. It was assumed that voids still remained after silylation and extrusion or that the large pore size of the zeolite precluded a molecular sieving effect.

3.1 Fabrication of mixed-matrix membranes

Figure 5 below shows the complete fabrication of the mixed-matrix membrane while the homogeneous blend of polymer and zeolite membrane is illustrated in Figure 6.

It is difficult to obtain a homogeneous blend of polymer and zeolite membrane since the previous attempts had failed due to the presence of voids between the polymer and zeolite. In this case, adhesion between polymer and zeolite is essential. Incomplete blend of polymer and zeolite can be illustrated in Figure 7 where the existence of voids are shown clearly.

So in this case, amine–carboxylic acid interaction will promote adhesion via acid-base interaction between –OH and-NH_2. A polyimide-zeolite mixed-matrix membrane was successfully fabricated without defects as shown in Figure 8. Attractive molecular forces exist between the polymer and modified zeolite.

Yong *et al.*, indicated that interfacial void-free Matrimid polyimide (PI) membranes filled with zeolites were prepared by introducing 2, 4, 6-triaminopyrimidine (TAP). TAP enhanced the

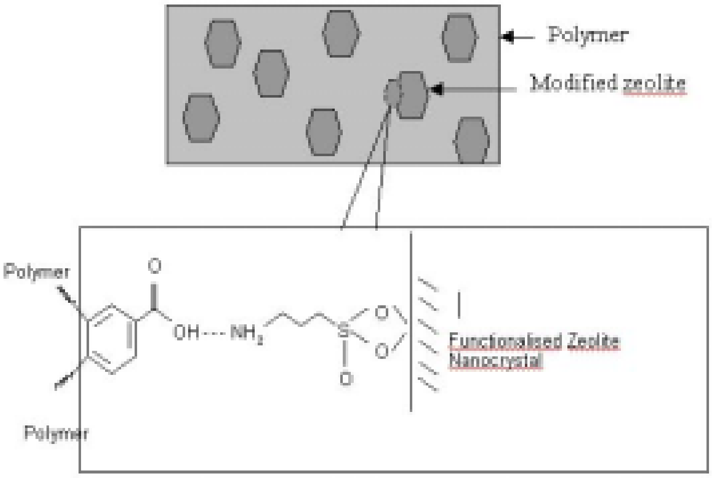

Figure 8. Modified zeolite in mixed-matrix membrane

contact of zeolite particles with polyimide chains presumably by forming hydrogen bonding between them. 2, 4, 6-triaminopyrimidine (TAP) is introduced as a kind of compatibilizer to eliminate the interfacial voids. This chain essentially enhanced the contact between the two components. The resulting membranes displayed an increase in permeability without much change in the selectivity. In fact, filling the space between zeolite particles and polymer chains would be more convenient and effective than surface treatment of zeolites (Duval *et al.*, 1993).

4. Development of high performance asymmetric membrane for gas separation through rheological approach

The phase inversion process determined the general morphology of a membrane such as skin layer thickness and surface porosity. Hence, it determined the basic capability of the membrane for gas separation. Besides the inversion process, another aspect that is equally important is the rheological conditions during manufacturing. These parameters involved the shear and elongation experienced during casting or hollow fiber spinning. The degree of shear can be studied by altering casting speed or the dope extrusion rate and the effect of elongation can be studied by altering the jet stretch ratio in spinning that is the ratio wind-up speed to extrusion speed.

The physical properties of films and fibers, such as tensile strength and Young's modulus, were related to molecular orientation induced during the various steps in fabrication. The separation performance of membranes is also significantly affected by molecular orientation. Therefore, it is important to closely relating the product performance to the fabrication process and to fully understand the mechanism behind the development of molecular orientation. In amorphous polymeric materials, molecular orientation was defined as a preferential alignment of randomly coiled chain molecules (Cleeremen, 1974). Various mechanisms have been postulated in the literature. There are three main mechanisms established named, phase inversion, shear flow and elongational or stretching flow.

By phase inversion, Serkov and Khanchih (Serkov and Kanchih, 1977) examined the development of molecular orientation during the precipitation process of polymer solution. They found that preorientation was developed during precipitation, which significantly determined the subsequent stretchability, structure and physical properties of the spun fibers. Molecular orientation by ionotropic coagulation is only applied to poly electrolyte precipitation. Due to this limitation, the mechanism cannot be adopted to explain the structural alignment in polymeric solutions generally. Serkov and Khanchih suggested that as the front moves through the solidifying medium, orientation is developed. They also postulated that as the polymer rich phase solidifies, spherulites could form if the energy of interaction with the solvent is high. This process can lead to highly ordered structure at the molecular level. Referring to shear flow, Takuechi *et al.* (Takuechi *et al.*, 1988) studied the morphological development in a copolyester fiber with increasing shear rate. They observed a skin-core structure in the resultant extrudate and characterized this in terms of band pattern, which were monitored through a polarizing microscope. Bousmina and Muller (Bousmina and Muller, 1996) also proposed a mechanism responsible for the development of ordered structure in an extruded filament according the influence of shear. They described a process which particles become aligned in the shear direction. Serkov and Khanchih (Serkov and Kanchih, 1977) also postulated that shear-induced orientation was frozen into the skin of a fiber during formation, while the molecular orientation was induced by elongation flow. Perepelkin (Perepelkin, 1977) outlined the principle aspects in the structural reorganization of polymer solutions that are; 1) a change in the orientational and three dimensional order of the structure, 2) an increase in the degree of orientation of the crystalline and amorphous sections of the structure, 3) a change in the conformational arrangement of the molecule chain and 4) a change in the molecular structure.

In gas separation membrane, it has been acknowledged that molecular orientation in the active layer will affect the selectivity. In recent years, besides the phase inversion process being the primary factor to determine the separation performance of gas separation membrane, more researches have been focusing on the rheological aspect. For that reason, rheological conditions during manufacture will affect membrane performance by altering molecular orientation. The shear during casting is one of the important rheological factors. It was shown that molecular orientation was intensified with the shear rate increment during casting and spinning and that there is a favorable effect on selectivity. The shear rate for flat sheet membrane varies by drag time. On the other hand, the hollow fiber membrane varies by dope extrusion rate.

Shilton *et al.* found that permeability and selectivity rose with increasing dope extrusion rate for coated fibers due to the combined effect of enhanced polymer selectivity and increased in surface porosity (Shilton *et al.*, 1994). However, elongation experienced during spinning was found to be detrimental to membrane performance. Permeability increased but selectivity decreased with increasing jet stretch ratio or elongation. This was due to increase in porosity in the skin layer and unfavorable polymer structure. To explain their findings, Shilton *et al.* suggested that shear and elongation affected the selectivity of the solid polymer in the membrane by altering molecular orientation (Shilton *et al.*, 1994). The actual rise in selectivity of the coated membranes with increasing dope extrusion rate could be explained by observing the increase in the selectivity of the polymer itself. This was related to the rheological behavior of the spinning dope under shear.

Aptel *et al.* (Aptel *et al.*, 1985) spun polysulfone ultrafiltration hollow fibers and found that the performance of the membrane depended on the extrusion rates of the polymer solution and on the bore liquid. According to them, shear forces in the spinneret caused orientation of polymer molecules which in turn affecting pore shape. If gelation of the solution due to contact with the coagulant liquid is faster than the relaxation time of the polymer solution, the polymer chain alignment is frozen into the membrane wall.

Ismail *et al* indicated that increasing molecular orientation occurred in the high-shear membranes. Furthermore, the selectivity of these membranes was heightened and even surpassed the recognized intrinsic selectivity of the membrane polymer. The results suggested that increased shear during spinning would increase molecular orientation and, in turn, enhance selectivity. The selectivities were much greater for high shear membrane (Ismail *et al.*, 1997 and 1998).

The shear-induced oriented structures phenomenon had been treated well by Takuechi *et al.* (Takuechi *et al.*, 1988) and more recently by Bousmina and Muller (Bousmina and Muller, 1996). Takuechi *et al.* studied the morphological development in a copolyester fiber with increasing shear rate. They observed a skin-core structure in the resultant extrudate and characterized this in terms of band pattern. Takuechi *et al.* also studied the texture of the extrudate by birefringence and showed that with shear rate induced, molecular orientation was concentrated only in the skin layer. Both Takuechi *et al.* and Bousmina and Muller suggested that understanding and quantifying, whenever possible, the relationship between extrudate morphology and rheology was of the outmost importance in optimizing processing conditions.

Spectroscopy has become an important tool to investigate the morphological characteristics of a membrane at the molecular level. Polarized transmission infrared spectroscopy has been used previously to study molecular orientation in thin polymer films, but transmission spectroscopy is applicable only if the polymer films are sufficiently transparent in the wavelength regions of interest. Fourier transform infrared spectroscopy technique has also been employed to study the deposition of polymide outer layer in composite gas separation membranes (Ancelin *et al.*, 1992). The authors used non-polarized infrared spectroscopy to analyze the polyimide polymerization mechanism using various polyamic acid precursors. Then, they tried to relate chemical structure to the selectivity of the prepared membranes. Their study did not involve direct measurement of molecular orientation in the membrane. By using FTIR, plane polarized infrared absorbed more strongly when the plane polarization was parallel. There was a difference in absorption between parallel polarized and perpendicularly polarized radiation and this phenomenon is known as linear dichroism (Shilton *et al.,* 1996).

Molecular orientation in membranes can now be directly measured by spectroscopic techniques (Khulbe *et al.*, 1995). Khulbe *et al.* employed electron spin resonance and Raman spectroscopy techniques to study the different morphologies in integral-asymmetric and symmetric membranes of poly(phenylene oxide) (PPO) and polyamide (PA). They found that molecular orientation existed in the skin layer of the asymmetric membranes and this was responsible for greater selectivities. This orientation was subsequently related to molecular vibration in specific bonds in the membranes. Pronounced infrared dichroism (the difference in absorption between parallel and perpendicularly polarized light) indicates that the alignment of molecules, with the absence of dichroism showed that a sample had been randomly orienting the molecules. Polarized IR spectra of hollow fiber membranes had been recorded by IR reflection from samples of the fibers wound several time round a KBr plate of rectangular cross section. In this study the membranes were cast at low and high shear rate. Both membranes exhibit dichroism in the infrared, but the effect was more pronounced in the high shear membranes suggesting greater molecular orientation (Ismail *et al.*, 1997).

Molecular orientation in the active layer of these membranes was directly and quantitatively measured using plane-polarized reflectance infrared spectroscopy. This technique could reveal anisotropy on the molecular level within a sample by pronounced infrared (Ismail *et al.*, 1997 and 1998 and Lai, 2002). Shear and elongation during spinning have been shown to affect the permeation performance of polysulfone hollow fiber membranes (Shilton *et al.,* 1996 and Aptel *et al.*, 1985) and this was attributed to molecular orientation in the active layer. If special skin formation conditions prevail, increased shear can create an oriented and highly ordered membrane active layer which can exhibit selectivities significantly greater than the recognized intrinsic value for the isotropic polymer. In addition, the membranes have been tested recently using positron annihilation lifetime spectroscopy (PALS) to further investigate the conformation of the active layer at the molecular level (Ismail *et al.*, 1997).

The calculated results suggest that hollow fiber membranes spun with high shear rates apparently have a thicker dense skin layer, indicating increasing gas transport resistance because of shear-induced chain orientation and packing. This result might also imply that a high shear rate may yield a hollow fiber with a "denser" selective layer with a lower permeability (Wang and Chung, 2001).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been used to characterize the surface structure, in particular the molecular orientation, in wide variety of polymer films, fibers and glass fibers. In polymer films, DRIFTS was capable of providing good quality spectra and structural information of polymer surfaces up to nanolevel thickness (Jansen and Haas, 1988). Reflection infrared spectroscopy had the advantage of being able to analyze the surface layers of opaque films or fibers. Recently, the technique has been developed to determine orientation of polymer molecules in asymmetric hollow fiber and flat sheet membranes for gas separation.

5. Chemical cross-linking modification of polymer membranes for gas separation

From previous researchers, experimental results suggested that cross-linking modification imparted membranes with anti-plasticization, good chemical resistance and even with good long-term performance. Besides, the gas permeabilities or permselectivity relationships of some cross-linked polymers such as polyimides were higher than the normal trade-off line (Liu *et al.*, 2001). Cross-linking modification can be induced by two methods. The first method is by using UV light induced photochemically cross-linking reactions and the second method is using thermal treatment by elevated temperatures. Cross-linking of the polymer matrix is a convenient way to improve resistance to chemical dissolution while simultaneously enhancing the high temperature modulus of the material. However, cross-linking has been shown to result in a significant decrease in the gas permeability.

UV light or other energy sources induced photochemically cross-linking reactions is a method of cross-linking modification but the difficulties of implementing it uniformly for hollow fiber membranes limit the application of this method. The radiative processes can activate reactive groups primarily restricted to the incident surface layer, depending on dosage rate and exposure time (Dudley *et al.*, 2001). This is especially true for typical UV irradiation.

Ouyang *et al.* reported that a thin SiO_x surface layer was formed on porous Nylon® membranes coated with a cross-linked polysiloxane by exposure to UV light at room temperature in the presence of atmospheric oxygen (Ouyang *et al.*, 2000). The transformations manifest by changes in both the chemical and physical properties of the films. The majority of carbonaceous species are removed from the film surface, indicative of the conversion of an organic siloxanepolymer into an inorganic SiO_x surface film. The gas permeation result showed that before irradiation, CO_2/N_2 selectivity was 22 and after UV-ozone induced formation of the SiO_x surface layer, the selectivity for CO_2/N_2 increased to 48.

Liu *et al.* prepared a series of copolyimides and modificated copolyimides by UV irradiation to photochemically cross-linked copolyimides (Liu *et a*l., 1999). Photochemically cross-linking modification will result in decrease of gas permeability and increase in both, energy (E_p) and H_2/N_2 selectivity of all copolyimides. UV irradiation of the copolyimides can determine activation energies for gas permeation. The cross-linked copolyimides obtained exhibited higher gas permeabilitites and selectivities than normal polymers for H_2/N_2 separation.

Dudley *et al.* (Dudley *et al.*, 2001) studied the cross-linking of polymer blend membranes containing a reactive additive using a variety of energy sources (UV, γ and electron bean irradiation) into integrally skinned asymmetric membranes. They reported that polyetherimide as the primary membrane component and the polymer was cross-linked by blending with an ethynyl-terminated monomer (ETM). The thermosetting

ETM can be cross-linked to provide materials with improved solvent resistance without evolution of volatile products and in the absence of catalysts. Results fall into two categories, depending upon the activation procedure employed: surface treatments and thermal treatments. Surface treatment resulted in improvements in separation selectivity with only modest reduction in fast gas flux. Thermal treatments were conducted at a temperature well below the maximum reaction temperature of the ethynyl unit (180°C) and at a temperature near the peak reaction temperature (279°C). In general, increasing the time or temperature of the annealing process resulted in an increase in the glass transition temperature and an increase in the extent of reaction. Complete conversion of the ethynyl units resulted in marked improvements in the resistance to chemicals, thermal stability and gas selectivity.

Thermal treatment at elevated temperatures is another method of cross-linking modification. The thermal process activates reactive groups uniformly throughout the material. The major drawback of thermal treatment at an elevated temperature is it decreases the fine structures of asymmetric membranes and their gas permeation properties. Therefore, cross-linking methods performed at a low temperature are necessary for the successful modification of asymmetric membranes (Liu *et al.*, 2001). Figure 9 describes the cross-linking modification process step-by-step by using immersing polyimide film in p-xlenediamine methanol solution (Liu *et al.*, 2001).

Most of previous researchers used cross-linking method at high temperature. Bos *et al.* used homogenous matrimide films as the model material and successfully stabilized the membrane by forming a semi-interpenetrating network with oligo-polyimide containing acetylene end groups at 265°C and by cross-linking with a heat treatment at 300°C without curing agents (Liu *et al.*, 2001). Staudt-Bickel and Koros found that cross-linking reaction between ethylene glycol and the carboxylic acid groups in the diamino benzoic acid by thermal treatment is much better than antiplasticization at 150°C. Liu *et al.* studied the fundamentals of the chemical cross-linking modification of a polyimide with p-xylenediamine at ambient temperature (Liu *et al.*, 2001). The advantages of this method are the room temperature curing process and the easy usage. The cross-linking modification result in significant decrease in gas permeabilities of cross-linked polyimides to He, O_2, N_2 and CO_2. The decrease in diffusion coefficients plays a dominant

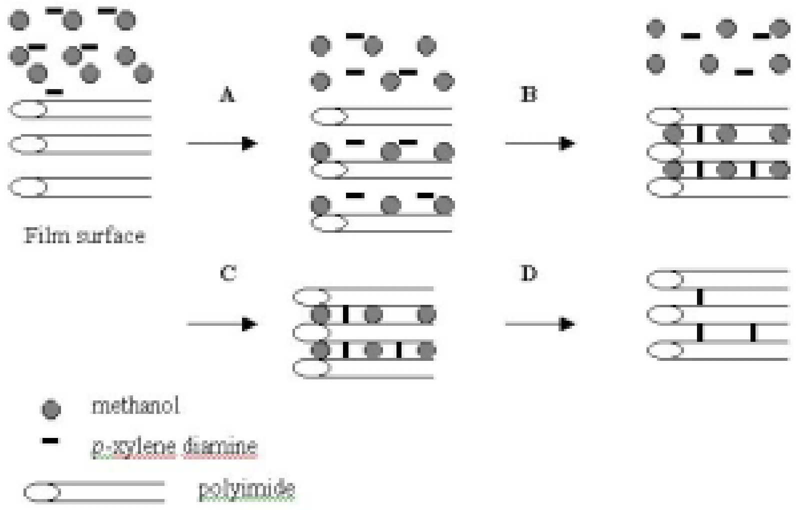

Figure 9. Schematic representation of chemical cross-linking process by thermal treatment. A) swelling B) cross-link C) removing from the solution D) drying (Liu *et al.*, 2001).

role to the decrease in gas permeability. With increase in the degree of cross-linking, the permselectivies of He/N_2 and O_2/N_2 increase too but CO_2/N_2 selectivity decreases (Dudley *et al.*, 2001).

Rezac *et al.* analyzed the influence of solid-state cross-linking polyimides to achieve this unique properties combination (Dudley *et al.*, 2001). They did comparison to other cross-linked polymer system. As a result, they found out that cross-linking *p* polyimide blend resulted in a material which simultaneously had outstanding permselectivity properties and chemical resistance, as well as no measurable decrease in permeability observed upon cross-linking by annealing at 240°C.

One specific technique is to synthesize polymers with cross-linkable groups on the polymer backbone, enabling the polymer to be cross-linked during a reactive post-treatment step after membrane formation. To avoid magnifying existing defects during the cross-linking step, it is highly desirable to start with a defect-free selective layer. Various other attractive membrane materials are also being developed though successful commercialization of any potential membrane material relying on retaining its intrinsic dense film properties in an integrally skinned asymmetric hollow fiber structure. Therefore, the issue of being able to produce an essentially defect-free asymmetric membrane structure represents one of the major problems in the gas separation membrane industry (Carruthers, 2001).

In order to improve gas separation performance, thus, to obtain a high performance membrane, the combination of the above mentioned three techniques should be adopted. Various and different modifications from many inventors will direct this technology toward the production of good performance membrane with high selectivity and high permeability or high permeability with constant selectivity.

6. Development of defect-free and ultrathin-skinned asymmetric membranes for gas separation

The fabrication of polymer membranes having both high gas permeability and selectivity has become a subject of strong research interest because of its importance for the development of the membrane gas separation process. One way of the achieving the gas transport performance is to fabricate asymmetric polymer membrane consisting of a defect-free skin layer, which has high gas permeability without a significant decrease in gas selectivity (Niwa *et al.*, 2000). Asymmetric flat sheet and hollow fiber membranes were defined to be "defect free" if the ideal A/B for example O_2/N_2 selectivity was found to be greater than 80% of intrinsic O_2/N_2 selectivity of dense polysulfone membrane film (Pesek and Koros, 1993). Interestingly, the asymmetric membrane exhibited greater gas selectivity than the dense membrane. The following are researchers that have done studies on the development of defect-free and ultrathin-skinned asymmetric membranes for gas separation.

Lai (Lai, 2002) did the study by using a casting solution consist of 22.0 wt.% polysulfone (polymer), 31.8 wt.% N,N-dimethylacetamide (less volatile solvent), 31.8 wt.% tetrahydrofuran (more volatile solvent), and 14.4 wt.% ethanol (nonsolvent). Manipulation of rheological factors and evaporation time in membrane formation process is a novel approach in membrane technology, which provides a potential platform to develop defect-free and ultrathin-skinned asymmetric membranes for gas separation. Rheological factors would affect morphology, physical properties and separation performance of asymmetric membrane. Therefore, this study investigated the effects of rheological factors with regard to membrane properties and structures (Lai, 2002). Molecular orientation is enhanced by shear during casting and this has a favorable effect on membrane selectivity. Molecular orientation of opaque polymeric films was directly measured using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), which was first reported by Fuller and Griffiths (Ismail, 1997). By manipulation the evaporation time, typical range time that lay within 9s to 21s were chosen in this study to investigate their effects on membrane properties and structures. The result elucidated that by increasing the evaporation time during casting cause a decreased in pore size and surface porosity with an increased in skin thickness. Decreasing the evaporation time during casting will cause an increase in both pore size and surface porosity accompanied by a decrease in skin thickness. A combination on both of the effects of phase inversion and rheological factors has successfully developed defect-free and ultrathin-skinned asymmetric membranes for gas separation. Overall, the optimum conditions for fabricating an approximately high performance, ultrathin polysulfone flat sheet asymmetric membrane from the results obtained in this study was the membrane cast at highest shear ($367s^{-1}$) and at 20s of forced convective evaporation in dry phase inversion steps.

Kurdi and Tremblay (Kurdi and Tremblay, 1999) have developed defect-free asymmetric polymeric membranes for separation of oxygen from air, by using dry/wet phase inversion process with polyetherimide (PEI) as polymer, Anhydrus N-methyl-2-pyrrolidinone (NMP) as solvent and lithium nitrates ($LiNO_3$) salt additive. They discussed the effects of polymer concentration, additive salt concentration and drying process on oxygen permeance and the actual separation factor of the membrane. The small amount of solvent in the coagulation bath improved the leaching of the salt additive and produced membranes with are more open structure. The skin formation is achieved by a diffusion-driven process and then by using forced convection instead of normal evaporation and produced a defect-free ultrathin-skinned asymmetric membrane suitable for gas separation. The highest productivity, defined as the highest simultaneous oxygen permeance and oxygen separation factor was obtained for membrane produced from casting solutions containing 23% by weight PEI. Increasing $LiNO_3$ / PEI ratio to >2% leads to a more open structure, which causes a large increase in gas permeance accompanied by a large decrease in the gas selectivity, due to increase in pore size. The rigidity of the membrane increases on drying at 90°C under vacuum.

Niwa *et al.* fabricated asymmetric polyimide hollow fiber with a completely defect-free thin skin layer. They focused on effects of the composition of spinning solution and the air gap height on the formation of the skin layer. The hollow fiber showed a microporous structure on the inner surface and a defect-free skin layer at the outer surface. The outer diameter of the fiber was 500 μm, with a wall thickness of 45 μm and the calculated apparent skin layer thickness was 470 nm. Selectivity of O_2 and N_2 for the hollow fibers at 35°C and 76 cm Hg was 5.4 and exhibited a larger value than that measured in the dense and asymmetric polyimide flat membranes.

Hachisuka *et al.* (Hachisuka *et al.*, 1996) had developed a new type of asymmetric membrane that has a hyper thin skin layer and sponge like porous matrix 6FDA-BAAF polyimide was used as one of the membrane materials. The skin layer had hardly any defects and the thickness of the membrane was 40-60 nm. The skin layer and sponge like porous matrix, which had finger void free morphology, were formed as one body. This suggests that the formation of such hyper-thin skin layers depends on the dissolution property between a dope solvent and water as a solidification solvent. The selectivity and permeation rate of the 6FDA-BAAF polyimide asymmetric membrane had an α 27 for CO_2/CH_4 and a permeation rate of 1.3 [Nm^3/m^2 h atm] (= 5.5×10^{-4} [cm^3(STP)/ cm^2 s cmHg]) for CO_2. (The maximum value had an α of 35 for CO_2/CH_4 and a permeation rate of 1.6 [Nm^3/m^2 h atm] (= 5.8×10^{-4} [cm^2 s cmHg]).

Kawakami *et al.* (Kawakami *et al.*, 2002a) studied the gas permeation stability of an asymmetric polyimide membrane with a thin and defect-free skin layer. The polyimide used in this study was synthesized from the fluorinated dianhydride (6FDA) and the aromatic diamine not containing a CF_3 group. The apparent skin layer thickness of the asymmetric membrane was 55 nm. They specifically focused on the CO_2 permeation stability of the asymmetric polyimide membrane with a 55 nm skin layer exposed to a

CO_2 pressure of 760 cmHg.

In addition, by Kawakami *et al.* (Kawakami *et al.*, 2002b) synthesized the isomeric polyimides, 6FDA-m-DDS and investigated the gas selectivity of the asymmetric polyimide membranes with an oriented surface skin layer. In particular, they focused on the effect of the chemical structure of the polyimide on the molecular orientation. The molecular orientation in the asymmetric polyimide membranes was measured using polarized ATR–FTIR spectroscopy. The gas selectivity of the asymmetric 6FDA-m-DDS membrane increase with an increased in the shear stress and were greater than that of the dense membrane. They also clarified that a parallel oriented surface formed on the asymmetric 6FDA-m-DDS membrane caused an enhancement in gas selectivity of the membrane.

Ren *et al.* (Ren *et al.*, 2002) found that when ethanol (ternary system) as a nonsolvent additive was added to the spinning solution contained 6FDA-2,6 DAT /NMP, the resultant fibers had less dense skin thickness compared to fibers spun from the binary dope (6FDA-2,6 DAT/NMP) system at the same shear rate. However interestingly, the selectivity in the ternary dope system increased slightly with an increase in shear rate. The hollow fiber membranes became more compact with an increase in shear rate. From their result, they made a conclusion; the reduction in permeance is mainly due to elongational induced molecular orientation, while the reduction in selectivity is probably due to elongational induced defects.

Chung *et al.* (Chung *et al.*, 2000) found that at low shear rates, the permeances of non-polar molecules such as H_2 ,O_2 ,N_2, and CH_4 decreases, while their relative selectivities increase with an increase in shear rates. Once a certain shear rate is reached, all permeances increase, while their selectivities decrease with an increase in shear rates. In low shear rate regions, the decrease in permeance or increase in selectivity with increasing shear rates arises from the better molecular orientation and chain packing induced by shear. With increasing shear in high shear rate regions, the increase in permeance or decrease in selectivity is mainly attributed to relatively porous skin structures induced by the low viscosity nature of a power-law spinning fluid at high shear rates, fracture, and modified thermodynamics and kinetics of phase inversion process. This work suggests that there may exist an optimum shear rate to yield optimal membrane morphology for gas separation. An increase in CO_2 permeance with increasing shear rates are possibly due to enhanced coupling effect between CO_2 and the highly oriented and closely packed fluoropolyimide molecular chains induced by shear. Chung *et al* (Chung *et al.*, 2002) also applied the shear rate application to the ultrafiltration membrane. They demonstrated the effect of shear rate on the outer surface morphology of polyethersulfone (PES) hollow fiber ultrafiltration membrane by an atomic force microscope (AFM). They varying shear rates from $1305s^{-1}$-$11,066s^{-1}$, and indicated that at low shear rates, the outer surface have revealed that nodules in the outer skin appeared to be randomly arranged at low shear rates but formed bands that were aligned in the direction of dope extrusion when the shear rate increased.

The pure water flux of the membranes was nearly proportional to the mean roughness and resulted in lower separation membranes. AFM data also imply that there was a certain critical value of shear rate around $3585s^{-1}$, the roughness decreased significantly with an increase in shear rate below $3582s^{-1}$ and almost leveled off or in a much slower pace above this shear rate.

7. Future direction

Formation of defect-free and ultrathin-skinned layer asymmetric membrane for gas separation seems to be the most challenging aspect in the production polymeric asymmetric membrane for gas separation due to its high permeability and selectivity. It is foreseen that in the future, this aspect will be concentrated in the development of defect free skin layer from various type of polymer especially polyimide, polysulfone, cellulose acetate, polyethersulfone and polyaramide.

Since the permeation properties of carbon membranes have been improving from the past 20 years, the future mixed-matrix membrane production is preferably to use the polymer. The carbonization polymer blend will lead to the formation of porous structure due to the thermally unstable polymer (pyrolyzing polymer) decomposing to leave pores in the carbon matrix formed from the stable polymer (carbonizing polymer) (Ismail and David, 2001). Proper materials selection is the initial step to attaining mixed matrix gas separation membranes with performance exceeding the upper bound trade-off curve. Failure to eliminate defects probably resulted in unfavorable performance. The upper bound trade-off curve still defines the approximate upper bound today, despite insensitive theoretical and practical structure-permeability studies. However carbon molecular sieving (CMS) lies well above the upper bound polymeric trade-off curve and in or near the commercially attractive region. These materials were expensive and difficult to process as membranes (Zimmerman *et al*., 1997). In addition, mixed-matrix membrane will not only be used in the design and development of mixed matrix membranes for specific gas separations applications, but will also have implications in the development of various other new and valuable materials for sensor, optical and electronic devices. Besides that, current studies clearly demonstrate the versatility of chemical cross-linking modification of polymer technique for formation of membrane and the potential utility of this technique seems limitless.

Conclusion

Increasing amount of research in the formation of gas separation membrane indicates that membranes technology is growing and becoming another alternative for industrial gas separation processes. The fabrication of asymmetric polymer consisting a defect-free and ultra-thin-skinned layer has become the strong subject of research interest because it stresses on the importance of having high permeability and selectivity gas separation membranes. High performance zeolite materials as a filler for mixed-matrix membranes can further take gas separation membranes into uncharted areas. Membrane separations employing mixed-matrix materials have the potential to meet demanding gas separation in a world with shrinking energy resources and increasing environmental concerns. These zeolite crystals, which are embedded in a polymer matrix, serve as the supporting material and offer processing flexibility unmatched by inorganic materials. As for chemical cross-linking modification by UV light and thermal treatment, this promising technique will be widely used in the near future. Covalent cross-linking has been reported to be an effective approach for stabilizing membranes while retaining very attractive transport properties. The degree of cross-linking can be controlled by the amount of carboxylic acid moieties incorporated into the polymer backbone and the thermal treatment given to the polyimide films. Though a lot of efforts were being devoted to membrane formation for gas separation in a number of promising area, more research and development strategies are still needed in order to exploit the full potential of this technology in order to produce high performance membrane for gas separation in the next decade.

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