A PRELIMINARY STUDY OF FLAT SHEET ASYMMETRIC MEMBRANE FORMATION FOR GAS SEPARATION APPLICATIONS

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Abstract

The common technique for the preparation of polymeric membranes with asymmetric structure is the phase inversion process. In this process, a polymer is dissolved in an appropriate solvent before casted on a suitable support. The casted film is then immersed in a non-solvent bath and the coagulation process taking place to form a membrane. The asymmetric membrane structure and its properties are influence by many experimental parameters such as the thickness of membrane, the polymer solution composition, coagulation bath composition, choice of solvent and non-solvent, the membrane casting speed and the knife shape which inducing casting shear rate can be determined in the membrane casting procedure. In order to produce a good quality flat sheet asymmetric membrane, a unique pneumatically-controlled flat sheet membrane casting system were designed and fabricated in this study.

The present study seeks to optimize those parameters suitable for membrane making, which will exhibits good separation performance in gas separation application. To achieve the above objective, a few framework have been drawn such as optimizing the initial membrane solution formulation, characterizing the thermodynamic and rheological properties of the polymer solution. The orientation of the polymer molecules is also important in membrane making and will also investigated in order to enhance membrane selectivity.

Keywords: Flat sheet membranes; Gas separation; Phase inversion; Asymmetric membranes

1. Introduction

Even though there are a large number of potential applications for gas separation with polymer membranes [1-4], only few of the selected polymers have become applied in practice, such as polysulfone, polyimide and polycarbonate [1]. Recently, many applications of membranes for gas separation and purification are well developed, however still have not been successfully introduced into practical use. Only integrated asymmetric and composite membranes are currently used in the separation of gases. These types of membranes are characterized by very thin non-porous layers which as gas selective and are deposited onto highly porous materials which will provided the necessary mechanical strength, but do not contribute to transport resistance. Currently, majority of commercially available and laboratory scale studied membranes operate according to the solution-diffusion mechanism. In this particular mechanism, the material transport occurs in the three steps namely, absorption, diffusion and release [4].

Gas membrane separation is a straightforward process concept. Gas membrane separation is a concentration-driven process which the gases is directly related to the pressure of the feed and the permeate streams. The feed air is compressed to provide a driving force and the filterable air stream will be passed across the membrane surface. The degree of separation is determined by the selectivity of the membrane and by the conditions of the separation, including pressure, temperature, flow-rate and membrane area.

There are two types of membrane that can be used for gas separation. The first is a porous membrane in which the gases are separated on the basis of their molecular size by small pores through the membrane. This mechanism is not commercially useful because of the low separation factors. The majority of commercial applications are based on non-porous gas separation membrane. These membranes are containing no pores in the conventional sense and the gases will be dissolving in and diffuse through the membrane. Two or more gases able be separated because of different gases exhibit different rates of transport through membrane. There
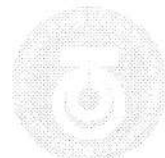
are many polymeric materials that exhibit good permeation and separation factors for gas separation applications, but the real challenge was fabricating polymeric membranes that have both economically high permeability rates and high durability in the gas stream environment [15]. The potential application of a polymer as a separation membrane depends upon the possible throughput and the purity of the product. This means that the both of the permeability coefficient and the selectivity of the gas should be transported more rapidly and as large as possible. As a basis, the polymers with permeability coefficient of oxygen values greater that 1 barrer and the permselectivity of O_2/N_2 values greater than 5 are interested for gas separation application requirements [4].

2. Membrane Formation

In the past, asymmetric membranes are almost prepared by a wet phase inversion process [1,5], by direct immersion of a cast film in a quench medium. An ideal asymmetric membranes for gas separations as considered here, must have the following requirements: 1) the skin layer must be defect free to ensured that the gas transports is controlled exclusively by a solution/diffusion mechanism, 2) the skin layer should be as thin as possible to maximize the membrane productivity, and 3) The sub-layer should be provide sufficient mechanical strength to support the skin layer and not contribute any resistance to the gas transport. Pinnau and Koros had found that the defect free integrally skinned asymmetric membrane with thin skin 200A can be formed by the dry/wet phase inversion process using forced-convective evaporation. They had summarized the empirically developed rules for the formation of optimized asymmetric membranes made by the dry/wet phase inversion process as follows: 1) The casting solution must consist of at least three components: polymer/solvent/non-solvent. The solvent must be have a higher vapor pressure than the non-solvent component, so that phase inversion can be induced during an evaporation step, 2) The composition of the casting solution should be as close as possible to the thermodynamic instability limit: bimodal composition, 3) The evaporation should be carried out by forcing a gas stream across the cast membrane to induce phase separation in the outermost region of the cast film (dry phase inversion process), and 4) The quench step (wet phase inversion) should be carried out in a thermodynamically strong non-solvent for membrane forming polymer. The quench medium must be miscible with the solvents and non-solvents of the casting solution [5].

3. Dry/wet phase inversion

The dry/wet phase inversion technique requires multi-component casting solutions consisting of polymer, at least one volatile solvent and one less volatile non-solvent then bringing the solution to phase separation by means of solvent outflow and/or non-solvent inflow [12]. However, it has been found that the used of two solvents, a primary volatile solvent and a secondary less volatile solvent, allows finer control of solvent evaporation and polymer coagulation rates. All of the solvents and non-solvents should be miscible with the coagulation bath medium and the non-solvent is added to the casting solution until the solution nears its phase boundary [7,11]. The evaporation process for a typical ternary casting system used for the preparation of membranes made by dry/wet phase inversion is illustrated schematically in Figure 1.
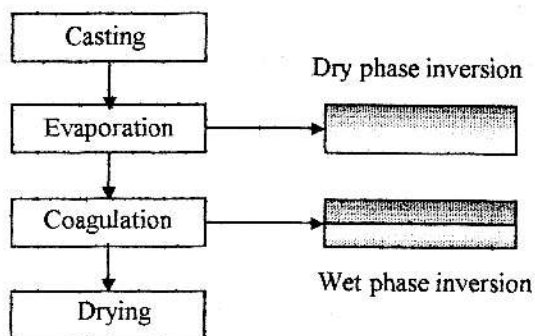

Figure 1. Process steps for the preparation of dry/wet phase inversion membranes.

4. Preparation Parameters And Their Effect On Membrane Structure And Performance

The mechanism for the formation of skin type asymmetric membranes by dry/wet phase inversion allows many of the variables of the membrane preparation procedure to be rationalized. Those parameters determining the structure and properties of phase inversion membranes are as follows:

i) Choice of Polymer Material

There are many polymeric materials that exhibit good permeation and separation factors for gas separation applications, but the real challenge was fabricating polymeric membranes, which have both economically high permeability rates and high durability in the gas stream environment [3]. The type of membrane structure depends on the nature of the selective materials. Glassy polymers are commonly formed into high-performance anisotropic (skinned) membranes by variants of the solution-precipitation procedure invented by Loeb and Sourirajan. In general, mass transfer in gas separation processes will be greater in amorphous polymers than in highly crystalline or cross-linked polymers as well as rubbery polymers [1].

ii) Polymer Concentration

Polymer concentration in the casting solution is another parameter in the dry/wet process. The casting solution with more polymer composition will increasing its viscosity and tends to promote more selective but less productive in the absence of offsetting casting conditions or other solution component changes. The viscosity for flat sheet casting solution is preferable only in 1000 to 2000 cP.

The effect of increasing polymer solution concentration with increasing the polysulfone content from 14 to 26wt.% at a constant DMAc/THF solvent ration of 1/1 showed the increased in O_2/N_2 selectivity and decreased in O_2 the pressure-normalized flux of O_2 [7]. Paulsen had reported that the increased polymer concentration will promoting the formation of macrovoids and this macrovoids can be suppressed by increasing the duration of the evaporation step or decreasing the initial casting solution thickness sufficiently [6].

iii) Choice of Solvent

Water miscibility is a primary requirement for the choice of solvent and non-solvent in an aqueous quenched membrane formation system. Since the solution dope typically require high solids contents, both volatile and less volatile solvents should be sufficiently strong to allow dissolution of high polymer concentrations (25-35wt%). The volatile solvent along with being miscible with water, must have sufficient volatility to permit ample evaporation from the nascent membranes [8].

The additional of volatile solvent was designed to enhance solvent evaporation, leading to skins with fewer defect [8]. Tetrahydrofuran (THF) is one of the only convenient high volatility solvents that was found to be both miscible with water and a strong solvent for Polysulfone and Polyimide Matrimid® in room temperature casting operations [7].

The most common less volatile solvents include 1-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc) and dimethylforamide (DMF). Each of these solvents mixes very well with water and each has a different degree of interaction with the polymer. Three solvents above are able dissolve a wide range of glassy polymers and able promote a rapid quench while providing sufficient THF to maintain a defect-free selective skin layer. As evidenced by intrinsic viscosity measurements, NMP having the strongest interaction and DMF having the weakest [7]. Wang defined that the NMP and DMAc were the good solvents (higher PVs) used to form membranes, which exhibit a dense skin layer and good selectivity, whereas the porous skin layer tends to form from the poor solvent [10].

iv) Choice of Non-solvent

Introduction of a suitable non-solvent (alcohols or acids) in the polymer solution plays the rule in preparing asymmetric membranes with good gas separation performance and the desired membrane morphology. The addition of a non-solvent to the membrane casting solution brings the initial composition of the casting solution nearer to the precipitation point. Water is frequently used as a non-solvent but other non-

solvent can also be used [10,11,25]. The early stage of phase separation in a polymer/solvent/non-solvent system can be identified by determined the cloud point of the dilute polymer solution based on a simple titration method [10,11,12]. The term "precipitation value"(PVs) has been defined as the grams of non-solvent required to cause visual turbidity in a solution containing of weight known polymer and solvent [10]. With studies on the phase separation of a polymer/solvent/non-solvent system, it able to provide the information for the determination of the membrane dope composition.

Kim had proposed that 3-10wt% of water needed to achieve liquid-liquid phase separation in PSF/THF/water and PSF/NMP/water system [9]. Wang had reported that the precipitation values (PVs) of non-solvents increased in the order $H_2O<EgOH<MeOH<2-PrOH<EtOH<DegOH<1-PrOH<AA<PA$. Water is a much stronger non-solvent compared to the alcohols and acids. With increasing temperature, the PVs of all the non-solvents in the PEI/NMP system were increased [10]. In addition, he also introduced the concept of precipitation values measurement to obtain easily on the phase separation of polymer solution with different non-solvent at different temperatures [14]. Whereas, Han used 1-2wt.% of water content enough to phase separate the 16wt.%PSF/DMF system [13].

Ethanol (EtOH) had been chosen as the non-solvent used in most of research works due to its strong interaction with water and its relatively nature and these aliphatic alcohols are commonly used as non-solvent in spin dopes.

v) Coagulant Used In Wet Phase Inversion

After dry phase inversion, the membranes are coagulated and undergo the traditional wet phase process during which not only creates a porous substructure, but also controls the thickness propagation of the evaporation-induced phase separation occurred at the skin layer and prevents the newly formed ultra-thin skin layer from redissolution, explained by Koros' group [22]. During the stage of wet phase separation, all of the solvent and non-solvent are miscible with the coagulation medium, the non-solvent will diffuse into the polymer solution, whereas the solvent diffuses into the bath and liquid-liquid demixing occurs at the interface of the medium and the cast membrane [27]. Pinnau and some others researchers had demonstrated that the fast coagulation of the cast polymer films resulted in asymmetric membranes with thin, but microporous skin layers supported by substructures containing finger-like macroporous. On the other hand, slow coagulation led to membranes consisting of rather thick dense layer supported by sponge-like substructure [23,24].

Water is the most common coagulant in making asymmetric membranes by the wet phase inversion process; in practice, organic non-solvents for polymers have also been used to adjust the membrane morphology [23-25]. Clausi and Koros had proposed that the solvent exchange procedure was found to have a significant impact on final membrane performance and to achieve optimum performance (i.e., high selectivity and high permeance), membranes were solvent exchanged in MeOH followed by hexane before drying [8]. Temperature of the coagulation bath is also one of the parameters influenced the coagulation rate and substructure forming in the membrane.

5. Optimization of gas separation membrane performance

Effect of shear rate

Only recently, scientists gradually recognize that the rheological conditions established in membrane making also play an important role on membrane performance. The effect of shear induced orientation has been observed in the separation performance of ultrafiltration and gas separation membranes. For example, Chung [16] found that the selectivity increased with increasing dope extrusion rate in hollow fiber spinning while the gas permeation rate reduced. In other words, the membrane spun with high shear had a higher selectivity but a lower permeance due to the greater molecular orientation induced in the high-sheared membranes. In the next report, Chung reported that the relative selectivities increase with an increase in shear rates. Once a certain shear is reached, all permeances increase, while their selectivities decrease with an increase in shear rates [17]. Ismail and Shilton had measured the molecular orientation in the active layer of polysulfone membranes and demonstrated that there was an increased molecular orientation in the high sheared membranes enhanced the gas selectivity [18-20], as shown in Table 1. Shilton et al. had also exhibited the similar trend in their study [21].

Effect of forced convection residence time

In the early 1990s, Koros et al. had developed a theory for skin formation and developed a forced convection technique to produce thin defect-free active layer. At low residence times, skin formation and coalescence of the polymer-rich phase will tend to be incomplete. As the residence time was increased, the skin matures and forms properly. This had reflected in the increase in selectivity and decrease in permeability as the residence time is increased from 0.237 to 0.426s [5]. Wang et al. had demonstrated that the effect of air-gap distance as residence time in the natural convection spinning process for the production of polyetherimide gas separation membranes. He reported that the length of the air-gap plays an important rule in the spinning process and greatly affect the membrane separation performance [28]. Sharpe et al. had reported that the residence time increases, the non-solvent concentration front from the lumen side penetrates deeper into the fiber and eventually begins to approach the outer skin. The advancing presence of water from the lumen side may begin to affect the phase inversion dynamics at the rear of the coalescing outer wall and this may result in an opening of the void-free nascent thin skin structure in that region. Thus, the rear of the skin begins to 'erode', causing the active layer to thin. This mechanism may also begin to cause perforations in the delicate membrane skin. This would account for the increase in pressure-normalized flux and slight decrease in selectivity as the residence time is increased from 0.426 to 0.710s [20].

The residence time in the forced convection process is used to optimize the membrane performance for gas separation. If the membranes were cast at an optimized residence time, then the surface imperfections would be minimized and allowing thinner and defect-free active layer to be produced.

Effect of membrane coating

Coating is a standard procedure, which allows the membrane exhibit permeation properties closer to the inherent characteristics of the membrane itself. The membrane coating is widely used to repair any defects or pores that may arise in the active layer which will rendering membranes useless for gas separation [26]. By blocking these cavities will results in a decrease in permeability but improving the selectivity of membranes performance, as shown in Table 1 [19]. The flat sheet membranes were coated with a highly permeable elastomeric silicone polymer, which have a high permeability and low selectivity elastomer, which simply plugs the defects but plays no part in the separation of gases. Coating may be regarded as a standard procedure to repair gas separation membranes.

Table 1: Effect of shear rate on gas permeation properties of uncoated/coated polysulfone hollow fiber membranes [19].

Module	Uncoated		Coated	
	P_{CO_2}	P_{CO_2}/P_{CH_4}	P_{CO_2}	P_{CO_2}/P_{CH_4}
		Low shear		
LA1	17.6	6.45	14.3	41.1
LA2	17.0	9.70	16.4	34.9
LA3	17.9	2.91	14.4	46.5
LA4	18.4	3.65	13.7	37.5
LA5	17.7	4.82	14.4	33.1
LA6	16.8	5.51	14.6	46.7
LA7	120	1.54	35.7	33.6
		High shear		
HA1	30.5	2.94	32.6	70.0
HA2	58.2	3.11	33.4	73.0
HA3	34.2	6.13	20.8	54.4
HA4	62.1	2.15	22.8	41.6
HA5	72.6	1.91	35.3	82.8
HA6	102	1.62	38.5	83.1
HA7	85.6	1.73	43.4	54.0

P= pressure-normalized flux $\times 10^6$ (cm^3 (STP)/(s.cm^2.cmHg)), measured at 25°C, at pressure differential of 5 bar.

6. Final remarks

Membrane formation is a challenging field of research with still many unexplored aspects. Recent advance in membrane research by Membrane Research Unit, University Technology Malaysia has concentrated in gas separation membrane formation from a ternary systems with using a high potential membrane making polymers and polymer blends. Recently, a development of flat sheet asymmetric membrane from a polymer blends was investigated. Two different polymer resins with suitable ingredients were added to improve the properties of membranes in gas separation application. The membrane will be prepared using the newly designed pneumatically-controlled flat sheet membrane casting system. With the development of a novel polymer blending suitable for membrane making, there are a few framework have been drawn such as like identifying the miscibility of polymer blends, optimizing the initial membrane solution formulation, characterizing the thermodynamic and rheological properties of the polymer blends in order to produce a good membrane. The orientation of the polymer blend molecules is also important in membrane making. All the framework will be used to improve membrane performance in terms of its selectivity and permeability.

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