Precursor Selection for Carbon Membrane Fabrication: A Review

N. Sazali[a,b,c,d*], W. N. W. Salleh[a,b], M. Nur Izwanne[e], Z. Harun[d], & K. Kadirgama[e]

[a]Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Faculty of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[c]Advanced Manufacturing and Materials Centre (AMMC), Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, Malaysia
[d]Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600 Pekan Pahang Darul Makmur
[e]Barrer Centre, Department of Chemical Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, United Kingdom

ABSTRACT

The rapid expansion of gas separation technology since it was first introduced is promoted by the beneficial selective permeability capability of the polymeric membranes. Up to the currently available information, a large number of studies have reported polymeric membranes permeability and selectivity performances for a different type of gasses. However, trends showed that separation of gases using as per in synthesized polymers had reached a bottlenecks performance limits. Due to this reason, membranes in the form of asymmetric and composite structures is seen as an interesting option of membrane modification to improve the performance and economic value of the membranes alongside with an introduction of new processes to the field. An introduction of new polymers during membrane fabrication leads to a formation of its unique structure depending on the polymers. Thus, structured studies are needed to determine the kinetic behavior of the new addition to membrane structures. This review examines the ongoing progress made in understanding the effects of the different polymers additives to the structural modification and the gas separation performances of the carbon membranes. A reduction of defects consisted of pore holes, and cracks on carbon membranes could be minimized with the right selection of polymer precursor.

Keywords: Carbon membrane, polymer blending, polyvinylpyrrolidone (PVP), microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC)

1.0 INTRODUCTION

Various types of new membrane materials have been studied [1-4]. Among them, polyimides received much attention as the choice of precursor due to their rigidity, high melting point, high glass transition temperature (T_g), outstanding thermal stability as well as attractive separation performance [5-7]. Generally, polyimides are produced through the polycondensation of aromatic acid dianhydrides and diamines in which the chemical structure of the constituent monomers could pose significant effects on their final properties. Various classes of polyimides with different dianhydrides such as Kapton with pyromellitic dianhydride (PMDA) [8-

* Corresponding to: N. Sazali (email: melya.jandi@yahoo.com)

10], Matrimid and P84 with benzophenone tetracarboxylic dianhydride (BTDA) [11-13], UIPR and UIP-S with 3,30 ,4,40 -biphenyl tetracarboxylic dianhydride (BPDA) [14, 15], as well as pyralin with hexafluoroisopropylidene (6FDA) [16, 17] have been synthesized and investigated for their suitability as the membrane materials. A recent study demonstrated the effective use of statistical analysis and modeling in the selection of carbon membrane precursors [18]. Table 1 demonstrates the list of carbon membranes fabricated from different polymeric precursors.

The aromatic polyimide type polymer is seen as an attractive option which could enhance the properties of carbon membrane for high gas separation performance. Unfortunately, due to the amorphous structures of the aromatic polyimide type, the sample preparation for traditional characterizations of the carbon membrane derived from this group possess an additional challenge [20, 29, 30]. A study published by Kim *et al.* (2016) demonstrated that polyimide derived carbon membrane was defect-free and could withstand high carbonization temperature without experiencing softening and continuous decomposition [31]. Furthermore, high carbon yields membranes which contribute to a better mechanical strength can be produced with polyimide. Polyimide's mechanical characteristics such as outstanding chemical and thermal resistance contribute to their capability in sustaining structural shapes after high-temperature heat treatment.

Fuertes and co-workers developed carbon membranes from the commercially available polyimide, Kapton, and Matrimid [32]. The membranes were prepared through coating on macroporous carbon supporting material with a polymeric

Table 1 Carbon membranes prepared from various polymeric precursors by previous researchers

Polymer Precursors	Gas performance (Selectivity)	Ref
Matrimid	$CO_2/CH_4 = 38.5$ $C_2H_4/C_2H_6 = 12.3$	[18]
Polyimide, 6FDA/DETDA: DABA (3:2)	$CO_2/CH_4 = 71.5$, $O_2/N_2 = 8.0$	[17]
Polyimide,6FDAmPDA/DABA (3:2)	$CO_2/CH_4 = 118$	[19]
Matrimid	$N_2/CH_4 = 7.7$	[20]
Sulfonated poly (phenylene oxide) (SPPO)	$CO_2/CH_4 = 173$	[21]
Matrimid	$H_2/N_2 = 4.46$, $H_2/CO = 4.70$, $H_2/CH = 410.62$	[22]
Phenolic resins	$O_2/N_2 = 5$, $C_3H_6/C_3H_8 = 15$	[23]
Sulfonated poly (aryl ether ketone), SPAEK	$H_2/N_2 = 220$, $CO_2/CH_4 = 67$	[24]
Polyethylenimine (PEI)	$H_2/CH_4 = 174.6$ $O_2/N_2 = 8.05$ $CO_2/CH_4 = 56.4$	[25]
Perfluoroalkoxy alkanes (PFA)	$H_2/N_2 = 24$ $CO2/N_2 = 11$ $O_2/N_2 = 5.3$	[26]
Matrimid	$N_2/CH_4 = 7.69$	[20]
Phenolic resins	$H_2/N_2 = 65.6$ $CO_2/N_2 = 35.1$ $O_2/N_2 = 4.7$ $H_2/CO_2 = 1.8$ $He/N_2 = 29.7$ $H_2/O_2 = 13.4$ $C_3H_6/C_3H_8 = 18.5$	[27]
Phenolic resins	$H_2/N_2 = 445.6$ $He/N_2 = 413.8$ $O_2/N_2 = 8.7$	[28]

solution followed by subsequent gelation of the film via phase inversion technique. The membranes were then carbonized at different temperatures ranging from 450 to 700˚C under vacuum. It was reported that the carbon membranes derived from Kapton exhibited the permeability of 92 and 45 Barrer for CO_2 and O_2, respectively at

25°C and were more permeable than those from Matrimid. However, the carbon membrane produced from Matrimid precursor possessed better permselectivity of 33 for CO_2/CH_4, 15 for CO_2/N_2 and 6 for O_2/N_2 [32]. The selection of polymer precursor could play an important role in the development of highly selective carbon membrane. In recent years, the use of carbon membranes produced via carbonization of polyimides (P84 copolyimide) for application of gas separation has increased in numbers [33, 34]. This review provides an overview of the progress made in understanding the effects of additives added to the carbon membrane. Different polymer precursors selected are discussed.

2.0 POLYMER BLENDING PRECURSOR

With motivation for a low-cost environmental pollution abatement strategy, fabrication of carbon membrane derived from polymer blends was investigated. Polymer blending is carried out by the addition of the second polymer; which tends to change the membrane morphology. The introduction of polymer blending could contribute to the compositional changes of constituents due to the mass transfer in the system. The use of polyimide, which is a versatile polymer that can be synthesized from a various dianhydride and diamine monomers should be the main attention in future studies on the preparation of carbon membrane.

Polyimide membranes have been the most widely used membranes in carbon dioxide separations with different permeation mechanisms. For instance, polyimide membranes demonstrated outstanding performances at different separations such as CO_2/N_2 and CO_2/CH_4 [34]. The structural properties of polyimide can be improved through

different chemical modifications such as acidization, sulfonation and cross-linking. Interestingly, polyimide-based carbon membranes can be constructed and prepared in different ways to produce distinctive physicochemical properties for specific separation tasks. However, these chemical modifications lead to an increase in the preparation costs of polyimide precursors. On the other hand, polymer blending could be an effective technique in modifying the polyimide precursors at a relatively lower cost to tailor the structure and properties of polyimide carbon-based membrane. The matrix-forming polymer precursor could affect the carbonization behavior of the membranes. Also, the pore structure of the resultant carbons can also be influenced by the selection of blended polymers which can be vaporized or decomposed into gases to leave pores in the matrix (labile polymer). Hence, the suitable pairing of polymer blend preparation plays a crucial role in tailoring its membrane properties for an enhanced gas separation performance.

Recently, Pirouzfar and colleagues prepared carbon membranes from polymer blends of polybenzimidazole (PBI) with different PIs. The membrane preparation conditions were optimized and optimum conditions were achieved at PI/PBI blending composition of 94% with carbonization temperature of 620°C under the pressure of 10-7 Torr. It was reported that the permeability and selectivity of CH_4/CO_2 were 26.7 with 310 Barrer and 77.5, respectively under such conditions. As a result, greater separation efficiency values were achieved with polyimide content in the range of 0.88-0.97 in these blends. The polymeric precursors were sandwiched between two metallic wire meshes and carbonized at temperatures of 600, 700 and 800°C under vacuum (2 mmHg) [35]. The performance of these prepared membranes surpassed several

separation performance trade-offs including CO_2/CH_4 ($\alpha = 203.95$) and H_2/CO_2 ($\alpha = 33.44$) thus exhibited great potential for various industrial applications.

Polymer blend film of PI (6FDA/TMPDA) and azide (2,6-bis(4-azidobenzylidene)-4methylcyclohexanon) was prepared through casting on Si wafer followed by annealing at 250˚C. At carbonization temperature of 800˚C, the film prepared with azide: PI ratio of 10:90 showed high CO_2 permeability and CO_2/CH_4 selectivity, thus can be a potential material in capturing CO_2 [36].

Hossieni and co-workers found that the augmentation in PBI composition in PBI/PI blends enhanced the membrane gas separation performance due to the effect of diffusivity selectivity. The selectivity performance of the membrane was slightly improved with the modification of PBI phase with p-xylene dichloride. On the other hand, significant improvement of the membrane selectivity was observed after cross-linking of Matrimid phase with p-xylene diamine. The outcomes of their study revealed promising features of the developed membranes for gas separation applications with great potential for hydrogen separation and purification applications on industrial scale [37]. Mesoporous carbon membranes can be fabricated by using the blending of polymer such as PI PMDA/ODA with poly(ethylene glycol) (PEG) and N, N-dimethylacetamide (DMAc) as the basic formulation. The polymer blends were then cast onto a glass substrate and imidized at 300˚C followed by further carbonization at 600˚C. An increase in the content of PEG in the blend could increase the pore size of the membrane. Hence, the mesoporous structure of the membrane could be tailored by manipulating the composition of the blended polymers. However, the

average molecular weight of PEG contributed little effect in controlling the pore structure [38].

Table 2 Carbon membrane prepared from Polyimide blends from previous studies

Polymer Precursor	Carbonization Condition			Ref.
	Temp	Heating rate	Gas flow	
Kapton/ PBI	620°C	10 °C/min	vacuum	[39]
Matrimid/PBI	800°C	15°C /min	vacuum	[34]
Poly-diimide /azide	800°C	12 °C/20 min	vacuum	[36]
Matrimid, Torlon and P84 /PBI	800°C	-	atmosphere	[8]
Matrimid/PBI	250°C	20 °C/0.5 h	vacuum	[37]
PI PMDA/ODA /PEG	600°C	3 K/min	Argon	[38]

It is worth to note that most of the polyimide achieved the abovementioned features through proper imidization prior to carbonization process. The completion of the imidization process is crucial to prevent the reaction of labile polymer such as PVP during the gasification process. This helps to avoid the alteration of carbon matrix structure and ensure the effective pore formation. The carbon matrix structure and cross-linking of the labile polymers with PI can be controlled through several process conditions such as imidization conditions, temperature, residence time and atmosphere. Table 2 shows the list of previous studies on the preparation of carbon membrane from polyimide blends with available precursors. However, there are limited studies on blending technology for carbon membrane fabrication. It is important to note that previous study that has been published might be reflected towards these approaches. The next section briefly discussed on the precursor blending technique that involves several promising materials such as

polyvinylpyrrolidone (PVP), microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC), and inorganic material to enhance the carbon membrane performance. Applications of this blending technique are simple but efficient and effective in explaining the carbon membrane properties.

2.1 Polyvinylpyrrolidone (PVP)

Kim and his research group have successfully prepared carbon membranes using aromatic PI and PVP polymer blends [40]. The characteristics of the carbon structure and gas permeation properties of the carbon membranes carbonized at 500 and 700°C were investigated in terms of the molecular weight of PVP (the thermally labile polymer). In an argon atmosphere, PVP underwent complete decomposition first at 350–450 °C, while the thermal degradation of PI occurred at 550–650 °C. It was found that the carbon membranes with a higher molecular weight of PVP pyrolyzed at 550°C exhibited an enhanced O_2 gas permeability from 4200.28×10^{-18} to 6075.405×10^{-18} m2 s^{-1} Pa^{-1} (560 to 810 barrers) and a reduced O_2/N_2 selectivity of 10^{-7}.

A study by Salleh and Ismail (2012) on the preparation of carbon hollow fibre membranes derived from polymer blends of polyetherimide (PEI) and PVP showed that PVP composition strongly influenced the gas permeation properties of the membranes. The membrane prepared from the polymer blends with 6 wt% of PVP demonstrated the highest CO_2/CH_4 and CO_2/N_2 selectivity of 55.33 and 41.50, respectively. Blending a thermally stable and thermal labile polymer is preferable in carbon membrane preparation.

In the recent years, the blending of two polymers with different thermal properties such as PPO/PVP [41, 42], PBI/Polyimides [8, 34], and poly (ethylene glycol)/ phenol formaldehyde novolac resin [43] have been reported for the fabrications of carbon membranes. All reported studies suggest that the addition of blending polymer will enhance the performance.

The pore structure of the carbon membranes prepared via polymer blending method can be controlled by manipulating the vaporization and gasification processes causing the labile polymer leaves pores in the matrix-forming polymer. This manipulation should be conducted before the pyrolysis and carbonization processes of the matrix-forming polymers. PVP has been the most popular thermal labile polymer. The incorporation of a thermally labile polymer such as PVP in carbon membranes could enhance the gas permeability of the membrane [44].

Studies have shown that the transport of gas species across the PVP derived carbon membrane did not only affected by the molecular sieving effect, but the permeation performances were also strongly dependent on the carbonization temperature and PVP molecular weight. The gas permeability of the carbon membranes increased with higher molecular weight due to the enhanced diffusion pathways in the thermally labile polymer region. Hence, the presence of the thermally labile polymer could be effective in controlling the pore structure of the carbon membranes [40, 42, 45]. The precursor with large molecular weight could lead to the formation of bigger pore size on the thicker skin layer. The addition of PVP in the solution could act as the suppressing agent against the formation of macro-pores in the membrane during phase inversion process. It has been proven by Mohsenpour et al. (2016) who reported that PVP exhibits non-solvent characteristics (demixing enhancer)

that suppresses the formation of macropores (demixing hindrance) [46].

PVP has also been used in many technical applications such as for the production of membranes used for dialysis and water purification and acts as a special additive for batteries and ceramics, an aid for increasing the solubility of drugs in liquid and semi-liquid dosage forms (syrups, soft gelatine capsules) as well as an inhibitor of recrystallisation. Lee and research partners developed carbon membrane using PPO/PVP with the PVP concentration of lower than 0.6 wt%. [44]. It was reported that the membrane demonstrated lower gas permeances and enhanced permselectivity due to the decrease in the pore volume and surface area. In conclusion, the introduction of PVP as thermally labile polymer could contribute to controlling the pore structure of the carbon membrane prepared from the polymer blend.

2.2 Microcrystalline Cellulose (MCC)

Microcrystalline cellulose (MCC), which can be isolated from cellulose fibre, has been used as suspension stabilizer and water retainer in cosmetic, food and pharmaceutical industries. In recent years, a significant number of studies have been reported on the fabrication of MCC concerning both bulk structure and surface properties. According to Ummartyotin and Pechyen, cellulose exhibits microwavable properties and is an effective material for various applications due to its outstanding reinforcing capability, excellent mechanical properties, low density and environmental benefits. The development of high performance bio-based composite materials has increase rapidly [47]. However, the applications of MCC in the fabrication of carbon membrane are still limited until today.

Rhim and co-worker investigated the changes in the thermophysical properties of MCC as a function of carbonization temperature [48]. MCC can be converted into porous carbon through carbonization process which then could be used as filtration membranes and adsorbents for air and water purifications. The first introduction of MCC as an additive for the fabrication of tubular carbon membrane could be found in a previous paper [49]. The surface of MCC polymer can be modified through physical and chemical routes by blending with P84-copolyimide. In this study, the feasibilities of MCC (Merck, 50: 9004-34-6) as the additives for various applications has been determined. Figure 1 shows the chemical structure of cellulose as well as the morphological structures of MCC and NCC. Recently, there has been a great deal of research interest in promoting the MCC for industrial commercialization. The use of MCC as pore performing agent would increase diffusion pathway for the transport of gas molecules across the carbon membrane.

2.3 Nanocrystalline Cellulose (NCC)

Recently, nanocrystalline cellulose (NCC) or also known as cellulose nanocrystal (CNC) have garnered great attention in various applications due to its availability of processing economical and agricultural waste-based concept [52]. During the extraction of cellulose, further purification is needed to obtain pure cellulose which is free from lignin, hemicellulose and other impurities. NCC has been applied in membrane field to enhance the membrane properties.

For instance, Laila *et al.* successfully fabricated nanocrystalline cellulose reinforced polyvinylidene fluoride -co-

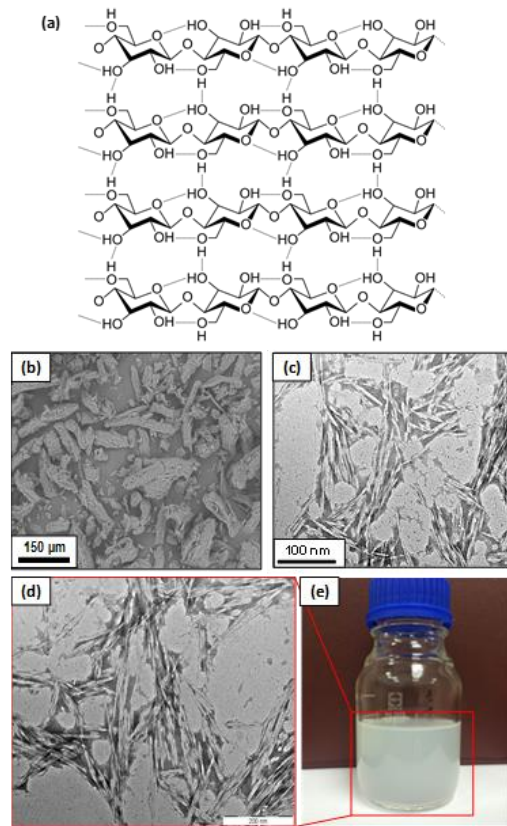hexafluoropropylene (PVDF-HFP) membranes via electrospinning method

Figure 1 (a) Chemical structure of cellulose, (b) FESEM image of commercial MCC, (c)-(d) TEM images of NCC isolated from kapok fiber [50] and recycled newspaper [51] (e) shows a photograph of a dispersion of NCC in water [51]

with improved physicochemical properties for membrane distillation (MD) [53]. The incorporation of NCC in PVDF-HFP matrix improved the tensile strength and Young's modulus as well as reduced the pore size distribution of the membranes. Besides, polylactide–polyglycolide/cellulose nanocrystal (PLGA/CNC) composite nanofiber membranes which have high mechanical properties are the new promising materials for skin tissue engineering [54].

A recent study by Mohammed and colleagues [51] showed that NCC could be fabricated as self-assembled NCC

membrane for water treatment application. The incorporation of NCC in the fabrication of carbon-based membranes could improve the thermal and mechanical properties of the membranes [49]. NCC has been used as pore performing agent due to its low glass temperature properties. Satyamurthy and co-workers reported that the incorporation of inorganic particles into the polymer precursor resulted in better separation performance [55]. It also consists of nano-gaps between the matrix and nanoparticles and is high in mesopore volume.

The addition of additives in the polymer solution would cause kinetic and thermodynamic variations during the phase inversion process. It is known that the crystallinity of the dope increases when the demixing of the blending dope is delayed. The additives which act as the demixing enhancers fasten the phase inversion thus reducing the crystalline structure of the membrane precursor. Hence, the finger-like macrovoids could be stretched down from the beneath of the membrane skin to the bottom of the sub-layer. By increasing the optimum additive composition, the gas permeation of the membrane becomes lower rather than increase, indicating that the kinetic effects become more dominant than the thermodynamic enhancement. The presence of additives does not only disturb the polymer chain packing and increases the free volume, but also facilitates the transport of CO_2 at the same time which results in the membrane performance improvement.

2.4 Inorganic Material

Rao *et al*. [56] prepared the polyetherimide (PEI)/multi-wall carbon nanotubes (MWCNTs) composite carbon membrane via spin coating method using PEI as the main precursor.

The results achieved O_2, CO_2 and H_2 permeances of 74.5, 88.0 and 545.5 mol m^{-2} s^{-1} $Pa^{-1} \times 10^{-10}$, respectively. The membrane precursor was carbonized at 500°C, and the prepared carbon membrane exhibited CO_2 permeability of 1463 Barrer and O_2/N_2 selectivity of 24.16 at 26°C. It was also found that MWCNTs could improve gas diffusivity by increasing the micropore volume, even when the MWCNTs were not well dispersed in carbon membrane.

In 2014, Li and research partners successfully prepared a carbon interlayer between the thin separation layer and carbon membrane support via the soft-templating method. It was reported that the OMC layer could effectively minimize the surface defects of the support with large pore size and enhance the interfacial adhesion of the thin separation layer to the support. Besides, they also introduced the ordered and uniform mesoporous channels which further enhanced the gas permeation properties of the supported carbon membranes. The supported carbon membranes were obtained via one-step coating on the support modified by the OMC interlayer and demonstrated the O_2, CO_2 and H_2 permeances of 74.5, 88.0 and 545.5, respectively. [57]. Table 3 shows the list of studies of various polymer/inorganic based carbon membranes.

The mesoporous silica/carbon composite membranes were successfully fabricated by incorporating the SBA-15 or MCM-48 into the microporous carbon matrix. These novel membranes exhibited better gas separation performance compared to the ZSM-5/C and zeolite T/C composite membranes in terms of the permeability of CO_2 and selectivity for the separations of CO_2/CH_4 and CO_2/N_2. This was attributed to the presence of additional pore channels in the mesoporous silica/carbon composite membranes which give lower gas diffusion resistance. Higher gas selectivity was also achieved due to the disordered ultra micropore networks in the carbon matrix. Hence, these new membranes could be of great potential for the applications of CO_2 separation and recovery from natural gas and exhaust gases from coal-fired power plants and chemical factories [58].

Table 3 Polymer/inorganic-based carbon membrane

Polymer/ inorganic	Carbonization Temp.	Performance	Ref
Polyetherimide (PEI)/MWCNTs	500°C	CO_2 permeability: 1463 Barrer O_2/N_2 selectivity: 24.16	[56]
OMC membranes	800°C	O_2, CO_2 and $H2$ permeances of 74.5, 88.0 and 545.5	[57]
Silica/PAA	373, 473 & 623 K	CO_2/N_2= 66 CO_2/CH_4= 170	[58]
Phenolic resins/ boehmite (γ-AlO(OH)) and Ag	550°C	C_3H_6/C_3H_8=38	[59]
Mesocarbon microbeads/ carboxymethyl cellulose	700 °C	Pore size becomes smaller, Pore distribution becomes narrow	[60]
PFAs synthesized by oxalic acid and iodine catalyst	900 °C	Performance of PFA-I > PFA-OA	[61]

Recently, Teixeira and co-workers studied the preparation of composite carbon membranes from the phenolic resins loaded with two different inorganic fillers (boehmite (γ-AlO(OH)) and silver (Ag)) [59]. After carbonization, the Ag loading enhanced the performance of the carbon membrane for several gas pairs of interest especially the separation of C_3H_6/C_3H_8 in which the permselectivity of C3H6/C3H8 increased from a maximum of 15 to 38.

Zhang and co-workers introduced the impregnation method to adjust and control of porous structure in the inner face of a tubular carbon membrane (TCM). It was reported that the increase of impregnant concentration and impregnation time resulted in smaller pore size and narrower pore size distribution of the TCM [60]. Song and co-workers prepared the carbon membranes from two types of PFAs synthesized with different catalysts, oxalic acid, and iodine. Those PFAs were composed of similar functional groups with different cross-linking styles, as indicated by their similar FTIR spectra and slightly different TG curves. The resultant carbon membranes exhibited different microstructures and gas permeability. The PFA-OA carbon membrane possessed high carbon yield, smaller d002 value (interlayer spacing) and short, slightly irregular but roughly parallel fringes. In contrast, the PFA-I carbon membrane demonstrates higher gas permeability and lower gas permselectivity [61]. As a conclusion, the blending of polymer/inorganic membrane will reduce the cost of the production as well as enhanced gas separation performance.

3.0 CONCLUSION

Carbon membranes derived from several additives were discussed for several gas separation. The presence of additives in carbon membranes provides superior pore structural properties due to the decomposition of additives during carbonization process. The permeation results of all the carbon membranes showed that the molecular sieving mechanism controlled the gas transport. The addition of NCC, MCC and PVP to the precursor as an additives produced better gas permeation performance as compared to the pure

precursor. The thermally labile polymer can control the overall pore structure of carbon membranes by fixing carbonization temperatures as well as precursor composition. The addition of additives such as cellulose makes the carbon membranes restrict the transport of easily condensable gases (e.g. CO_2). Consequently, varying different types of additives might lead to the different pore size, pore volume and diffusional pathway in carbon membranes.

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