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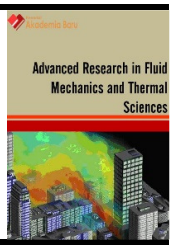

PI/NCC-Based Tubular Carbon Membrane: Influence of Aging Times Towards Oxygen Separation Performance

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ABSTRACT

Tubular carbon membrane was prepared from carbonization of P84 co-polyimide (PI) and nanocrystalline cellulose (NCC) which had been carbonized under Argon atmosphere at 800°C with a heating rate of 3°C/min. The resultant TCMs were aged for a specified duration (new, three days, one month, and three months) to study the effects of aging times on the oxygen separation properties (permeance and perm-selectivity) of TCMs. The investigation finding reveals that the aging times could be a factor that affects the transport properties of the fabricated membrane. The pores of the fabricated TCMs samples tend to shrink over time to reach a stable thermodynamic state. The results also showed that newly fabricated TCMs (no aging) possess the highest gas permeance and perm-selectivities over the aged TCM samples. The highest selectivity was achieved at 9.29° 2.5.

1. Introduction

Blending of PI with NCC is a promising approach in the fabrication of robust tubular carbon membranes (TCMs) for oxygen separation applications. In comparison to PI/NCC polymeric membranes, TCMs has been shown to have higher selectivity [1]. Till date, several investigators have described the fabrication of carbon membrane using different types of polymeric precursors [1-4]. Principally, a carbon membrane is composed of a thin film of porous carbon with a thickness below 10µm that possessed micropore size below than 1 nm [5-7]. The separation capability of carbon membrane is based on the adsorption characteristic and molecular sieving which relies on the membranes effective micropore size (EMS). In gas separation application, carbon membranes with EMS below than 0.5 nm are known as Molecular Sieve Carbon Membranes (MSCM) while carbon

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membranes with EMS in the range of 0.5-1 nm are known as Adsorption Selective Carbon Membranes (ASCM). A small change in the EMS can significantly influence the separation properties and the permeation rate of the carbon membrane [8].

Lately, most of the investigators have concentrated their efforts on developing new approaches in the production of TCMs with improved gas separation performances. In 2006, Lee and co-workers steered research on poly (2,6-dimethyl-1,4-phenylene oxide (PPO)-derived carbon membranes and their gas permeation performance [9]. In their study, they found that the molecular sieving is the dominating mechanism governing the gas transport through their PPO-derived carbon membranes. One of the significant synthesis parameters affecting the permeation performance of carbon membrane is the carbonization temperature [10-12]. For instance, at low temperature, the pore structure was developed, and their characteristic values increased with increasing temperature up to a certain threshold where further elevating the temperature will deteriorate their particular values. These derived carbon membranes from PPO show higher values with correlation to the permeability versus permselectivity and excellent performance as compared to polyimides-derived carbon membranes.

Zhang and co-workers have employed an impregnation method to adjust and control the porous structure in the inner face of TCMs. In their study, the pore size distribution of TCMs was examined by modifying the impregnation time and concentrations. From the obtained SEM micrographs, they found that the pore defects on TCMs surface can be repaired through impregnation treatment. Also, the resultant data on the distribution of micropore size shows that the pore size becomes narrower and smaller as the impregnation time and concentration increased. These results proved that the impregnation conditions could affect the structural parameters of the TCMs [13]. According to Briceno and co-workers, TCMs can be fabricated through a single-step polyimide coating method as a carbon layer precursor without needing a prior modification of TiO_2 macroporous support. Membranes produced by this method and carbonized at 650°C showed to have excellent gas selectivities of 4.46 for H_2/N_2, 4.70 for H_2/CO_2 and 10.62 for H_2/CH_4 which is higher than Knudsen theoretical value. In the hydrogen permeation test, the permeance results also showed to have improved value, which is more than 9.82x10-9 mol/(m^2.Pa.s) [14]. Despite their chemical and thermal resistance, fabricating a stable TCMs still possess a challenge. TCMs permeation systems are vulnerable to humidity and oxidation [15]. Carbon membrane appears as an amorphous nanoporous skeleton with a sharp pore size distribution (critical size ranging from 0.3 to 0.7 nm) [16]. This structure is composed of small and poorly aligned nanocrystallites with their faces comprised of graphene layers. Several nanocrystallite edges can be terminated either by thermally stable C-H groups or oxygen surface groups. Others are believed to be more reactive as they can be terminated either by relatively stabilized π–σ electron pairs or by free radicals which are commonly known as active sites. The precursor and the history of thermal treatment can be used to identify the quantity and the nature of active sites on the carbon surface [17]. Exposure of these active sites with oxygen molecules in the air could lead to the formation of oxygenated functional groups on the membrane surface even at room temperature. Thus, it can be said that the oxygen chemisorption can reduce the open porosity towards gas transport and the results obtained offers additional limitation towards diffusion which known as carbon aging.

A few numbers of investigation have been conducted in highlighting the aging factors on TCMs performance. As carbon being exposed to air, an irreversible chemisorption of oxygen would happen [18]. Small changes in the effective pore size constriction of carbon molecular sieve (CMS) can severely influence the permeability of an adsorbing gas molecule. Moreover, the presence of oxygen chemisorption and strong adsorption by pore constrictions in the pore system can lead to very low diffusivity. It was also reported that the complete removal of chemically bonded oxygen could be

achieved by performing heat treatment at 800°C under an inert environment. Facing the demands of efficient gas separation [19], the selection of membrane materials and membrane fabrication techniques is very important after considering the adsorption and transport properties of the gases [8]. Currently, there are very limited works studying the relationship between membrane aging and membrane performance.

Broad study on physical aging has been transpired mainly on glassy polymers, however aging in carbon membrane has beforehand centered essentially on adsorption: either physical adsorption of water or chemical adsorption of oxygen, as well as the nature of pore make-ups [20-24]. Physical aging gives off an impression of being the essential driver for quick variations of transport attributes in initial times after membrane fabrication for tests got from high fractional free volume forerunners [25]. Tentatively, in this examination, for the examples considered, the majority of the above aging factor concentrates on maturing times as huge factors through the sharp exploratory outline. TCMs pores remain accepted to age comparable to the glassy polymers' ''unrelaxed free volume''. After some time, these pores tend to recoil keeping in mind the end goal to accomplish thermodynamically more steady states. Menendez and Fuertes studied the aging behaviors of carbon membrane at the different atmospheric condition. From their study, the carbon membrane exposure to both humid and dry atmospheric condition had resulted in rapid loss of permeability. The long-time membrane exposure towards air has reduced the membrane separation ability by narrowing the pore structure, thus increasing the diffusion resistance of gas. Menendez and Fuertes [8] reported that freshly prepared membrane showed excellent separation of O_2/N_2, but later experiencing poor separation after being kept in ambient conditions. Physical aging can be defined as the notable change in polymer properties in response to parameters such as storage time and constant temperature without external factors influence [18]. On the contrary, carbon aging happens due to the presence of oxygen groups on the carbon surfaces via oxygen-carbon interaction during the membrane exposure towards air at room temperature [8, 16, 26]. Therefore, this work focuses on the separation properties of ceramic tube-supported TCMs prepared via the carbonization of PI/NCC [1].

2. Methodology

2.1 Materials

PI (ρ = 1.31 g/cm^3, Tg = 315 °C) was supplied by Sigma Aldrich. N-methyl-2-pyrrolidone was obtained from Merck Millipore. NCC was self-synthesized from the newspaper [27] whereas a porous tubular ceramic (TiO_2) support (length = 8 cm, thickness = 3 mm, pore size = 0.2 µm, porosity = 40-50%) was procured from Shanghai Gongtao Ceramic Co., Ltd.

2.2 Dope Preparation

15 wt.% of PI was dissolved in NMP under constant stirring at 80°C, followed by a gradual addition of 7 wt.% of NCC. The solution was used to form a uniform layer of polymeric precursor over the external surface of the tubular support as reported in our previous study [28]. The dope solution was stirred for 24 hours and followed by sonication for degassing purposes.

2.3 Formation of Tubular Polymeric Precursor Membranes

The supported polymeric membranes were prepared via dip-coating of the tubular support into PI/NCC dope solution for 45 minutes, followed by drying at 80°C for 24 hours in an oven.

Subsequently, the membranes were equilibrated in methanol for 2 hours before finally being dried at 100°C for 24 hours.

2.4 Formation of Carbon Membranes

The porous tubular ceramic alumina was coated via the dip-coating method using PI/NCC dope solution. The tubular then dried in an oven overnight at 80°C before it was heat treated in Carbolite's horizontal tubular furnace. Before carbonization, the polymeric membranes were stabilized at 300°C for 30 min under 200 ml/min Ar gas flow at a constant heating rate of 3°C /min. The purpose of the stabilization stage is to avoid the melting of the membrane when it undergoes the carbonization stage. Later, the stabilized membranes were carbonized at 800°C for 30 min with the sweeping of 200 ml/min flowing Ar at a heating rate of 3°C /min. After cooling, four samples at different aging stages were prepared by manipulating aging time ranges (fresh, three days, one month, and three months), respectively.

2.5 Membrane Characterization

Scanning electron microscopy (SEM) was used to observe the membrane structure and morphology. Before the observation, the samples were coated with gold. By employing TM3000, Hitachi SEM with a potential of 10 kV was used to capture images. Fourier transform infrared (FTIR) spectroscopy (PerkinElmer, L1600107) was used to determine the functional groups.

2.6 Pure Gas Permeation Measurements

The TCMs were tested in gas permeation system as described in our previous study [17]. A 14-cm length tubular stainless-steel module was used to place TCMs, fitted with a rubber O-ring. Next, pure N_2 (0.364 nm) and pure O_2 (0.346 nm) were channeled into the prepared module at a pressure of 8 bars. The permeance, P/l (GPU) and selectivity, α of TCMs were determined by respective equations as described beforehand [1, 29]. Typically, the aging of membranes was categorized into two types which are the physical and chemical aging. Up to now, despite the sorption and chemisorption studies on aging, there are insufficient studies available on the physical aging of CMS materials [16, 21]. As such, the research related to the physical aging of polymeric membranes have gained the interest of many investigators [22].

3. Results

3.1 Morphological Structure Analysis

The membrane surface and cross-section prepared at different aging times were observed using SEM. From the observation, it can be evidently noticed that the carbonization process has removed the functional group, the sp^2-hybridized condensed carbon sheets have taken into shape, and the pores would form from those pressing imperfections. The performance of PI/NCC carbon membrane under various aging times are deliberated in Figure 1. A few active carbon atoms are seen in the pores where it can react with a volatile molecule such as water as shown in Figure 1(a).

Figure 1(b) shows the fresh PI/NCC CM while Figure 1(c) to (e) shows the CM with one day, one month, and three months aging times, respectively. CM with the most extended aging times (3 months) shows membrane with the most defect, both on the surface and cross-section micrograph. The surface and cross-section were rough with the presence of defect formation. This morphology

evaluation suggested that fresh PI/NCC CM structure is the preferable CM which contributed to the better selectivity performance.

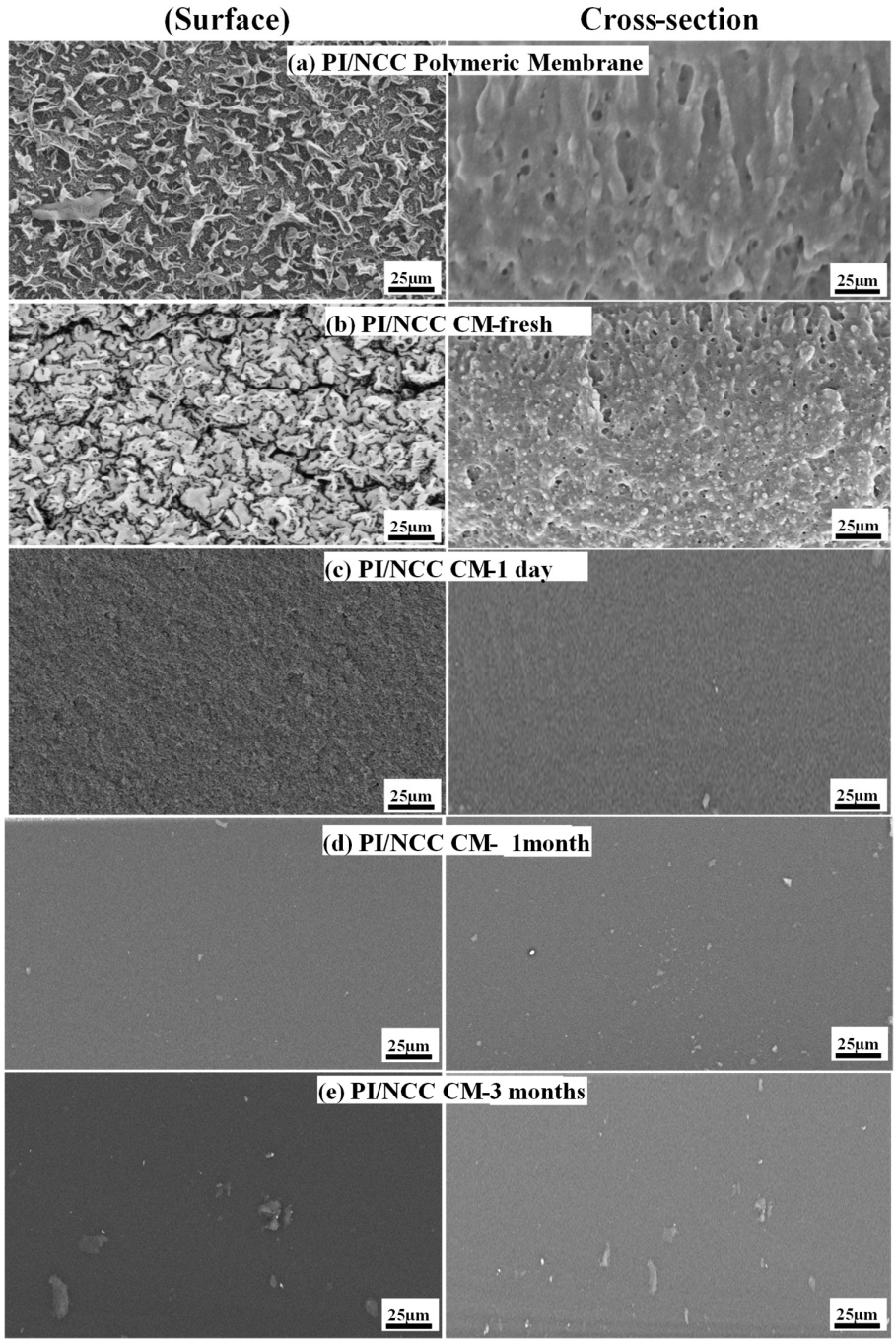

Fig. 1. Surface and cross-section micrograph under various aging times for (a) PI/NCC polymeric membrane, (b) PI/NCC CM-fresh, (c) PI/NCC CM-1day, (d) PI/NCC CM-1 month, and (e) PI/NCC CM-3months

3.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of all the membranes are shown in Figure 2. It can be observed that PI/NCC polymeric membrane spectrum shows the presence of amorphous structures. In comparison with the other PI/NCC carbon membrane samples, the highest peak appeared in the polymeric membrane has been removed due to the removal of non-carbon elements during carbonization process and leaving only the carbonaceous elements in the crystalline state. Eight peaks can be noticed in all PI/NCC carbon membranes which are 897, 1053, 1247, 1505, 1595, 1730, 2918 and 3333 cm-1. The presence of a peak at 897 cm-1 indicates the association of O-H and Cl-H bending while 1053 cm-1 peak indicates the presence of C-O-C pyranose ring stretching vibration in the membrane. According to Mohamed and co-workers [27], the peak discovered at 1247 cm-1 represents the acyl-oxygen CO-OR stretching vibration in hemicellulose PI/NCC polymeric membrane. Another peak that appeared at 1505 and 1595 cm-1 is referred to C=C stretching and C=C unsaturated linkages of the aromatic rings that appeared in the PI/NCC polymeric membrane lignin, respectively. A peak that appeared at 2918 and 3333 cm-1 represents the C=H stretching and the existence of intermolecular hydrogen bonds among the cellulose samples, individually.

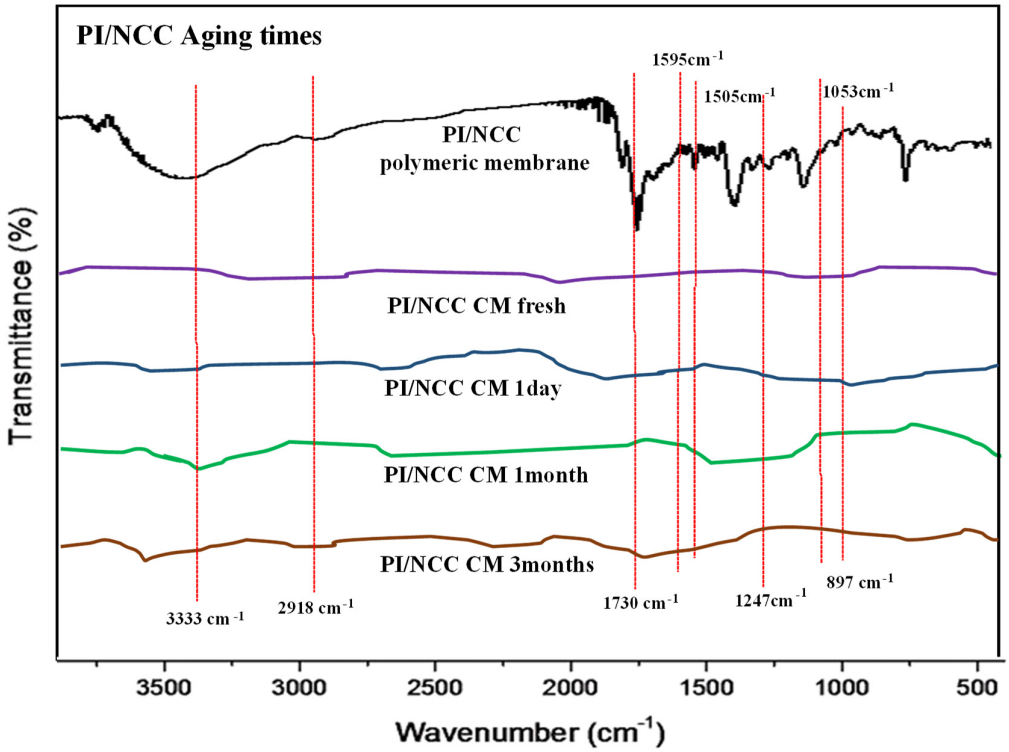

Fig. 2. FTIR analysis of (a) PI/NCC-based polymeric membrane, PI/NCC CM (a) fresh, (b) 3days, (c) 1 month, and (d) 3 months prepared using different dope formulation

As can be seen in Figure 2, the polymeric membrane that underwent high heat treatment faces a reduction in peaks depending on the aging times applied, and the vilest scenario happened in the fresh PI/NCC carbon membrane which showed the most peaks. These are because the spectrum of the fresh membrane showed almost a straight line indicating complete conversion of the polymer into carbon materials. These also happened due to the elimination of N, O and H elements during the carbonization process as well as the removal of the existing functional groups by leaving only the carbon elements. From the results, it can be concluded that the variation in aging times applied on

the PI/NCC carbon membranes could influence the rearrangement of the morphological structures of the carbon membranes and this differs with PI/NCC polymeric membrane.

3.3 Gas Permeation Measurements

Polymeric and carbon membrane of PI/NCC-based TCMs were synthesized at different aging times (freshly-prepared, three days, one month, and three months) to analyse the changes in gas permeation properties. The further introduced heat treatment process is expected to interrupt the hydrogen bonds between polymer chains which results in intra- and inter-molecular cross-linking and endorsing to more open structure [35]. The gas permeation properties of the PI/NCC polymeric and carbon membranes was calculated using gas permeation test at 8 bars in room temperature. The permeation measurement was done with pure gases composed of different molecular sizes, which were N_2 (3.64Å), and O_2 (3.46Å) for different membrane aging times. Table 1 shows the properties of gas permeation of all polymeric and PI/NCC-based TCMs. It was observed that the selectivity of membrane drops significantly after long storage duration. As can be seen in Table 1, the fresh PI/NCC CM possess high O_2/N_2 selectivity at 9.29±2.54 but lowest permeance of N_2 at 3.22±3.21 and O_2 at 29.90±2.98, respectively. After being aged for 3 months, the carbon membrane exhibited two times higher O_2 permeation than fresh counterpart PI/NCC CM. It appears that the water had reacted with the active carbon locales of the PI/NCC CM fresh membrane and formed oxygen functional groups that reduce the pore size.

Table 1
Gas permeation performance of carbon membranes produced from aging times

Sample	Carbon membrane		
	Permeace		Selectivity
	N_2	O_2	O_2/N_2
PI/NCC Polymeric membrane	0.70 ±5.23	0.77±3.22	1.10±5.12
PI/NCC CM fresh	3.22±3.21	29.90±2.98	9.29±2.54
PI/NCC CM 1 day	3.96±1.27	31.44±4.12	7.94±2.41
PI/NCC CM 1 month	7.01±2.83	43.90±3.61	6.26±3.28
PI/NCC CM 3 months	12.33±1.76	48.21±2.87	3.91±3.85

During the aging times, the observed performance of the membrane was reduced due to the adsorbed water molecules into the membrane structure. However, it is believed that the removal of these water molecules can recover the performance of the TCMs, in term of gas transportation and also separation properties. Also, the features of the carbon membrane can be partially regenerated after the Ar treatment at 800°C, which could increase the surface stability. However, the microporosity of the membrane will be affected by the introduction of severe heat treatment either through annealing or carbon gasification. Moreover, the impact of different aging time on room temperature dried membrane is also studied. Aging times was translated in term of permeability loss and the addition of simultaneous selectivity, a customarily observed as a trade-off. Table 1 demonstrates the losses over O_2 permeability which outweighed those additions in O_2/N_2 selectivity at different aging times of the PI/NCC TCMs. It may be imperative to note that permeability of PI/NCC TCMs was obtained at two stages. The initial phase is recorded and characterized by rapid permeability decrease for ~30 days and used to determine the excess nonequilibrium free volume. At this point, previously termed as “aging-knee,” slower and more gradual permeability reduction occurs due to the revamp of the “intrinsic” microporosity. The final phase is slower because of those confined mobilities of the PI/NCC TCMs chains profound over their glassy states. Significant

redistributions in free volume ensued in the last phase is denoted by extending the permeability loss and selectivity gain over long times. However, the reduction of gas diffusivity and solubility coefficients was due to the densification of the microstructure amidst the physical aging. These, in turn, reduce the permeability and indicates that the overall process is dominated by diffusion which is implied by the more substantial modifications in both diffusivity and selectivity.

Adequate research focusing on customizing the carbon atomic sieve characteristics for higher perviousness and selectivity is required. Also, till date, the very minimal effort has been put into improving the strength of carbon membrane materials [36]. The lack of work in this area is to some extent was contributed by the inflexible quality of TCMs membranes in addition to their improved thermal and chemical endurance contrasted with polymeric substances [37]. Therefore, successful execution of TCMs membrane technology is vital to comprehend the operational strength of TCMs membranes to develop the handling and processing amidst manufacturing and operation properly [38-43].

4. Conclusions

From this study, the influence of aging times on PI/NCC carbon membrane was investigated. The critical points of the findings can be summarized as follows:

1.The pores of the fabricated TCMs samples tend to shrink over time (the longer the aging time, the smaller pores are produced) to achieve thermodynamically stable states.

2.Fresh TCMs (shortest aging time) possesses the lowest gas permeance with N_2 of about 3.22 ± 3.21, and with O_2 of about 29.90 ± 2.98, respectively. The highest selectivities over other TCM samples (longer aging time) showed a permeation value of 9.29 ± 2.54.

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