



Gas Separation Performance through Carbon Membrane: The Effect of Polymer Composition

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Mohd Syafiq Sharip¹, Norazlianie Sazali^{1,2,*}, Ahmad Shahir Jamaludin³, Mohd Nizar Mhd Razali³

¹ Faculty of Mechanical & Automotive Engineering Technology (FTKMA), Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia

² Centre of Excellence for Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

³ Faculty of Manufacturing & Mechatronic Engineering Technology (FTKPM), Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia

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ABSTRACT

A comprehensive requirement in terms of efficient strategies in collecting reasonably high purity of H₂ is predicted due to the development of hydrogen (H₂)-based economy. The purpose of a H₂-selective membrane is to exploit the high diffusivity features of H₂ and also to limit the consequence of lower solubility. Owing by its highly permeable and selective characteristics, carbon membranes provide great potential in gas separation industry. Hence, the objective of this study is to examine the effect of carbonization parameter, in particular the composition of polymer on the properties of gas separation. Matrimid 5218 was used as a precursor for the fabrication of carbon tubular membrane to manufacture a carbon membrane with high quality through the process of carbonization. The surface of tubular ceramic tubes was coated with polymer solution via dip-coating technique. The dip-coating method provides an excellent potential in the manufacture of defect-free carbon membrane. The resultant Matrimid 5218-based carbon tubular membranes were characterized in terms of structural morphology using scanning electron microscopy (SEM), chemical structure using Fourier transform infrared (FTIR), thermal stability, and gas permeation properties using pure gas permeation system. The best formulation for Matrimid 5218-based carbon tubular membrane fabrication was shown by the polymer solution containing 15wt% of Matrimid 5218. The highest H₂/N₂ selectivity of 401.08±2.56 was achieved by carbon membrane carbonized at 800°C with 2°C/min of heating rate.

Keywords:

Hydrogen separation, carbon membrane, Matrimid 5218 type polyimide, and polymer composition

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1. Introduction

Despite the fact that the idea of membrane utilization had been made earlier, the practical and effective use of hollow fiber membranes with small diameter was introduced only in the late 70s

* Corresponding author.

E-mail address: azlianie@ump.edu.my (Norazlianie Sazali)

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before DuPont pioneered its implementation. Nonetheless, the yields of hollow fibers of the first generation were very limited to satisfy the necessity for economical gas separations. Monsanto Co. addressed the problem by producing multicomponent polysulfone hollow fiber membranes for the recovery of hydrogen. Restriction of the discerning and dense fiber areas to a very limited space has greatly improved the transport properties of the fibers. The utilization of such asymmetric membranes for hydrogen recovery from ammonia purge gases has been effective in industrial-scale. Subsequently, Separex Corp. created the Separex[®] spiral, a wound cellulose acetate membrane targeting the same types of separation as previous technology, besides purification and dehydration of natural gas [1]. Cellulose acetate membranes exhibit great performance mainly because of their high resistance to impurities from hydrocarbon. Membrane technology was typically found in the mid- 1980s to advance other applications such as hydrogen recovery from recycling of refining gas. In Japan, a polyimide membrane with the best solvent and heat resistance characteristics was initially introduced by Ube. The first application of this membrane was made by Seibu Oil's Onoba City refinery.

Recently, the economic development of H₂ is the main factor contributing to the growing interest in hydrogen recovery, which has been seen as the key option for energy sources, benefiting the industrialized nations with various energy-intensive industries. Proton-exchange membrane (PEM) fuel cell is a strong candidate for power generation to replace the combustion of fossil fuel [2]. PEM uses hydrogen as the basis for the transformation of chemical energy into electrical energy. There are several remarkable benefits of the aforementioned fuel cells such as high fuel efficiency compared to internal-combustion engines, almost zero carbon monoxide, NO_x or HC emitted, and low level of carbon dioxide generated [3]. Indeed, effective distribution of hydrogen supply is necessary for these fuel cells to be widely implemented. The potential for gas separation membranes to be deployed in this process is essential. Solution-diffusion mechanism is ineffective to remove completely the trace contaminants which restrict the economic competency of the polymeric substance, especially for high purity products. Nevertheless, the demand for further enhancement in the application of membranes for the separation of hydrogen gas is rational.

The membrane-based separations process plays a very important part in various industrial processes for instance in the gas separation process. A great deal of effort is needed to develop new membrane formulations with great features in terms of selectivity and permeability. At the present time, carbon membranes are acknowledged as a viable option to be used in gas separation mainly because of their prominent separation properties. In fact, owing by its excellent selectivity and permeability properties, multiple reports have presented evidence that carbon membrane is a strong candidate for gas separation [4]. In addition, carbon membrane shows a superior performance without an increase in energy and cost of processing, as the cooling step is skipped [5]. The increase in ultra-micro porosity and free volume are prompted by the orientation dislocation of aromatic micro in glass-like matrix. Typically, microspores are almost slit-shaped with dimensions of the porous mouth as wide as the small molecules diameter [6]. The mechanisms of gas transport rely on both membrane and permeate properties. There are a few of separation mechanisms that are considered important for the process of gas separation, which are solution and Knudsen diffusions, and the molecular sieve effect. The above-mentioned mechanisms are found to be appropriate for material systems and limited number of gases. The solution-diffusion mechanism operates in line with the concept of high diffusion rate and high solubility of mixture component, in which it will dissolve and then diffuse through the membrane regardless of the component size. Moreover, solution-diffusion membranes are comprised of free volume sites that are not occupied by polymer chains because of their restricted motion and packing density [7].

The components are transported through the membrane by uninterrupted movement of the transient free volume gaps close to the feed side with those close to the permeate side induced by the thermal motion of segments of the polymer chains. The previous works reported that the development of various mechanisms can be accomplished by transportation of gases through the porous membrane. These works provide a graphical diagram for mechanisms of gases permeation through porous and dense membranes [8]. Following the advances in the technology enhancement, separation requirements and its application, the requisite for new membrane materials is crucial to achieve the promising productivity and separation effectiveness. The morphology of the final membrane obtained is remarkably distinct, in which the main differences are from the properties of materials and process conditions.

The pore size of carbon membranes must be greater than 30 Å in the pore diameter range to achieve a superior selectivity [9]. In its carbon matrix, carbon membranes have constraints which reach molecular dimensions of absorbing species [10]. The molecular sieve selectively permeates the three-dimensional molecules smaller than the size of planar shape with small cross-sections or slit widths [11]. Thus, gas molecules of the same sizes will be effectively separated by carbon membranes. The typical molecular sieving transport mechanism is shown in Figure 1. Through this mechanism, the separation occurs when the smaller molecules from the gas mixture pass through the pores while the larger molecules are simultaneously blocked. It shows the high permeability of the gas mixture and components selectivity [12].

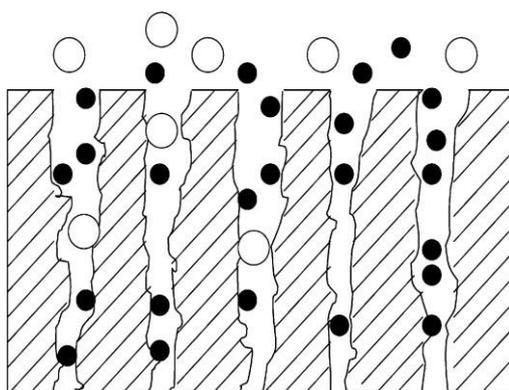


Fig. 1. Typical mechanism of molecular sieving transport [12]

In the early 1970, the concept of membrane for gas separation was discovered through the formation of polysulfone and cellulose esters [13]. The manufacturing process of inorganic membranes is usually done using pyrolyzed carbon, metals or ceramics. There are numerous studies reported on the compression of micro porous carbon particles into stainless steel plugs and the analysis of diffusion coefficients for various gases for example hydrogen (H₂), nitrogen (N₂), argon (Ar), helium (He), and krypton (Kr) [14]. Later in the 1980s, the growing interest in the production of carbon membranes started when previous researchers successfully fabricated the crack-free carbon molecular sieve membrane from cellulose hollow fiber membrane carbonization [15]. Since then, the number of research conducted and publications produced related to carbon membranes have been increasing [16]. In contrast to polymeric membranes, carbon membranes have higher selectivity and permeability; however, large-scale production of carbon membranes involves high cost and complicated process [17]. Therefore, the trade-off between good selectivity and permeability of membrane with the options of producing low-cost membrane is very much required.

The utilization of carbon membranes correlated to gas separation can be found in various industrial operations. The competency of gas separation process depends on the permeability and selectivity of a membrane material.

There are two types of membranes according to their selectivity and density, namely porous membranes and nonporous membranes. Porous membrane has a rigid and highly voided structure which can facilitate the distribution of inter-connected pores. The separation of substances via porous membrane is generally a function of both of membrane and permeates characteristics, in particular the pore size distribution and the molecular size of membrane polymer. Fundamentally, membranes with micro porous structures can effectively separate molecules with a large size difference. A porous membrane is relatively comparable to the normal filter in terms of its function and configuration. In gas separation, porous membranes have high level of density with low selectivity value. Micro porous membranes characterization can be classified in accordance to membrane porosity, average diameter of pore, and membrane asymmetry. They show distinctive properties of carbon dioxide permeability with high selectivity towards methane, carbon dioxide and nitrogen. Carbon membranes consist of amorphous porous structure created by the evolution of volatile gases during the carbonization of polymeric precursor. Meanwhile, the carbon membrane porous structure consists of apertures or pores of near molecular dimension identical to the diffusing gas molecules [18]. The pore system of carbon membrane is typically non-homogeneous because of the presence of large opening in the midst of the unusual conditions.

In accordance to its configuration, the structure of inorganic membranes can be divided into two primary groups, namely dense (non-porous) inorganic membranes and porous inorganic membranes. Dense or nonporous membranes imply prohibitive selectivity properties although the ratio of gas transport on the medium is typically small. It is worth to note that non-porous or dense membrane can separate permeants with similar size if their solubility in the membrane differs substantially. Carbon membrane with superior selectivity and permeability along with the excellent properties in terms of mechanical and chemical, has the possibility to be acknowledged worldwide. Previous studies stated that the asymmetric membranes which mainly affected by its high gas permeance are the most desired membrane structure for industrial applications [19]. For most cases, asymmetric membrane is typically applied in various gas separation applications to improve the permeability of the manufactured membrane. The membrane manufacturing process involves the preparation of asymmetric structures membranes by phase inversion techniques relating to both wet spinning and dry-wet spinning [20].

Carbon matrix is deemed to be impermeable and hence the pore system has a strong impact on permeation across carbon membranes. Partial burn off or activation technique not only used to broaden the carbon pore system, but also to harden at high temperatures in inert atmosphere allowing the pore to close, which have been deployed recently to determine gas permeability through the molecular dimensional carbon membrane pore system. The pore system consists of relatively large openings with compact structures [21]. The main sections of the pore volume are openings that are responsible for the adsorption efficiency; meanwhile the constrictions are responsible for the stereo selectivity of the pore penetration by host molecules and for the kinetics of penetration [22]. Thus, the diffusivity of gases in the carbon membrane varies significantly depending on the shape and size of the molecules, attributed to the ultra micropores found in the carbon membrane which have the pore size and critical dimensions of pore mouth almost the same as the dimension of gas molecules. Pore size in the carbon molecular sieve depends on the equilibrium between the removal of O₂ containing groups on the surface around the pore mouth (pore enlargement) and crystallite rearrangement enhancing sintering (pore shrinkage).

2. Steps Involved in Carbon Membrane Preparation

The carbonization of aromatic polymers is usually used in the preparation of carbon membranes [23]. Carbonization is the most important method, and is often considered to be the center in the production of carbon membranes. Enhancing the performance of carbon membranes involve a few critical steps including precursor selection, membrane preparation and carbonization conditions. Additional advancement in terms of separation and technology development and its applications results in further obstacles such as the need for new membranes to achieve highly efficient and high productivity separation. The manufacture of carbon membranes is performed to overcome the limitations of the polymeric membranes. Figure 2 shows a schematic diagram for the preparation of carbon membranes.

The selection of modified precursors may lead to different carbon membranes. Thus, the most important element is selecting the appropriate polymeric precursor. The choice of polymeric precursor materials is based on their chemical and thermal stability, a great combination of selectivity and permeability, and good mechanical properties to produce the desired carbon membrane. Polyimide-based carbon membrane shows promising maximum efficiency. The carbon-built membrane with defect-free characteristics is derived from the polyimide membrane with the ability to withstand high temperature treatment without softening and decomposing instantly and abruptly. The use of these materials leads to the production of carbon membrane with high carbon yield and the ability to preserve their structure even after being heated at high temperatures attributed to an abnormally robust and unforeseen chemical and heat resistance [24].

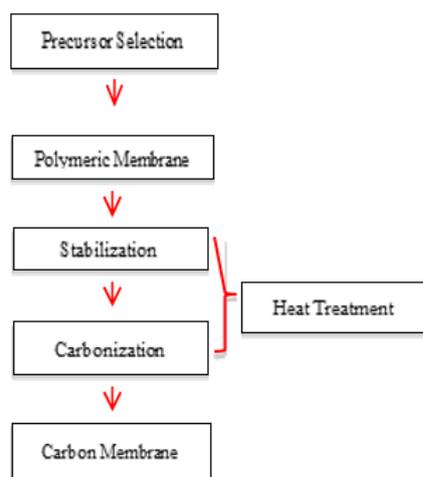


Fig. 2. Schematic diagram for the preparation of carbon membranes

3. Effect of Polymer Composition

During the process of carbonization, the membrane morphology can be modified by making some adjustments to certain elements. The precursor composition, temperature, and process atmosphere are the factors that influence the resulting membrane during the process of carbonization. In contrast to other factors, polymer composition is the most indicative element, as it plays a big part in determining the membrane separation efficiency. The carbon membrane morphology can be modified through precursor composition with varying solvent evaporation rates. In general, low composition of polymer results in membrane with a larger pore size in contrast to high composition of polymer which results in non-selective carbon membrane production [25]. This

is attributed to the rapid evaporation of solvent. On the other hand, with high composition of polymer, slower phase inversion leads in restriction of gas permeation and slow evaporation of solvent resulting in a membrane having a thicker dense layer or smaller pore size. The detailed description of the evaporation of membrane solvents is discussed in polymeric membrane development. The carbon membrane need to have a particular pore size, which is sufficiently small to enable the targeted gas to pass through the membrane, separating it from the larger penetrant. Studies on the efficiency of carbon membrane with varying compositions of polymer should be conducted to analyze their behavior during polymeric precursor preparation [26-28]. This section emphasizes on carbonization process at temperature of 800°C under N₂ condition, of five different Matrimid® 5218 compositions namely 5 wt.%, 10 wt.%, 13 wt.%, 15 wt.% and 18 wt.%. The resultant membranes will be characterized using FTIR and SEM. The separation competency of membrane with varying compositions of polymer precursor is evaluated through gas permeation test using N₂ and H₂.

4. SEM Analysis

The morphology structures of Matrimid-based membranes are determined using scanning electron microscopy (SEM), in which the structures significantly affect their performance in gas separation. Low composition of polymer typically results in rapid evaporation of solvent resulting in non-selective carbon membrane, meanwhile relatively slow phase inversion takes place at high composition of polymer resulting in the development of thicker dense layer caused by slow evaporation of solvent and limited gas permeation [29]. Such phenomena can be interpreted by the polymer chain entanglement prompted by polymer chain reorientation at different composition of polymer. Figure 3 shows the cross-sectional morphologies of carbon membrane prepared from varying compositions of polymer.

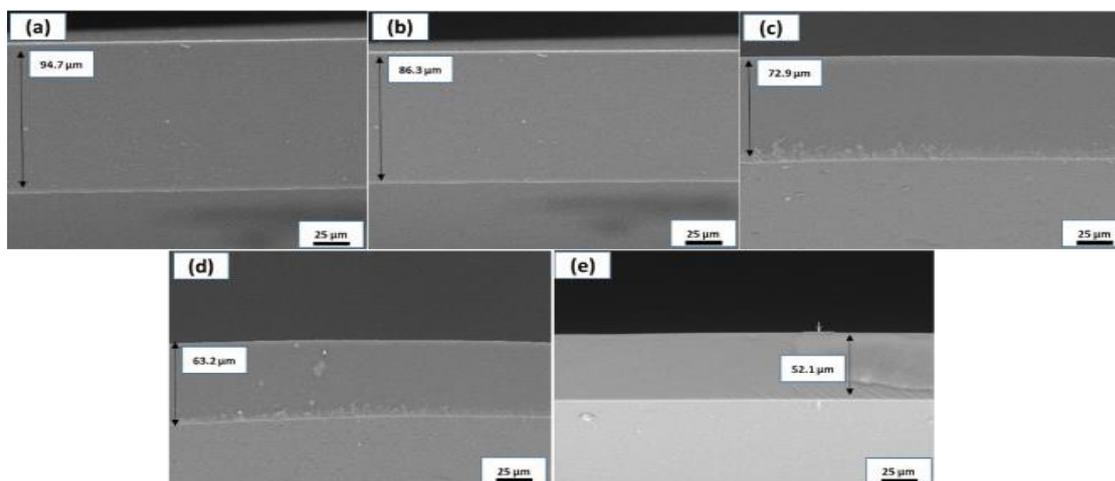


Fig. 3. Cross-sectional morphologies of Matrimid-based membranes with compositions of (a) 5 wt.%; (b) 10 wt.%; (c) 13 wt.%; (d) 15 wt.%; and (e) 18 wt.%

Characterization study via SEM was conducted on dense carbon membrane manufactured without tubular support due to the complicated method in producing supported carbon membrane. Such situations arise during the process of stabilization. Densification happens through further heating of the membrane. The thickness of the membrane with 5 wt.% Matrimid was about 94.7 μm. As the composition of polymer increased, the membrane thickness reduced. The membrane

thicknesses for the compositions of 10 wt.%, 13 wt.% and 15 wt.% were 86.3 μm , 72.9 μm and 63.2 μm respectively. Furthermore, the decreasing trend persisted with 18 wt.% Matrimid composition, in which the membrane thickness was 52.1 μm . The slow phase inversion allows the membrane thickness to decrease to a specific composition of polymer. The reason for this was that there was ample time for the polymer chain reorientation, resulted in a membrane with thinner dense layer [30]. On the other hand, because of the drastic polymer chain entanglement, a thicker membrane was generated if the composition of polymer was outside the range of the optimal composition. Similar compositions of polymer solution were used in the manufacture of tubular carbon membrane, in which its structure was developed during the dip-coating process. There were no major variations seen on the membrane structure at different compositions of polymer except for the variations in membrane thickness. Based on the composition of polymer accumulated on the ceramic support, varying structure of carbon membrane and gas permeation properties will be extracted after the process of carbonization. A substantial variation in the thickness of membrane was seen from the morphological images acquired from the SEM study, in which the evaporation of solvent was affected. The structure of the supported membrane acquired at the end of the process was determined by the degree of solvent removal and the composition of polymer.

5. FTIR Results

The molecular orientation of the Matrimid-based membrane was determined using Frontier Transform Infrared spectroscopy (FTIR). The spectrum derived from FTIR analysis for polymeric membrane produced at different compositions of polymer was displayed in Figure 4. FTIR was able to identify the variations in terms of chemical structure during the polymer to carbon transformation.

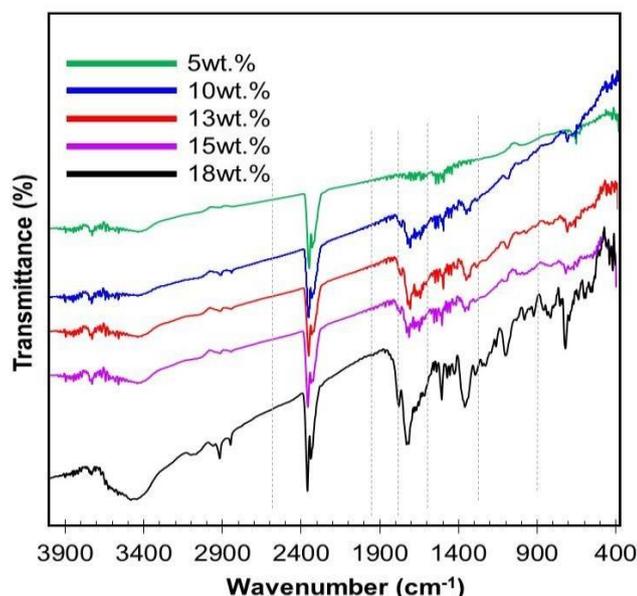


Fig. 4. FTIR analysis of polymeric precursor membrane fabricated at varying compositions of polymer

The presence of C-H aroma monosubstituted benzene can be identified with band magnitude ranging from 719.97 to 882.24 cm^{-1} , meanwhile the wavelengths approximately from 2718.08 to 3880.65 cm^{-1} corresponded to the imide groups with symmetrical and asymmetrical C=O stretching vibrations. Of all compositions, the imide groups consisting of aliphatic C-N stretch resulted in the band magnitude from 1363.12 to 1663.47 cm^{-1} . In addition, the wavelengths from 1506.71 to 1808.35 cm^{-1} and from 993.57 to 1399.30 cm^{-1} were attributed to the aromatic C=C bending vibration and C-N-C transverse stretch polymeric membrane, respectively. By referring to earlier studies, the band at 3461 cm^{-1} was corresponded to the amide group with C=O stretch, whereas the band approximately at 1339 cm^{-1} (100) represented amide group with C-N stretch or/and N-H bend [25].

Figure 4 shows the spectrum extracted from FTIR analysis for carbon membrane manufactured at multiple polymeric compositions. In contrast to polymeric membranes, there was no visible bond ranging from 400 to 3900 cm^{-1} shown in the FTIR results. Besides, the chemical structure and bond is reported to deconcentrates and breaks at the temperature of carbonization. Ismail has studied the characterization in terms of structure of the other polymers which have been modified according to the thermal history [31]. The result indicated that there was a significant reduction of peaks in higher composition of polymer during the process of carbonization for all carbon membranes. The intensity of transmission decreased as the membrane structure became compact and nearer to the interface of ATR crystal [32]. To summarize, the process of carbonization might occur regardless of the type of polymer formulation used [33].

6. Gas Permeation Characteristics

Table 1 shows the properties of gas permeation of carbon membrane manufactured at varying composition of polymer. The permeation properties of all gases increased when the compositions of polymer increased from 5 wt.% to 15 wt.%. Densification could occur due to the increasing composition of polymer which resulted in the permeance reduction for all gases. In spite of that, well-combined of selective layers was found and no increment in terms of mass transport resistance of the evaluated gases was identified [5]. Conversely, the permeance of all gases decreased at 18 wt.% composition of polymer. This situation arose as a result of the entanglement of polymer chain and its compact structure in a state beyond the optimum composition [34-36].

Table 1

Gas permeation properties of Matrimid-based carbon tubular membrane fabricated at varying compositions of polymer

Carbon membrane	Permeance (GPU)		Selectivity H ₂ /N ₂
	H ₂	N ₂	
CM-5 wt%	1156.44±1.34	3.45±1.88	335.20±3.42
CM-10 wt%	1170.35±1.23	3.40±2.51	344.22±2.63
CM-13 wt%	1189.78±2.41	3.37±1.53	353.05±3.37
CM-15 wt%	1247.37±1.52	3.11±3.59	401.08±2.56
CM-18 wt%	1209.44±1.86	3.35±3.59	361.03±3.12

The findings indicated high performance of the carbon membrane as opposed to the polymeric membrane. Except for 18 wt.% composition, it was found that the resultant membrane became more selective when the composition of polymer increased. The increment in H₂ permeance was noticeable because the kinetic diameter of H₂ (2.89Å) was comparatively smaller than N₂ (3.8Å). As a consequence, selectivity of H₂/N₂ increased when the composition of polymer increased to 15 wt.%. Owing to the failure of the subtraction and the formation of unselective voids, the selectivity of the resultant carbon membrane began to decline at 18 wt.% composition of polymer. The outcomes indicated that 15 wt.% of Matrimid was the most appropriate composition of polymer for the carbon membrane fabrication. Favvas's group reported similar findings of the same composition, using Matrimid 5218-based carbon hollow fiber membranes. Moreover, the findings suggested that the high selectivity properties of H₂/N₂ were because of the tighter structure of the macromolecules linkages, identical to those reported by Hosseini and co-workers [5]. Thus, the polymer membrane fabricated from 15 wt.% composition of Matrimid was deployed to study the consequence of the temperature of carbonization.

7. Conclusions

In conclusion, the carbon membrane was presumed to be the option for the separation process in the coming years. The deployment of carbon tubular membrane has revealed that the properties and characteristics of carbon have significantly contributed to the process of separation as opposed to the other membrane material based on the work performed using H₂ and N₂. In this sense, the future research on carbon membrane must be continued to enhance its commercialization. Carbon tubular membrane has been successfully manufactured and characterized particularly by means of thermal stability and structural morphology properties. The findings indicated that all the resultant carbon tubular membrane was dense in structure. 15 wt.% composition of Matrimid was the best formulation of polymer solution for the fabrication of carbon tubular membranes.

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