ORIGINAL ARTICLE

Development and characterization of polyacrylonitrile (PAN) based carbon hollow fiber membrane

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Abstract

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This paper reports the development and characterization of polyacrylonitrile (PAN) based carbon hollow fiber membrane. Nitrogen was used as an inert gas during pyrolysis of the PAN hollow fiber membrane into carbon membrane. PAN membranes were pyrolyzed at temperature ranging from 500°C to 800°C for 30 minutes of thermal soak time. Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and gas sorption analysis were applied to characterize the PAN based carbon membrane. Pyrolysis temperature was found to significantly change the structure and properties of carbon membrane. FTIR results concluded that the carbon yield still could be increased by pyrolyzing PAN membranes at temperature higher than 800°C since the existence of other functional group instead of CH group. Gas adsorption analysis showed that the average pore diameter increased up to 800°C.

Key words : carbon membrane, hollow fiber, gas separation, polyacrylonitrile

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Membrane technology is becoming more useful for separation of gas mixture and offers great advantages in its operations (Robeson, 1999). Polymeric membranes had been successfully used for this purpose. However, their permeability-selectivity combination is still not up to the industries satisfaction and their application is limited especially related to severe environment such as higher temperature and corrosive operation. At present, carbon molecular sieves membrane (CMSM) has been identified as a solution to this problem (Koros and Mahajan, 2000). It offers a balance on permeability-selectivity trade off and the separation can be maintained in the environment that was prohibited by polymeric membrane previously. Ismail and David thoroughly reviewed the advantages of carbon membrane and the potential application for gas separation (Ismail and David, 2001).

The interest in developing carbon membrane only grow after Koresh and Soffer (Koresh and Soffer, 1987; 1986; 1983) had successfully prepared apparently crack-free carbon hollow fiber membranes by carbonizing cellulose hollow fibers. CMSM contains narrow constrictions at the entrance of the micropores that approach the molecular dimensions of gaseous species. The constrictions allow the passage of the smaller species and restrict the larger ones as ruled in a molecular sieving mechanism (Fuertes and Centeno, 1999). It is believed that CMSM has a pore size in the range of 3Å to 6Å (Fuertes and Centeno, 1998) that enhance the discrimination between gas molecules of different sizes.

CMSM can be produced by pyrolyzing a polymeric membrane precursor in a controlled condition and atmosphere. Lately, numerous precursors have been used to form carbon membrane such as polyimides and derivatives, polyacrylonitrile, phenolic resin, poly (vinylidene chloride), poly (furfuryl alcohol), cellulose, phenol formaldehyde, polyetherimide and polypyrrolone. Many researchers used polyimides as their precursor for producing carbon membrane. Jones and Koros (Jones and Koros, 1994) reported that the best carbon membrane, in terms of both separation and mechanical properties, were produced from the pyrolysis of aromatic polyimides.

However, polyimides are commercially expensive materials and some can be obtained in laboratory scale only (Centeno and Fuertes, 1999; Fuertes *et al*, 1999). Therefore, in order to reduce the cost and time for carbon membrane fabrication, other alternative polymer must be considered. Therefore, the objective of this study is to report the development of PAN based carbon hollow fiber membrane. We have selected PAN as a precursor for carbon membrane based on many reasons as will be discussed in the following section. PAN is spun using dry-wet spinning process to form hollow fiber membrane. Inert gas pyrolysis system is used to pyrolyze the PAN membrane into carbon hollow fiber membrane.

Experimental

Polyacrylonitrile (PAN)

PAN is one of the versatile polymers that is widely used for making membranes due to its good solvent resistance property. It has been used as a substrate for nanofiltration (NF) and reverse osmosis (RO) (Kim *et al*, 2002). The thermosetting characteristic offered by PAN makes it suitable as a carbon membrane precursor. It usually does not liquefy or soften during any stage of pyrolysis and preserves its morphology upon the pyrolysis. The general molecular structure of PAN is shown in Figure 1.

In carbon fiber manufacturing, PAN is recognized as the most important and promising precursor for carbon fiber. It dominates nearly 90% of all worldwide sales (Gupta and Harrison,

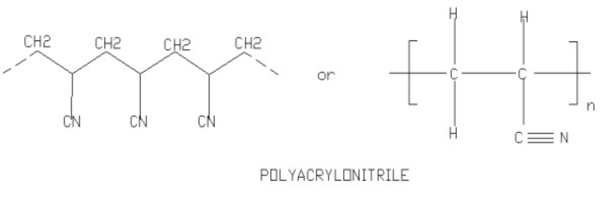


Figure 1. Molecular structure of polyacrylonitrile (PAN)

1999). There are numerous PAN fibers advantages including a high degree of molecular orientation, higher melting point (PAN fiber tends to decompose before its melting point, T_m of 317-330°C) and a greater yield of the carbon fiber (Donnet and Bansal, 1984). PAN fibers form a thermally stable, highly oriented molecular structure when subjected to a low temperature heat treatment, which is not significantly disrupted during the carbonization treatment at higher temperatures, meaning that the resulting carbon fibers have good mechanical properties (Donnet and Bansal, 1984).

On the other hand, it is possible to blend the PAN with other polymers to alter the final pore size distribution of carbon membrane. Linkov *et al.*, (Linkov *et al,* 1994a) prepared PAN hollow fiber membrane by varying the viscosity of the precursor solution by blending it with methyl methacrylate. They also applied phase inversion by casting PAN with poly (ethylene glycol) (PEG) and poly (vinylpyrrolidone) (PVP) in order to synthesize membranes with 50-400 nm pore sizes. The pore size distribution was very narrow in the case of the PAN-PVP precursor (Linkov, 1994b).

One of the main problems of unsupported carbon membrane (i.e. hollow fiber) is brittleness of the carbon structure. We believe that by the application of PAN precursors, which is widely used in the production of high strength carbon fiber, this problem can be minimized. However, in this case, first task is to develop PAN-based carbon membrane. Furthermore, some improvement and optimization must be done in the next stage in order to achieve high performance PAN-based carbon membrane.

Preparation of carbon membrane

Dry/Wet spinning process

A binary polymer solution consisting of 150g PAN (Aldrich 18131-5) and 850g dimethylformamide (DMF) was prepared for making 1000g of spinning solution. Dry/wet-spinning process was applied in preparing asymmetric PAN hollow fiber membranes precursor. Spinning solution and bore fluids were extruded simultaneously through a spinneret to form a nascent hollow fiber at an ambient temperature. The internal surface of hollow fiber was contacted with a bore fluid and experienced wet phase separation in order to form a circular hollow lumen. Water was chosen as bore fluid with flow rate of lml/min (Pesek and Koros, 1994; Clausi and Koros, 2000), which was controlled by high-pressure syringe pump.

The fiber was then directed to a force convective chamber, which provides a controlled force convective environment for inducing dry phase separation through an air gap. The inert gas nitrogen was used to allow the fiber skin formation. The hollow fiber was then immersed into nonsolvent (water) coagulation bath for wet separation and then the washing treatment bath. The coagulation bath temperature was controlled at 14°C by a refrigeration/heating unit to ensure rapid solidification, while the washing bath was kept at ambient temperature.

The resulting hollow fibers had an outer diameter of 600μm with a 300μm inner diameter. The fully formed PAN hollow fiber was subjected to solvent exchange in methanol for 2 days and hexane for another 2 days before being dry in ambient atmosphere.

Inert gas pyrolysis

Inert gas nitrogen was set up for pyrolysis of PAN hollow fiber membrane as shown in Figure 2. PAN hollow fiber bundles were inserted into a quartz tube and wrapped with stainless steel wire type 304 (outside diameter 3 mm) at both ends. Then, the quartz tube was inserted into Carbolite wire wound tube furnace (Model CTF 12/65/550) that can be set to a maximum temperature of 1200°C. The pyrex socket was connected at the front of quartz tube to channel the nitrogen gas during pyrolysis and the other side of quartz tube was located in a fume cupboard to purge the volatile gas evolved. All the connection were properly tighten to prevent air from entering the quartz tube which could interrupt the inert gas pyrolysis process.

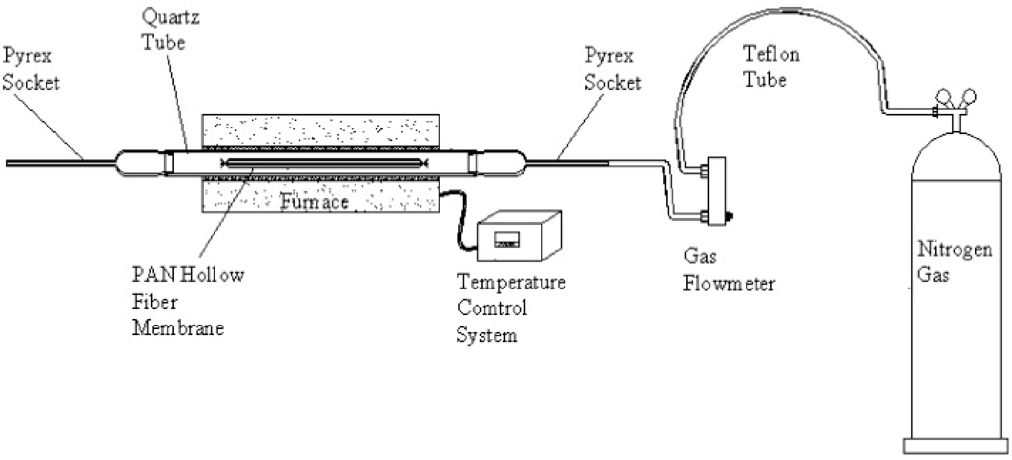


Figure 2. Nitrogen gas pyrolysis system

The PAN membrane was subjected to thermostabilization process in air at 250°C for 30 min at heating rate of 5°C/min before the pyrolysis was conducted. Thermostabilization is necessary in order to cross-link the PAN chains and to prepare a structure that can withstand high temperature process. This can also ensure both the molecules and the fibrillar orientation will not be eliminated during the final heat treatment process.

Before the pyrolysis process started, the inert gas needed to be purged into the pyrolysis system to remove the unwanted air or oxygen. This was to prevent the oxidation from occurring during high temperature pyrolysis process. Then, the precursor was heated to a required pyrolysis temperature in the range of 500-800°C and maintained at that temperature for 30 min by setting up the temperature control systems. The heating rate was set at 3°C/min and nitrogen gas flow rate was maintained at 200 cm^3/min. The resulting carbon membrane was cooled down to ambient temperature in an inert gas atmosphere.

Characterization of carbon membrane

Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) has been used to investigate the resultant membrane morphology. Images of fiber surface, skin layer structure and cross sections of membrane prepared under different carbonization condition can be viewed clearly. Before passing through SEM, the membrane samples had to go through the gold coating process. After that, the samples were imaged and photographed by employing a scanning electron microscope (SEMEDAX; XL40: PW6822/10) with potentials of 10kV in achieving magnification ranging from 500x to 5000x.

Fourier transform infrared spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a very useful tool to detect the existence of functional groups in a membrane. The FTIR results display changes of functional groups and elements in the membranes when they are heated from room temperature to pyrolysis temperature.

Gas sorption analysis

Nova 1000 Gas Sorption Analyzer, Quantachrome Corporation was used to determine the average pore size and micropore volume of carbon membrane. The sample was pretreated in a vacuum at 400°C for about 2 hours. The heated sample cell was immersed into liquid nitrogen to maintain the temperature at 77 K before testing. Nitrogen gas was used as an analysis gas.

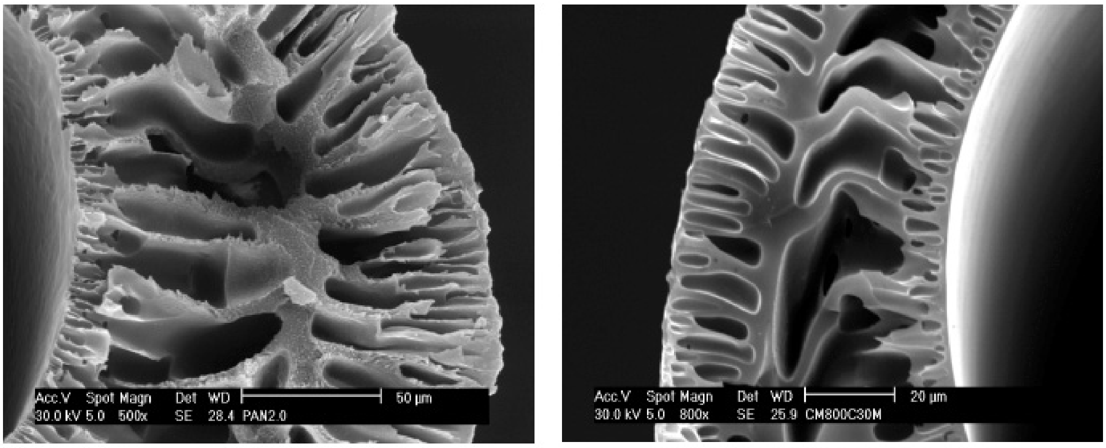
Results and Discussion

Effects of pyrolysis temperature on the morphology of PAN-based carbon membrane

Changing the high temperature treatment parameter can vary the permeation characteristics of a carbon membrane. This is in contrast to polymeric membranes, where such variations frequently involve the synthesis of a new membrane material (Koresh and Soffer, 1986). This unique characteristic is one of the advantages of carbon membrane for gas separation.

From SEM image in Figure 3, the structure of PAN carbon membrane changes greatly between the inner and outside diameter of the fiber (i.e. middle region) compared to PAN precursor. For the PAN-based carbon membrane, the outer selective skin is clearly separated from the inner wall by the larger macrovoid between it. Meanwhile for PAN membrane, the pores from the inner diameter are likely connected to the outer diameter pores. This structure could be a reason for the imbalance of permeability-selectivity in polymeric membrane, where the higher selectivity give the lower permeability to gas separation. On the other hand, the larger macrovoid presented in carbon membrane contributes to a higher permeability without interrupting the higher selectivity. Higher selectivity is determined by the pore constriction at the outer surface of the carbon fiber. Therefore, carbon materials not only have the ability to perform molecular sieving but also may allow a considerably higher flux of the penetrant through the material (Steel and Koros, 2003).

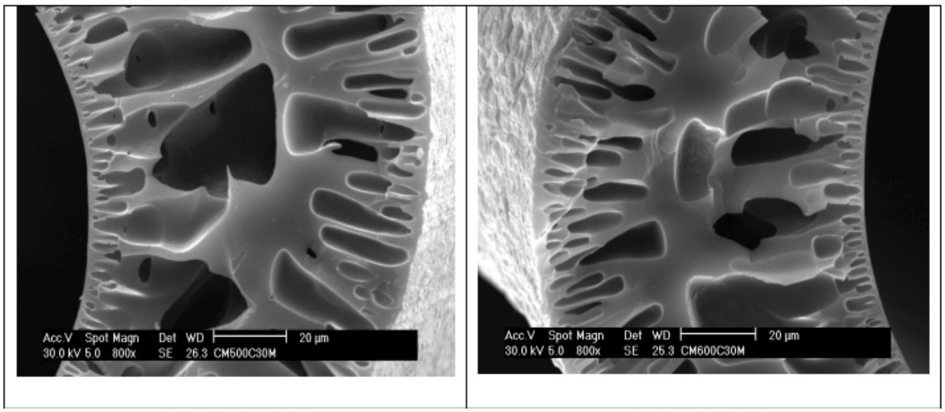
Pyrolysis temperature will greatly change the morphology and structure of PAN membrane. For PAN precursor, the membrane must be pyrolyzed at a minimum temperature of 400°C (David, 2001). Figure 4 shows the variations of the PAN-based carbon membrane structure with the pyro-lysis temperature ranging from 500-800°C. The entire SEM images were at 800X magnification. It can be observed that the amount of the outer pores skin was increased with the increasing pyrolysis temperature. During the pyrolysis, by-products of different volatilities are evolved and generate pores through the polymeric matrix (Steel, 2000). Therefore, as the pyrolysis temperature increases the amount of by-products also increases which enhances the pore formation. However, at relatively higher pyrolysis temperature, the pore structure becomes tighter which gives an increase of gas selectivity (Geiszler and Koros, 1996). Densification of the porous carbon matrix occurs at high pyrolysis temperature, which can be identified by an increase of shrink-



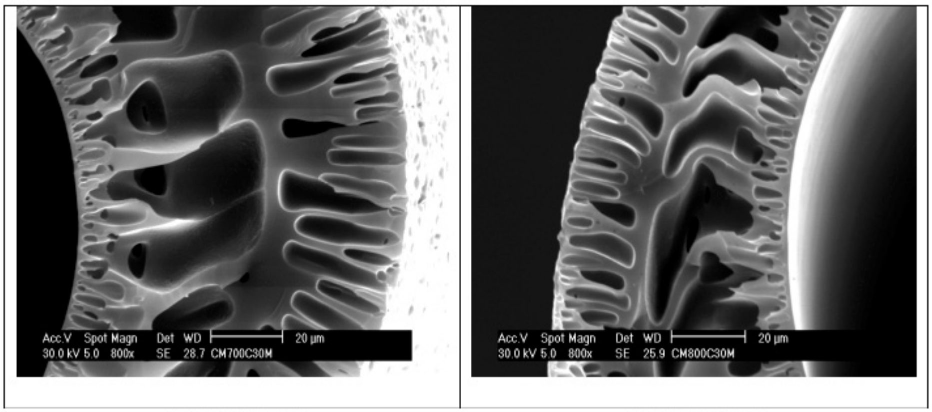
(a) PAN Membrane

(b) PAN Based Carbon Membrane

Figure 3. Cross section of PAN membrane and PAN based carbon membrane



(a) CM 500°C (b) CM 600°C



(c) CM 700°C (d) CM 800°C

Figure 4. Carbon membrane at a different pyrolysis temperature

age factor as shown in Table 1.

Effects of pyrolysis temperature on the functional groups evolution during pyrolysis

Generally, carbon membrane is known by its amorphous porous structure created by the evolution of gases generated during pyrolysis of the polymeric precursor. Though the membrane is amorphous in nature, one still finds carbon membrane subdomains, where the structure of the polymeric precursor is still recognizable. This subdomain structure determines, in part, the differences that are found in the performance of carbon membrane derived from various polymeric precursors. The extent of this subdomain structure also depends on the pyrolysis conditions (Sedigh *et al*, 1999).

Table 1. Percentage of shrinkage based on the variations of inside diameter of the fiber.

Pyrolysis temperature	Inside diameter (µm)	% Shrinkage
PAN membrane	300	-
CM 500°C	249	17.0%
CM 600°C	216	28.0%
CM 700°C	202	32.7%
CM 800°C	204	32.0%

The mechanism of carbon membrane formation from a PAN is a complex process and various reaction schemes have been proposed to occur especially by researchers involved in carbon fiber production. During oxidative stabilization

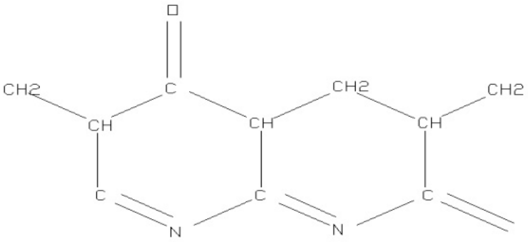


Figure 5. Structure of ladder polymer from PAN

process, cyclization and oxidation taking place to form a ladder polymer as shown in Figure 5 (David and Ismail, 2003). This ladder structure is thermally stable and ready to withstand high temperature of pyrolysis process.

Pyrolysis of PAN membrane involves many process such as chain scission, chain breakdown, by-products evolution or cross linking depending on heat treatment history. The principal scission products releases from PAN precursor in the temperature ranging from 400 to 1000°C are hydrogen cyanide (HCN), ammonia (NH_3) and nitrogen (N_2). Depending on the extent of pre-oxidation, various amounts of water (H_2O), carbon monoxide (CO) and carbon dioxide (CO_2) were also formed. In addition, small quantities of hydrogen (H_2) and methane (CH_4) were released during the carbonization process (Lewin and Preston, 1983). Figure 6 shows the proposed mechanism of the stabilization chemistry and carbonization of PAN-based carbon fiber.

Figure 7 and Figure 8 show the spectrum of pyrolyzed PAN membrane at different pyrolysis temperatures. Meanwhile Table 2 gives a summary of FTIR results for PAN membrane pyrolyzed using nitrogen pyrolysis system. The original PAN molecule consists of functional groups such as methyl (CH_3) and nitrile (C≡N). During oxidation, numerous new transition structures were formed, such as ketones, aldehydes, carboxilyc acid etc. as in Figure 6. After carbonization, all of these transition compounds were expected to evolve as volatilities and only carbon and hydrogen atoms remain. However, 100% conversion of polymer to carbon is not achieved due to the existence of other compounds.

Table 2. Summary of FTIR results for PAN membranes pyrolyzed at different temperature

Pyrolysis temperature	Functional group	Frequency (cm^{-1})
500°C	C≡N	2216.42
	C-N	1265.90
	C=C	1595.42
600°C	C≡N	2224.05
	C=N	1649.36
	C-N	1265.77
	C=C	1539.65
	N-H	3445.29
	C=O (Aldehydes)	1739.53
	C=O (Ketones)	1701.79
700°C	C=N	1653.23
	C-N	1021.84
	C=C	1540.69
	N-H	3442.13
	C=O (Ketones)	1701.01
	C-H	2924.63
800°C	C=N	1649.58
	C-N	1021.39
	C=C	1541.42
	N-H	3442.97
	C-H	2923.64

The C=C groups exist in all pyrolyzed PAN membrane. This group is formed by aromatization process that occurred during thermostabilization of PAN membrane. The nitrile groups (C≡N) disappear when PAN membrane is pyrolyzed at temperature of 700°C. Aldehydes and ketones can be detected at pyrolysis temperature of 600°C and aldehydes disappeared when reaching 700°C. A ketone group disappeared at 800°C spectrum but nitrogen atom can still be found at this spectrum. It can be concluded that pyrolysis temperature at 800°C seems not enough to remove all non-carbons atoms (i.e. N, O, etc) in PAN membrane because of the existence of other functional group instead of CH group as detected by FTIR spectrum.

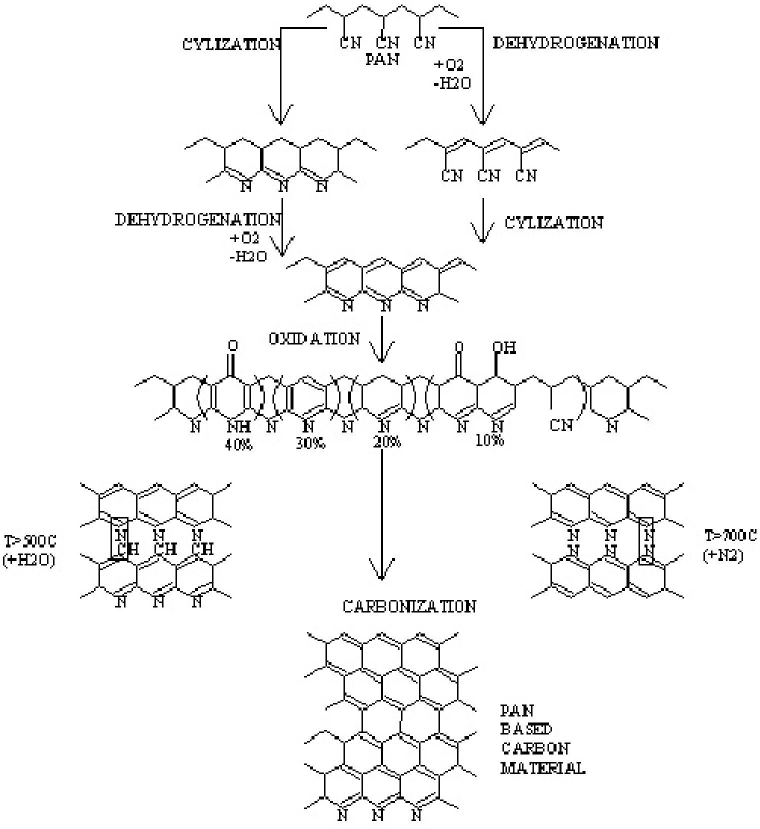


Figure 6. Proposed mechanism of the stabilization chemistry and carbonization of PAN based carbon fiber (Fitzer *et al*, 1986)

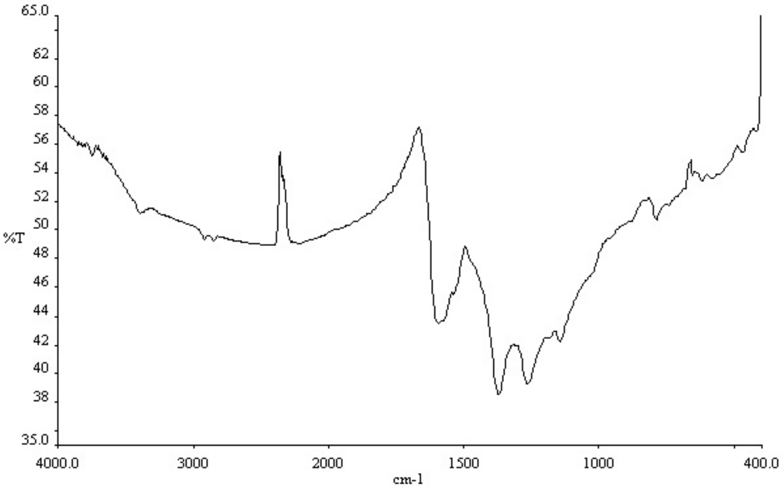
Effects of pyrolysis temperature on the porous structure of carbon membrane

The mechanism of gas permeation and uptake through porous solids is closely related to internal surface area, dimension of the pores and surface properties of the solid, rather than to the bulk properties of the solid as in the case with polymers (Koresh and Soffer, 1987). Therefore, it is important to study and analyze the porous structure in carbon membrane. The porous structure in carbon membrane contains pore or apertures that approach the molecular dimension of the diffusing gas molecules (Jones and Koros, 1994; Lafyatis *et al*, 1991). According to the IUPAC, three different types of pore have been defined; macropores that are larger than 50 nm; mesopores, between 2 and 50 nm in size; and finally, micropores, that are smaller than 2 nm.

Generally, the pore size of carbon membrane is non-homogeneous, comprised of relatively wide openings with a few constrictions (Koresh and Soffer, 1980). The pores are varying in size and dimensions depending on the morphology of the organic precursor and the chemistry of pyrolysis. The idealized structure of carbon material is shown in Figure 9. The pore mouth “d”, often referred to as an ultramicropore (<10Å) (Suda and Haraya, 1997; Centeno and Fuertes, 1999), which allows molecular sieving of the penetrate molecules. The larger micropores, “D” of the material (6-20Å) may allow for diffusion of gas molecules through the carbon material (Steel, 2000).

The extent and nature of the porous structure and the surface area will be largely dependent on the nature and morphology of the precursor

(a) 500°C



(b) 600°C

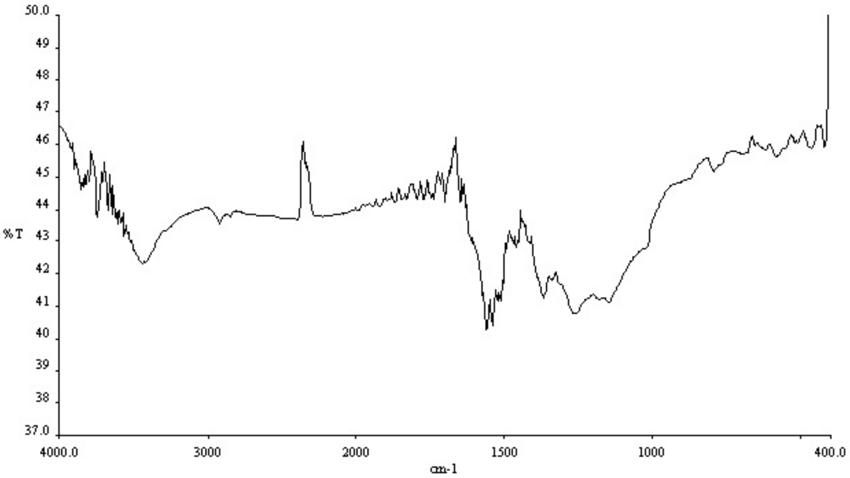


Figure 7. FTIR spectrum of pyrolyzed PAN membrane at (a) 500°C (b) 600°C

polymer and the history of its heat treatment (Donnet and Bansal, 1984). The imperfect stacking between the microfibrils of graphite basal plane in carbon fiber gives rise to empty spaces between the microfibrils that form pores or voids. Generally, low temperature carbon fibers have small but numerous pores that are distributed throughout the carbonized material (Donnet and Bansal, 1984).

This is in agreement with the results shown in Table 3. It can be observed that the average pore diameter increases with increasing the pyrolysis temperature up to 800°C due to the expelling of the carbon atoms as carbon monoxides (David, 2001). However, at a very high temperature, pore size start to decrease and eventually the pores will shrink and collapse owing to progressive annealing (Suda and Haraya, 1997; Centeno and Fuertes, 1999). The BET surface area is increased as the pyrolysis temperature reaches the maximum to a value of 103 m^2/g, and then decreases rapidly. This trend also agrees with the results reported by Lee and Tsai (Lee and Tsai, 2001).

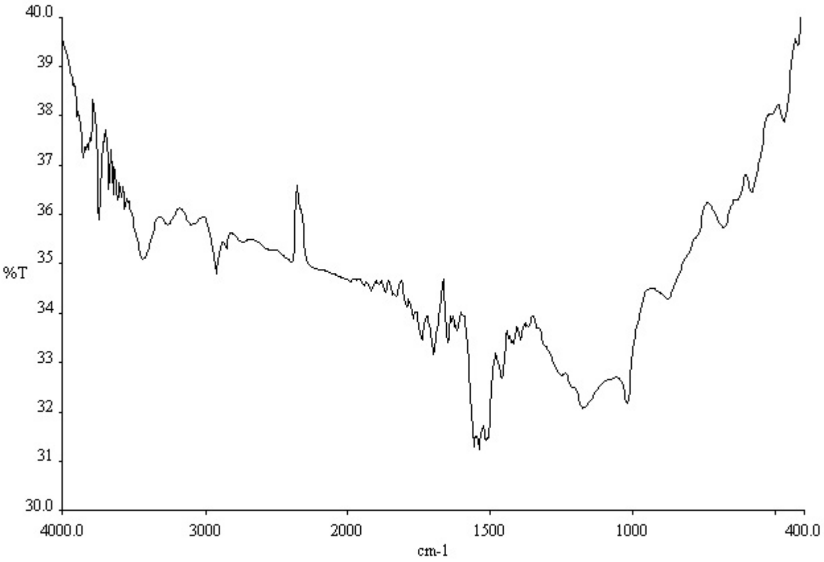
Conclusion

Based on the results presented, it can be

Table 3. Micropores properties of PAN membrane pyrolyzed at different pyrolysis temperature.

Pyrolysis temperature	Average pore diameter (Å)	Micropore volume (cc/g)	BET surface area (m^2/g)
500°C	11.19	0.039	108.29
600°C	10.20	0.032	95.47
700°C	12.43	0.040	102.98
800°C	13.13	0.034	85.66

(a) 700°C



(b) 800°C

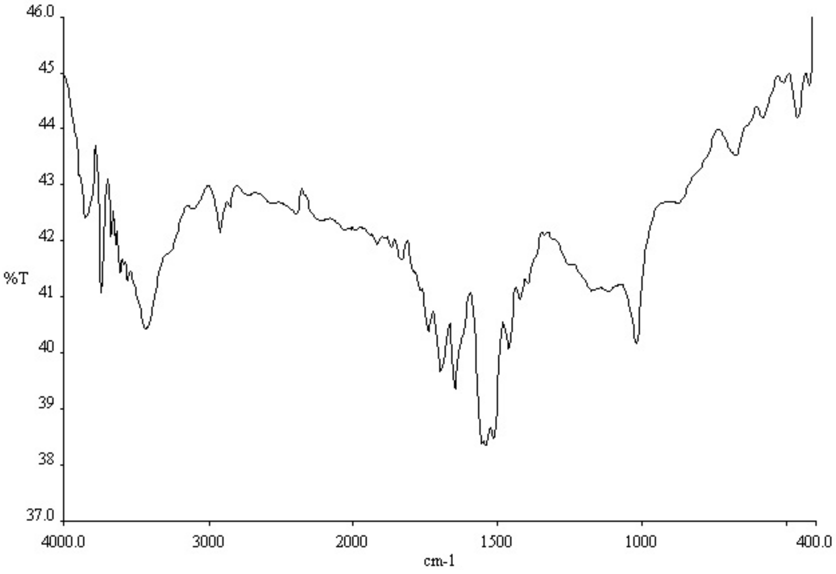


Figure 8. FTIR spectrum of pyrolyzed PAN membrane at (a) 700°C and (b) 800°C

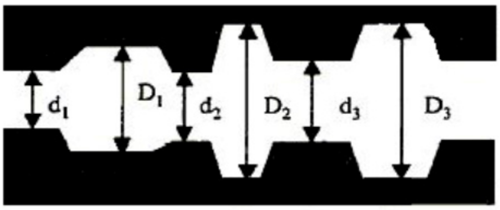


Figure 9. Idealized structure of carbon material (Steel, 2000)

concluded that PAN membranes can be successfully pyrolyzed into carbon membrane using nitrogen gas pyrolysis system. Pyrolysis temperature influences the resultant carbon membrane by altering the structure and pore properties of the membrane. FTIR results concluded that the carbon yield still could be increased by pyrolyzing PAN membranes at temperatures higher than 800°C because of the existence of other functional group instead of CH group. Gas adsorption analysis showed that the average pore diameter increased up to 800°C. This result encourages further research on higher pyrolysis temperature since it has been hypothesized that the pore diameter will shrink at relatively higher temperature.

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