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Enhancement of Gas Separation Performance of Carbon Nanotubes Mixed Matrix Membrane with Acid and Alkali Treatment

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Abstract

Carbon nanotubes have special properties according to the different diameter, length, and direction of 'twist' of the nanotubes. Recent experiments as well as numerical calculations indicate small interlayer corrugation in multi- wall carbon nanotubes (MWNTs), confirming theoretical prediction of frictionless sliding, along the common axis, of an infinitely long incommensurate. As a result, the permeability of O_2 and N_2 increased in proportion to the amount of open-ended CNTs in the polymer matrix. Furthermore, carbon nanotubes have been chosen to be an inorganic material in the gas separation in order to enhance the gas separation performance. However, it seems not easy to achieve the high performance in gas separation of carbon nanotubes mixed matrix membrane because polymer like polyethersulfone (PES) and molecular sieve could not have a good adhesion to each other in the gas separation. This problem does not help the gas separation to achieve the best performance. Other than that, atomic simulations results for both self and transport diffusivities of light gases such as H_2 and CH_4 in carbon nanotubes and in zeolites. They reported transport rates in CNTs to be orders of magnitude faster than in zeolites and the exceptionally high transport rates in carbon nanotubes are shown to be a result of the inherent smoothness of the carbon nanotubes. The objectives of this study are to fabricate and characterize treated and untreated carbon nanotubes (CNTs) MMMs in gas separation and to investigate the effect of sulfuric acid and sodium hydroxide treatment on the MMMs performance in gas separation. From the result, it was obtained that either treated by acid or alkali, both samples show better structure and thus increase membrane selectivity compared to untreated membrane and therefore, good performance was achieved in gas separation. As a conclusion, fabrication of treated and untreated flat sheet MMMs was successfully conducted and treatment by using sulfuric acid and sodium hydroxide increase the gas separation performance.

Keywords: carbon nanotubes, mixed matrix membranes, gas separation.

■1.0 INTRODUCTION

Carbon nanotubes have special properties according to the different diameter, length, and direction of 'twist' of the nanotubes. Recent experiments as well as numerical calculations indicate small interlayer corrugation in multi- wall carbon nanotubes (MWNT), confirming theoretical prediction of frictionless sliding,[1] along the common axis, of an infinitely long incommensurate. As a result, the permeability of O_2, N_2 and CH_4 increased in proportion to the amount of open-ended CNTs in the polymer matrix. Furthermore, carbon nanotubes have been chosen to be an inorganic material in the gas separation in order to enhance the gas separation performance. However, it seems not easy to achieve the high performance in gas separation of carbon nanotubes mixed matrix membrane because polymer like polyethersulfone (PES) and molecular sieve could not have a good adhesion to each other in the gas separation. This problem does not help the gas separation to achieve the best performance. Other than that, atomic simulations results for both self and transport diffusivities of light gases such as H_2 and CH_4 in carbon nanotubes and in zeolites.[2-3] They reported transport rates in CNTs to be orders of magnitude faster than in zeolites and the exceptionally high transport rates in carbon nanotubes are shown to be a result of the inherent smoothness of the carbon nanotubes. Recently, there is great interest in the modification of the porosity of MWNTs to improve the performance of these materials by using acid and alkali. Nitric and sulfuric acid (H_2SO_4) are effective to modify MWNTs surface by inducing formation of functional groups.[4] Hydroxide of alkali metal such as potassium hydroxide (KOH) is effective to develop porosity of membrane attributed to redox reactions between carbon nanotubes and KOH.[5] In gas separation, selectivity of membranes is independent of the membrane thickness. However, treatments using highly concentrated acid or other extreme oxidants can often disrupt their primary structures.[6]

■2.0 EXPERIMENTAL

2.1 Materials and solvents

Pristine MWNTs (purity >95%) are purchased from AMTEC, Universiti Teknologi Malaysia. The carbon nanotubes have a diameter of approximately 8-40 nm and a length of at least 200 Mm. concentrated sulfuric acid and alkali, n-methylpyrrolidone, polyethersulfone, acetone, and methanol are all analytical grade and used as received.

2.2 Characterizations

Scanning electron microscopy (SEM) and Field emission scanning electron microscopy (FESEM) were used in this study to reveal the chemical structure of untreated and treated membrane by using diluted sulfuric acid and sodium hydroxide. SEM was used at magnification of 15000 to view the upper surface of membranes while FESEM was used at magnification of 300 and 10000 to see the cross sectional area of the membranes.

■3.0 RESULTS AND DISCUSSION

3.1 SEM

SEM at magnification of 15000 shows a flat surface that confirms there is no MWNTs that fill in the PES membranes (Fig. 1). This SEM image is important for comparison with the other mixed matrix membranes.

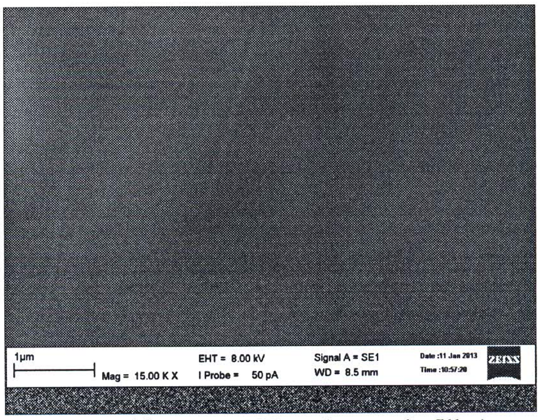

Figure 1 SEM of polyethersulfone membrane (without MWNTs as inorganic filler)

Untreated MWNTs membranes could not grab a good adhesion at the membranes surface. Most of the MWNTs tips are not disconnected and make them less ease to be filled in the membranes (Fig. 2). It seems like the MWNTs are scattered on membrane surface. It shows that MWNTs could not achieve good adhesion with polymer.

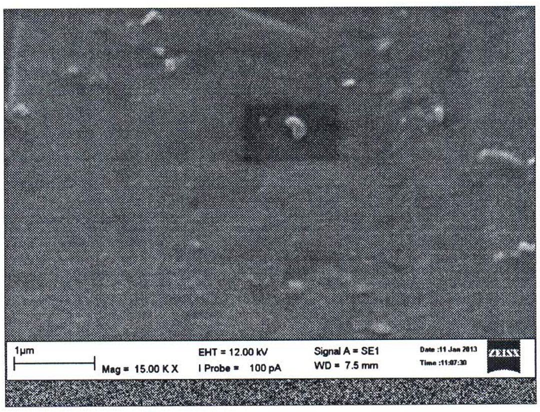

Figure 2 SEM of untreated mixed matrix membrane

From figure 3, the use of 2.0 M H_2SO_4 as MWNTs pretreatment helps the MWNTs to have better adhesion with PES. It does not scattered as untreated membranes otherwise have been distributed well through out the membranes.

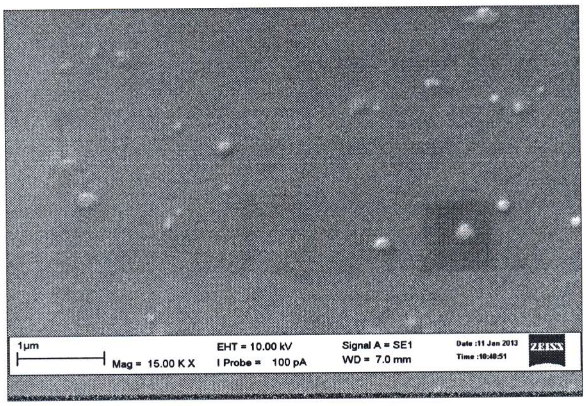

Figure 3 SEM of treated mixed matrix membrane by 2.0 M H_2SO_4

SEM image for MWNTs that have been treated by 2.0 M NaOH views that the tip of MWNTs was opened and MWNTs are ease to bend through the membrane surface (Fig. 4). This is because sodium is a member of alkali metal group in periodic table that might open MWNTs tips effectively.

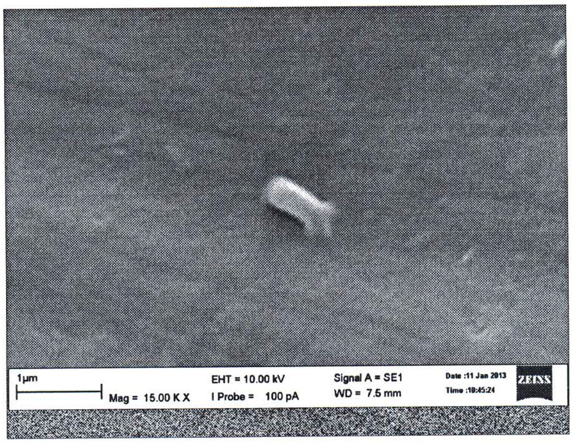

Figure 4 SEM of treated mixed matrix membrane by 2.0 M NaOH

3.2 FESEM

FESEM results a quite big micro porous pore at lower magnification of 300 (Fig. 5a). At 10000 magnifications FESEM shows that the average size of pores is about 1.10 μm (Fig. 5b). It might occur because no MWNTs are added to the membranes.

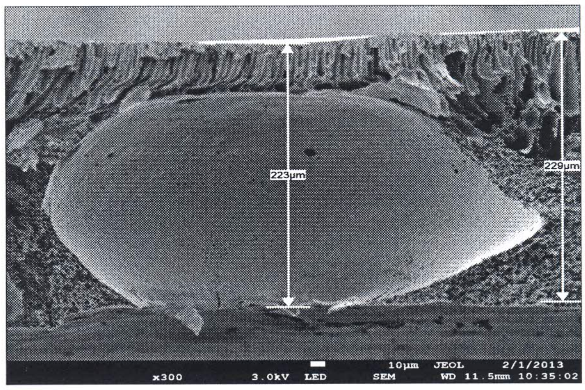

Figure 5a FESEM of polyethersulfone membrane (without MWNTs as an inorganic filler) at lower magnification

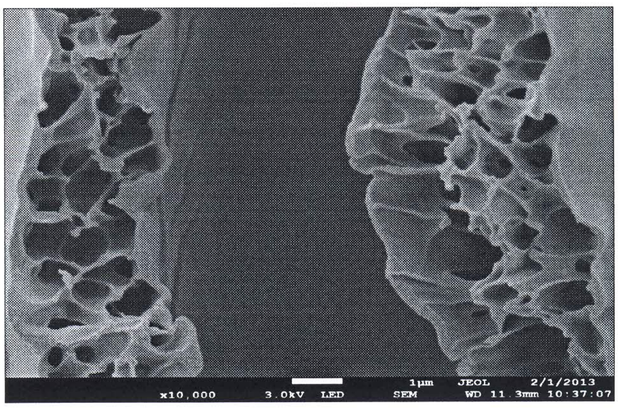

Figure 5b FESEM of polyethersulfone membrane (without MWNTs as an inorganic filler) at higher magnification

Figure 6a exposes that at lower magnification of 300, the structure of membranes are rather separated into two layers. The average pore size of untreated mixed matrix membrane is about 0.97 μm (Fig. 6b). It happens because polymer like PES and molecular sieve like MWNTs could not achieve a good adhesion to each other in gas separation.[2-3]

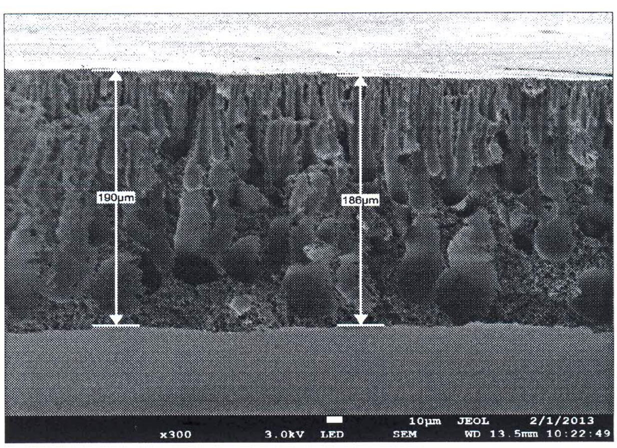

Figure 6a FESEM of untreated mixed matrix membrane at lower magnification

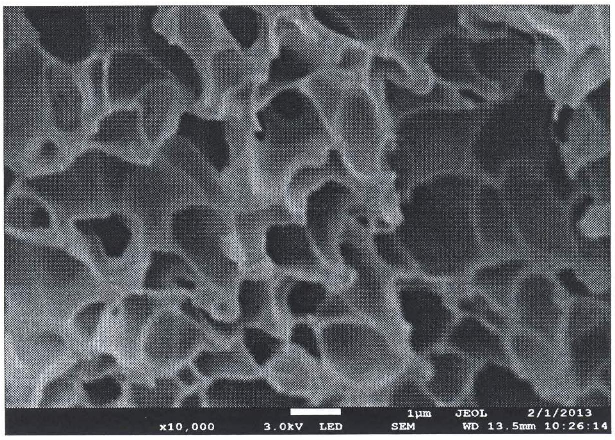

Figure 6b FESEM of untreated mixed matrix membrane at higher magnification

At magnification of 300, FESEM reveals that MWNTs that has been treated with 2.0 M H_2SO_4 produces two layers membranes (Fig. 7a). PES and treated MWNTs could achieve better adhesion to each other compared to untreated MWNTs. The use of acid might dissolved impurities and helps to open the carbon nanotubes tips.[7] Other than that, acid treatment provide functional group (carboxyl group) that will help the MWNTs to have good adhesion with PES.[8] FESEM with higher magnification also results the better discovery (Fig. 7b). The average pore size is 0.55 μm that is smaller than pore size that found in PES membranes and untreated mixed matrix membranes.

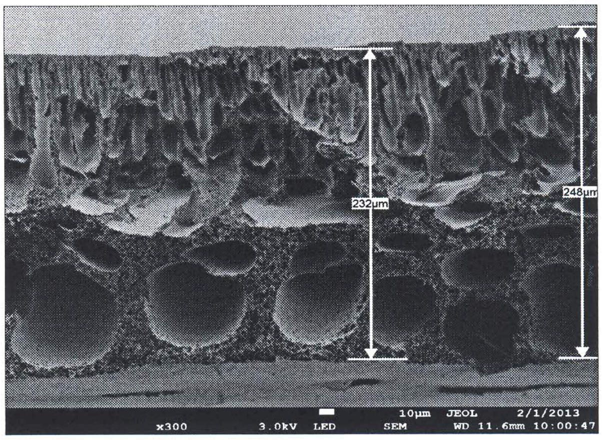

Figure 7a FESEM of treated mixed matrix membrane by 2.0 M H_2SO_4 at lower magnification

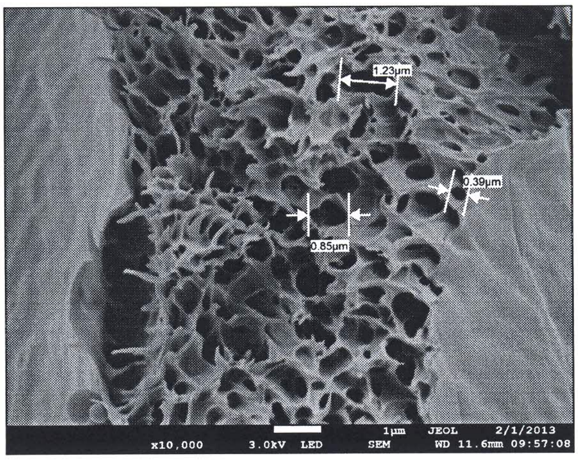

Figure 7b FESEM of treated mixed matrix membrane by 2.0 M H_2SO_4 at higher magnification

Figure 8a shows a quite compact structure of membranes. The MWNTs and PES achieve adhesion to each other tightly compared to the other three membranes and it was supported by the average pore size of 0.52 μm (Fig. 8b). This resulted by existence of NaOH that develop porosity of membrane.[5] Sodium which has character as alkali metal opens the tips of MWNTs and therefore PES becomes more ease to be filled by the MWNTs and thus gas separation can be done faster because most of the carbon nanotubes are ready for gases go through.

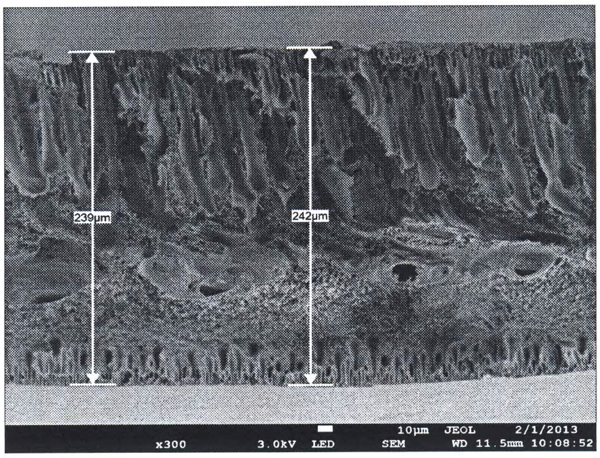

Figure 8a FESEM of treated mixed matrix membrane by 2.0 M NaOH at lower magnification

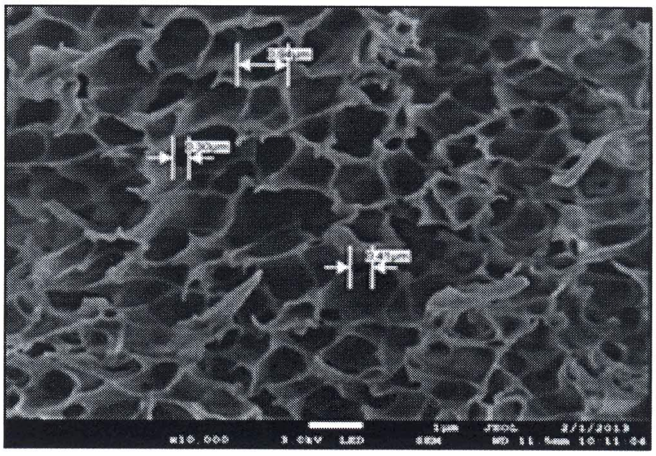

Figure 8b FESEM of treated mixed matrix membrane by 2.0 M NaOH at higher magnification

■4.0 CONCLUSION

From the result, it was obtained that either treated by acid or alkali, both of them show better chemical structure that are ready for enhancing gas separation performance. MWNTs pretreatment for membranes is a requirement to shorten and modify the MWNTs physical character. When MWNTs have been treated by H_2SO_4, MWNTs are distributed well throughout the membrane (Fig. 7a and 7b) while when MWNTs have been treated by NaOH, the MWNTs tips are opened and easy to be filled in PES (Fig 8a and 8b – shows compact membrane structure). The use of alkali metal is a good material to open the tips of carbon nanotubes and therefore it will accelerate the gas separation process because more tips can be opened compared to the use of sulfuric acid. However the use of acid and alkali must be at low concentration. It is because treatments using highly concentrated acid or other extreme oxidants can often disrupt their primary structures.[6]

Acknowledgement.

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