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Performance improvement of membrane distillation using carbon nanotubes

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Abstract. Although the bucky paper (BP) made from carbon nanotubes (CNTs) possesses beneficial characteristics of hydrophobic nature and high porosity for membrane distillation (MD) application, weak mechanical strength of BP has often prevented the stable operation. This study aims to fabricate the BP with high mechanical strength to improve its MD performance. The strategy was to increase the purity level of CNTs with an assumption that purer CNTs would increase the Van der Waals attraction, leading to the improvement of mechanical strength of BP. According to this study results, the purification of CNT does not necessarily enhance the mechanical strength of BP. The BP made from purer CNTs demonstrated a high flux (142 kg/m^2·h) even at low ΔT (50°C and 20°C) during the experiments of direct contact membrane distillation (DCMD). However, the operation was not stable because a crack quickly formed. Then, a support layer of AAO (anodic aluminum oxide) filter paper was introduced to reinforce the mechanical strength of BP. The support reinforcement was able to increase the mechanical strength, but wetting occurred. Therefore, the mixed matrix membrane (PSf-CNT) using CNTs as filler to polysulphone was fabricated. The DCMD operation with the PSf-CNT membrane was stable, although the flux was low (6.1 kg/m^2·h). This result suggests that the mixed matrix membrane could be more beneficial for the stable DCMD operation than the BP.

Keywords: bucky paper; carbon nanotube; membrane distillation; mechanical strength; mixed matrix membrane

1. Introduction

Carbon nanotube (CNT), which is a cylindrical structure of graphite, is famous for its high mechanical properties, high thermal conductivity, high electrical conductivity, chemical stability, large surface area, and high aspect ratio (Ruoff and Lorents 1995, Gonnet *et al*. 2006, Wang *et al*. 2006, Hilding *et al*. 2003, Zhang *et al*. 2014). In order to utilize these beneficial characteristics, a membrane was fabricated from CNTs in the form of bucky paper (BP), which found various applications such as bioengineering and electronic industries (Zhang *et al*. 2014, Zaeri *et al*. 2010, Whitby *et al*. 2008, Špitalský *et al*. 2009). The BP is also applied in water treatment as an electrode for capacitive deionization to remove ions from aqueous solution (Li *et al*. 2008, Pan *et*

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al. 2009). Yang *et al*. (2013) was able to remove humic acids (> 93%) from aqueous solution using the BP with porosity of 72.9% and pore size of 40 nm. Dumée *et al*. (2010) was able to increase the BP porosity (90%) and extended the BP application into membrane distillation (MD). They demonstrated the BP performance by producing the distillate at a flux of 12 LMH ($l/m^2/h$) under vapor pressure difference of 22.7 KPa during experiments of direct contact membrane distillation (DCMD) (Dumée *et al*. 2010). However, they also noted the limitation of BP resulting from ageing by delamination (Dumée *et al*. 2010). Similar problem was also reported by others (Sears *et al*. 2010). Sears *et al*. (2010) reported that the BP cracked quickly during experiments of DCMD and subsequently, the permeate quality deteriorated.

This study is aimed to fabricate the BP with high mechanically strength to improve its MD performance. The strategy is to increase the purity level of CNTs. It is assumed that the purer the CNTs, the higher the Van der Waals attraction, which would increase the mechanical strength of BP. Impurities could interfere with the hydrophobic interaction among CNTs. The purity level of CNTs was increased by removing their impurities in this study. Since CNTs are manufactured through the chemical vapor deposition method using catalysts such as Fe, Ni, and Co (Tripathi *et al*. 2014, Hou *et al*. 2008), they became impurities. Beside metal catalysts, amorphous carbons formed during the manufacturing process also become impurities. Therefore, the BP was fabricated with purer CNTs in order to promote the stable operation of DCMD.

2. Materials and methods

2.1 Materials

Multi-walled CNTs with 10~15 nm outside diameter, 0.5~2.0 μm long, and 90% purity manufactured by Hanwha (CM-95, Republic of Korea) were used in this study. The amount of CNTs was carefully selected because it was learned from a preliminary study that the amount of CNTs decides the hydrophobicity of BP. According to Fig. 1, using less CNTs resulted in the more hydrophobic BP. When 5 mg and 10 mg of CNTs were used, the hydrophobic BPs with contact angles of 157° and 126° were fabricated, respectively. As the amount of CNTs increased, the BP

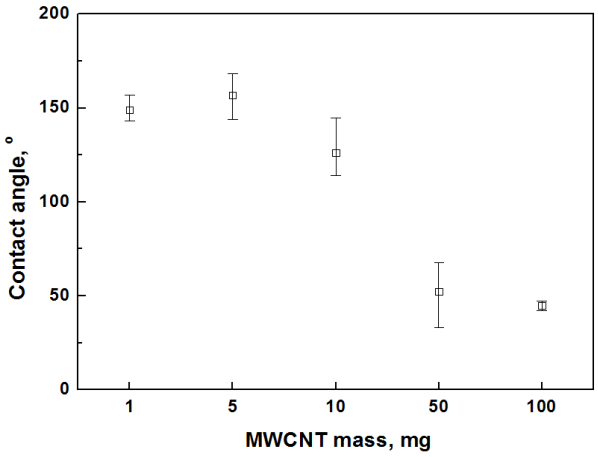

Fig. 1 Contact angles of BP as a function of CNT amount

became hydrophilic, as indicated by decreased contact angles. Therefore, 5 mg and 10 mg of CNTs were used to fabricate the BP in this study. The 98% of HCl (Daejung, Republic of Korea) was used to purify CNTs. The anoxic aluminum oxide (AAO, Anodisc 47, Whatman) filter paper with pore size of 0.2 μm, 47 mm diameter and 60 μm thickness was used for the purification of CNTs. The AAO filter was used to reinforce the BP. Either 99.5% N-Methyl-2-pyrrolidone (NMP, Daejung, Republic of Korea) and sodium dodecyl sulfate (SDS, L3771, Sigma) was used to disperse CNTs.

2.2 Methods

2.2.1 Purification of CNTs

Impurities of metal catalysts and amorphous carbons were removed from CNTs through the acid and heat treatment. The acid treatment intended to remove metal catalysts, while the heat treatment intended to remove amorphous carbons. During the acid treatment, 500 mg of CNTs were added into 200 mL of hydrochloric acid. The solution was sonicated at 140 W after 2 h of stirring. After the sonication, the solution was filtered through the AAO filter and washed using deionized water. The sonication and washing continued until the pH reached 6.5~7. During the heat treatment, acid treated CNTs were first dried at 100°C for 12 h. Then, the dried CNTs were put into the oven, at which Ar gas was flowing at 100 ml per min, at 500°C for 3 hr (Datsyuk *et al*. 2008, Kim *et al*. 2006).

2.2.2 Dispersion and filtration

It was found from a preliminary study that a mechanically stronger BP could be fabricated when CNTs were dispersed by NMP than by SDS. Therefore, NMP was used to disperse CNTs in this study. After the predetermined amounts of CNTs were added into 100 ml of NMP, CNTs were dispersed throughout the solution using the ultrasonic bath at 140 W for 90 min. The dispersion repeated five times before filtration. The resulting dispersed solution was then filtered through the AAO filter to fabricate the BP.

2.2.3 Mixed matrix membrane

The 50 mg of CNTs were dispersed in 82 g of NMP solution, and the dispersed solution was sonicated in the ultrasonic bath at 140 W for 90 min. The sonication repeated five times. After 18 g of polysulfone were added to the NMP plus CNT solution at 50°C, it was casted at 100 μm thick, and immersed in deionized water bath for 1 d. It was then dried at 50°C for 48 h to form the mixed matrix membrane (PSf-CNT).

2.2.4 Characterization

Raman spectroscopy (JP/NRS-3300, Jasco, USA) and Fourier Transform Infrared spectrophotometer (FTIR) with imaging system (FT/IR-6300, Jasco, USA) were used to detect the possible defects occurred in CNTs after the purification. The CNT purity level was measured by the thermogravimetric analysis (SDT2960, TA instrument, USA).

The contact angle of membrane was measured by the sessile drop method (Baek *et al*. 2012). The image taken from the scanning electron microscopy (SEM) with electronic data systems (S-4200, Hitach, Japan) was processed using the image-J software to calculate the pore size of BP (Wyart *et al*. 2008). The SEM images were also used to determine the membrane thickness. The porosity was calculated using Eq. (1) (Zheng *et al*. 2006). The tensile strength was measured using the universal testing machine (BESTUTM-00005MD, Republic of Korea).

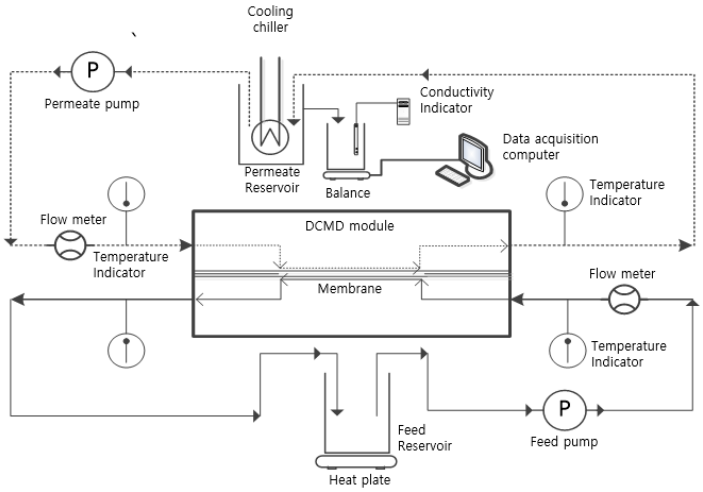

Fig. 2 Schematic of DCMD experimental set-up

$$\text{Porosity, \%} = (W_w - W_d)/\text{A}\cdot\text{h} \quad (1)$$

where, W_w: weight of wet membrane
W_d: weight of dry membrane
A: membrane area
h: membrane thickness

2.2.5 MD experiments

The DCMD experiments were conducted at ΔT of 30°C (50°C and 20°C). Fig. 2 shows the experimental set-up of DCMD. The hot feed was 2,000 mg/L of NaCl solution (3.18 mS/cm), and the cold feed was the deionized water (0.1 μS/cm). Both were circulated at 0.1 l per min. An area of the BP was 0.283 cm^2, and an area of PSf-CNT membrane was 4 cm^2. Flux and salt rejection were measured to evaluate the MD performances of various membranes.

3. Results and discussion

3.1 Purification

Fig. 3 shows the results of CNT purification. As explained above, the purification consists of two steps (acid treatment and heat treatment). The acid treatment was able to increase the purity level of CNTs from 90% to 93.4%. The heat treatment extended the purity level to 96.9%. CNTs were then examined any possible defects. The ratio of D and G peaks from the Raman spectroscopy was utilized to determine whether CNTs are damaged. It is assumed that the ratio for intact CNTs would be unity. According to Fig. 4, the ratio was close to the unity (0.99) for pristine CNTs, while the purification processes reduced the ratio to 0.92 (acid treatment) and to 0.93 (heat treatment). This result indicates that the purification processes could damage CNTs.

Two BPs was then fabricated with pristine CNTs (BP-R) and purified CNTs (BP-P) in order to examine possible enhancement in mechanical strength of BP. However, the comparison result of

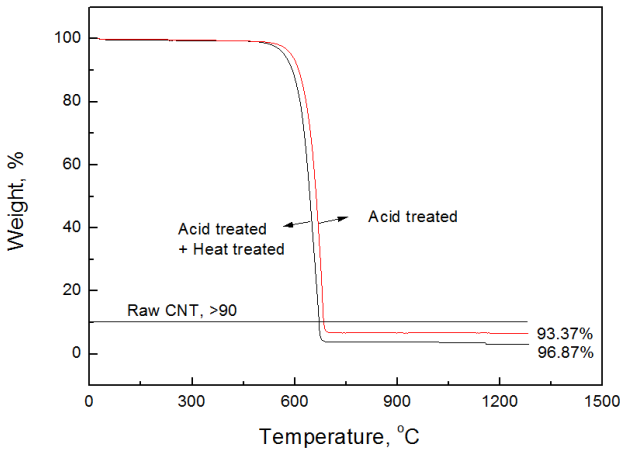

Fig. 3 Purification results of CNTs (TGA analysis)

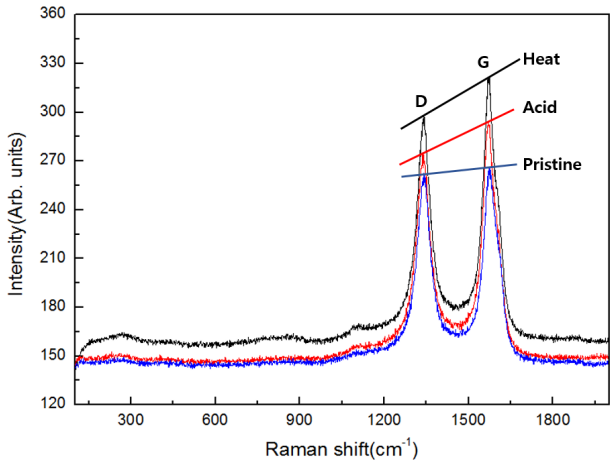

Fig. 4 Raman spectroscopy results of CNTs

their tensile strengths showed no difference. The tensile strength of BP-R was 34 ± 4.2 MPa, while that of BP-P was 34 ± 3.0 MPa. This result indicates that the purification of CNTs does not necessarily enhance the mechanical strength of CNTs.

The tensile strengths of CNTs obtained in this study are somewhere between the literature reported values. One group reported mechanical strength of 2.9~4.9 MPa (Špitalský *et al*. 2009, Arif *et al*. 2016), while other group reported substantially higher mechanical strength of 5.2 GPa (Dumée *et al*. 2010). They used different lengths of CNTs. Short CNTs (0.5~2.0 μm) were used in this study, and the Zhang group used longer CNTs (10~50 μm) (Zhang *et al*. 2014), and the Dumee group used the longest CNTs (150~300 μm) (Dumée *et al*. 2010). It is unclear whether the CNT length is related to the mechanical strength of BP, and if so, how the length affects their mechanical strengths.

The characteristics of BPs fabricated in this study (BP-P and BP-A) were compared with those of other BPs (Zhang and Dumee). According to Table 1, the BP-P was more porous (93%) than

Table 1 Characteristics of various membranes

Items*	Average pore size, nm	Porosity, %	Contact angle, °	Thickness, μm	Tensile strength, MPa	Liquid entry pressure (LEP), KPa
BP-P	19±15	93±7.9	125±3.2	28±2.2	34±3.0	23±5.0
BP-A	16±9.0	-	157±7.6	77±2.0**	334±30.6	42±3.0
Dumee	27.3	90	113.3	47±5.6	5,200	55.2
Zhang	10	87.2~89.1	-	~110	2.9~4.9	-
PSf-CNT	-	54±4.6	78±1.1	~100	4.4±0.2	>700

*BP-P indicates BP made of purified CNTs; BP-A indicates BP on AAO; Dumee indicates BP fabricated by Dumee group (Dumée *et al*. 2010); Zhang indicates BP fabricated by Zhang group (Zhang *et al*. 2014); PSf-CNT indicates mixed matrix membrane of polysulfone with CNTs.
**BP-A's real thickness is 17 μm since AAO is 60 μm thick

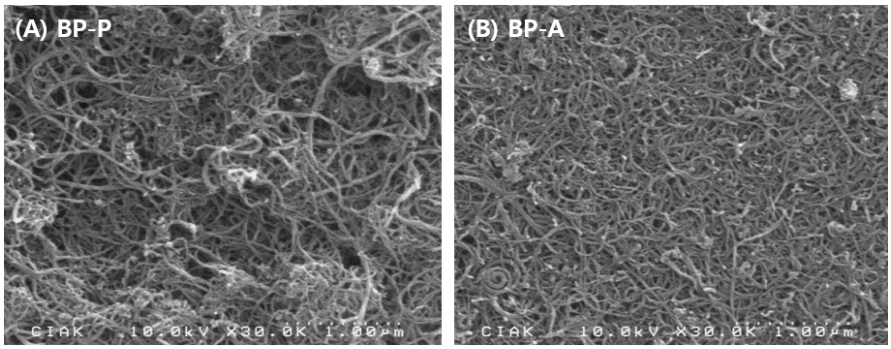

Fig. 5 Images of scanning electron microscope of BPs fabricated in this study

others (90% for Dumee group, 87.2~89.1% for Zhang group). They were also more hydrophobic than other BP. The BP-P (125°) and BP-A (157°) had higher contact angles than the Dumee group's BP (113.3°). They were thin (28 μm), compared to others (47 μm for Dumee group, 110 μm for Zhang group). The BP-P and BP-A had larger pore sizes (16~19 nm) than the Zhang group's BP (10 nm), but smaller than the Dumee group's BP (27.3 nm). All these characteristics are beneficial for high membrane permeation, except low pore size. However, the BP-P (23 KPa) and the BP-A (42 KPa) showed low liquid entry pressures, which indicates that the MD experiments with these BPs should be conducted carefully to prevent water penetration. Fig. 5 shows the SEM images of the BP-P and BP-A.

The DCMD experiments with BP-P and BP-A were then conducted. As shown in Fig. 6, the BP-P showed a flux (142 kg/m^2/h) at temperature difference of 30°C (50°C and 20°C), which is substantially higher than other BP (12 LMH). High porosity, high hydrophobicity and thinness are believed to contribute to such high flux. As shown in Table 1, the BP-P had the porosity of 93%, contact angle of 125° and thickness of 28 μm, while the Dumee group's BP had the porosity of 90%, contact angle of 113.3°, and thickness of 47 μm.. However, the operation was not stable because a crack formed quickly (25 min). Dumee *et al*. (2010) experienced a similar problem. Their DCMD experiment came to an end after 2 h (Dumée *et al*. 2010). BP was held together by the Van der Waals attraction, which might be insufficient to guarantee its integrity.

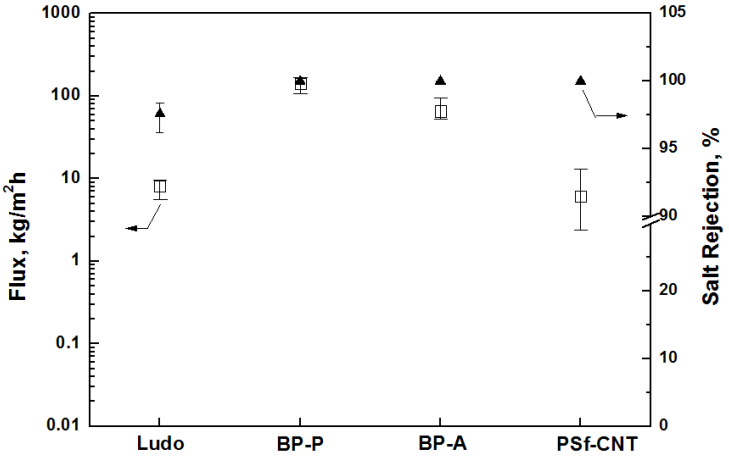

Fig. 6 Results of DCMD experiments

Therefore, a support layer was introduced to reinforce the BP. The BP was placed on the support layer of AAO filter to form the BP-A. The support layer reinforcement improved the mechanical strength of BP. According to Table 1, tensile strength of the BP-A (334 MPa) was significantly higher than the BP-P (34 MPa). The BP-A possessed comparable pore size and contact angle as the BP-P. The pore size of the BP-P was 16 nm and that of the BP-P was 19 nm. The contact angle of BP-A was 157° and that of the BP-P was 125°. The BP-A was thicker than the BP-P due to the support layer of AAO filter. When the BP-A was applied for the DCMD experiment, it showed a flux of 66 kg/m^2/h according to Fig. 6, which was considerably lower than that of BP-P (142 kg/m^2/h). The operation with the BP-A was not stable either. Wetting quickly occurred probably due to thin layer of BP. This result indicates that the support reinforcement of BP with the AAO filter did not necessarily lead to the stable operation of DCMD.

CNTs were then added as filler to the polymer matrix to form the mixed matrix membrane of PSf-CNT, instead of BP. The PSf-CNT had lower porosity (54%), contact angle (78°), and were thicker (100 μm) than the BP-P, according to Table 1. When the PSf-CNT was applied for the DCMD experiment, low flux (6.1 kg/m^2/h) was obtained according to Fig. 6. Low porosity, contact angle and high thickness are believed to result in such low flux. On the other hand, the operation was stable. There was no crack formed and no wetting occurred during 2 h of the DCMD operation with the PSf-CNT membrane. This result suggests that the mixed matrix membrane could be more beneficial for the stable DCMD operation than the BP.

4. Conclusions

This study aims to fabricate the BP with high mechanical strength to improve its MD performance. The strategy was to increase the purity level of CNTs, which would improve the Van der Waals attraction, resulting in enhanced mechanical strength of BP. In this study, the purity level of CNTs could be increased from 90% to 96.9% using the acid and heat treatment. However, such purification did not lead to enhancement of mechanical strength of BP as initially assumed. Nonetheless, the BP-P, which was fabricated with purer CNTs in this study, demonstrated substantially high flux (142 kg/m^2/h) even at ΔT of 30°C (50°C and 20°C) during the DCMD

experiments. However, the operation was not stable because a crack quickly formed. Subsequent support reinforcement using the AAO filter was able to enhance the mechanical strength of the BP, but wetting quickly occurred during the DCMD experiment. Therefore, CNTs were added as filler to polymer matrix to form the mixed matrix membrane of PSf-CNT. Although flux was low, this PSf-CNT membrane allowed stable DCMD operation. This study results suggest that the mixed matrix membrane could be more beneficial for the stable DCMD operation than the BP.

Acknowledgments

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