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PAPER

PVdF/graphene oxide hybrid membrane via electrospinning for water treatment application

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Membrane materials based on poly (vinyldene fluoride) (PVdF) have received a great attention recently due to their outstanding mechanical property and chemical resistance. However, this material can easily cauese a membrane fouling problem due to its hydrophobic nature. This paper describes how to overcome this problematic issue by incorporating hydrophilic graphene oxide (GO) into PVdF-based membranes. Herein, PVdF nanofiber membranes loaded with GO was prepared via an electrospinning method and the hybrid membranes were characterized for water treatment applications. Graphene oxide sheets were initially prepared by the Hummer's method. The pore property of the PVdF/GO hybrid nanofiber membrane for microfiltration (MF) applications was controlled by systematically increasing the number of nanofiber layers and thermal treatment. These resulting materials were characterized by SEM, FT-IR, UV-Vis, Raman spectroscopy, and tensometer. Overall results showed that the reliable formation of the composite materials which possessed controlled pore-diameters (~0.2 micron) and narrow distribution. Based on contact angle tests, these PVdF/GO nanofiber composite membranes exhibited very hydrophilic characteristics. In addition, the hybrid membrane showed high pure water flux results up to 3 times and outstanding flux decline with 0.1mg/L Kaolin solutions compared to a neat PVdF nanofiber membrane. Based on these results, it can be speculated that the incorporation of GO into PVdF could also improve antifouling ability of the membrane system and will allow for their use as a water-treatment membrane.

Introduction

Synthetic polymer membranes including poly (vilnylidene fluoride) (PVdF), Poly (sulfone) (PSf), poly (ether sulfone) (PES), poly (ethylene) (PE), and poly (propylene) (PP) have been widely used in water treatment processes due to their outstanding physical and chemical properties.[1,2] However, these materials often exhibit hydrophobic property causing some critical problems including the flux and rejection decline, and organic fouling.[3-6] In order to resolve some of these issues, various approaches have been developed to render hydrophilic property into these polymeric materials by introducing hydrophilic monomers by low energy plasma[7] and irradiation[8] as well as by blending hydrophilic organic and inorganic materials.[9,10]

Recently, nano-scale metal oxide particles,[11] carbon nanotubes,[12] and graphene[13,14] have been utilized to improve these polymer-based membrane properties with increased permeability, selectivity, and anti-fouling effect. In particular, graphene as an additive has many advantages for water purification due to its high surface area (2,630 m^2/g) and chemical stability.[15,16] As exfoliated graphene oxide (GO) can possess various hydrophilic functional groups such as carboxyl, expoxyl, and hydroxyl groups,[17] GO-incorporated membranes have been tested in waste-water treatment systems to remove heavy metal ions (e.g., Pb, Cd, and As ions).[15,18,19]

An electrospinning technique is relatively new approach to manufacture nanofiber-based membranes for microfiltration (MF) and ultrafiltration (UF) systems.[20] It has been introduced to prepare a nonwoven nanofibrous web or membrane by electrostatic charge to the polymer solution jet. This technique offers many advantages such as a high surface area-to-volume ratio, outstanding selectivity of polymer materials, and easy incorporation of various functional groups. In addition, this technology can reduce the environmental treatment cost as the membrane manufacturing process doesn't require to use non-solvent bath.[21-23]

Herein, GO was prepared by the modified Hummer's method and was hybridized into an electrospun poly (vinylidene fluoride) (PVdF) membrane to prepare composite materials for microfiltration (MF) application. We systematically controlled the pore property of the composite membrane, and investigated the changes of water flux and surface modification of nanofiber membrane as a function of GO contents.

Experimental section

Materials

Materials used to synthesize graphene oxide were graphite flake

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(Bay city, Michigan 48706), sulfuric acid (98%), potassium permanganate (Sigma-Aldrich), sodium nitrate (NaNO₃, ≥99.0%, Sigma Aldrich), hydrogen peroxide (H₂O₂, 35%, Samchen Co. Ltd. in South Korea). Materials used to manufacture hybrid nanofiber membrane were poly (vinylidene fluoride) (PVdF, Arkema, Kynar 761), N,N-dimethyl formamide (Duksan Pure Chemical Co. Ltd., Korea, >99.0%), acetone (Duksan Pure Chemical Co. Ltd.). The distilled water was purified through a Millipore system (~18 MΩ · ㎝). All of the chemicals and reagents were used as received without further purification.

Synthesis of graphene oxide (GO) and GO paper

GO was synthesized by the oxidation of natural graphite flake using the modified Hummer's methods.[24] Specifically, 2 g of graphite flake and 1.52 g of NaNO₃ were mixed with sulfuric acid (67.6 mL) under stirring at room temperature, and then 9 g of KMnO4 was gradually added into the mixture. The resulting mixture was putted into the ice-bath and stirred for 5 hours under 10 ℃. The mixture was additionally stirred at room temperature for 5 days which was eventually turned to brownish paste. The brown paste compound was fully dissolved by 5 vol.% of concentrated sulfuric acid and stirred for 3 hours, followed by the addition of 5 ml of H₂O₂ into the compound. The color was changed to bright yellow. A mixture of 4 vol.% of H₂SO₄ and 1.5 vol.% of H₂O₂ solution was added to this bright yellow solution to oxidize graphite flake. The oxidized graphite was washed several times with distilled water and centrifuged (Hanil Science Industrial Co., Ltd., FLETA 5) at 4,000 rpm for 10min until the pH of the top solution became neutral. To obtain the GO powder, vacuum drying was performed for 2 day. Exfoliation of graphite oxide to GO was achieved using a tip sonicator (Sonic VCX-750, Sonics & Materials, Inc.) with 1mg/mL of graphite oxide solution for 1 hour. Then, the final GO paper was obtain by filtering the graphene oxide solution with a vacuum filtration system with 0.45 ㎛ PVdF filter (Millipore Co., Ltd.).

Preparation of PVdF/GO hybrid nanofiber membrane

The PVdF (PNMs) and PVdF/GO hybrid nanofiber membranes (PGNMs) were prepared by the electrospinning method after the preparation of electrospinning solution consisting of 20 wt% of PVdF powder and the 0.1-0.4 wt% of GO in DMF and Acetone under sonication for 1 hour. The composition of the solution is listed in Table 1. The prepared solution was then filled into a 5mL syringe with a 22 gauge needle. The syringe was positioned vertically for 30 min. By pushing the end of syringe plunger, the air was completely removed. The ejection speed was controlled by KDS100 (KD Scientific Inc.), and the voltage supply equipment used was a CPS 60K02VIT (Chungpa EMT co., Ltd.). The following electrospinning conditions were used: flow rate 0.6 mL/h, voltage 15 kV, TCD (tip to collector distance) 10 cm, duration 6 h, and relative humidity 20~40%. To improve physical property and to control pore diameter, the PGNMs were thermally treated in a dry-oven at 120 ℃ for 24 hours after stacking PGNM's layers and placing between glass plates. After peeling off the membrane from the glass plates, the membrane was rinsed with methanol and distilled water to remove the residues.

Table 1 Composition of electrospinning solutions

Sample code	PVdF (wt. %)	GO (wt. %)	DMF (wt. %)	Acetone (wt. %)
PNM	20.0	0.0	64	16
PGNM01	19.9	0.1	64	16
PGNM02	19.8	0.2	64	16
PGNM03	19.7	0.3	64	16
PGNM04	19.6	0.4	64	16

Characterization of synthesized GO and PVdF/GO hybrid nanofiber membranes
Morphology and structure of synthesized GO and PVdF/GO hybrid nanofiber membranes

FTIR (JASCO, FT/IR-620) was used to observe the various functional groups of synthesized GO. Test samples were prepared by mixing of GO sheets and KBr disc.

The surface morphology of GO was observed by STEM (Scanning Transmission Electron Microscope, Hitachi, HD-2300). The GO solution was prepared by 0.1mg/mL density in ethanol dispersed about 10minutes by an ultra-sonicator, and the STEM samples were prepared by completely drying of 1-2 drops of GO solution on TEM grid with infrared. At this experiments, 400 mesh carbon was used for grid and the acceleration voltage was 200 KeV.

The SEM and EDS (Hitach, S-4800) analysis were performed to observe the surface morphology of the PNMs and PGNMs, and to confirm the presence of GO in nanofiber. These membranes were completely dried in a vacuum oven at room temperature for 1 hour and the osmium (Os) was coated for 5 second on the membranes by using a vacuum sputter. Raman spectroscopy (WITec project, alpha 300R) was used to determine whether the introduction of GO in the nanofiber membrane was successful or not. The sample was made of a 1cm × 1cm size and the membrane were mounted on a glass substrate, then the laser beam was focused on the center of membrane surface.

Pore size and porosity analysis of PVdF/GO hybrid nanofiber membrane

To analyze the pore-diameters of the PGNMs, Capillary Flow Porometer (porolux 1000, Porous Materials Inc.) was used and the Porewick solution with a surface tension of 16.0 dynes/cm was used as standard solution and then effective diameter of membrane was fixed at 1.9cm.

To analyze the porosity of membranes, the prepared nanofiber membranes (5 cm × 5 cm) were soaked in n-butanol (Junsei Chemical Co. Ltd.) at room temperature for 2 hours. The membranes were taken out from the solvent and wiped with Kimwipes to remove excess n-butanol from the surface. The mass of these wet membranes (W_{wet}) was measured. To determine the mass of dry membranes (W_{dry}) and volume (V_{dry}), the wet membranes were dried in the oven at 100 ℃ for 24 hours. The average water uptake values were determined based on five measurements. The porosity was then determined by the following Eq. (1).

$$Prosity(\%) = (W_{wet} - W_{dry})/(\rho_b \cdot V_{dry}) \times 100\% \qquad (1)$$

Where ρ_b is the density of n-butanol.

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Mechanical properties of PVdF/GO hybrid nanofiber membrane

The PGNMs' tensile strength was measured by a KYUNG-SUNG testing machine with 1 KN capacity load cell. The test was performed according to ASTM D882, and all samples were compared with neat PVdF membrane to evaluate the effect of GO on the mechanical properties. The samples were cut in a rectangular shape with dimension of 10 mm × 3 mm. The test was performed using pneumatic grips with 90 psi and 25 mm×25 mm rubber jawface at a crosshead speed of 50 mm/min.

Contact angle test of PVdF/GO hybrid nanofiber membranes

The contact angle measurements of the prepared nanofiber membranes were conducted using a Contact Angle Analyzer (Phoenix 300, SEO) to investigate the surface wetting characteristics of membrane as a function of GO contents. The measurements were carried out using distilled water and at room temperature. The contact angle values was obtained with the average of the five measurements to minimized experimental error.

Pure water flux test of PVdF/GO hybrid nanofiber membrane

The water flux of the membrane samples was performed by a dead-end-cell device with a filtration area of 38.5 cm^2. The schematic diagram of the filtration system is shown in Fig. 1. The distilled water was prepared in a bomb filter and mixed well using a magnetic stirrer to eliminate bubbles in the membranes. The filtration pressure was maintained by a compressed N_2. The filtrate was collected into a receiver on a balance. The mass of filtrate was recorded during the filtration, which was plotted against time. Water flux was then determined according to the following Eq. (2).

$$\text{Water flux (kg } / \ m^2 \cdot \ \text{h)} = m_x / \Delta t \cdot A_x \qquad (2)$$

Where m_x is the weight of the filtrate (kg), t is filtration time (hour), and A_x is effective area of membrane (m^2).

Turbidity and flux decline test of PVdF/GO hybrid nanofiber membranes

The 0.1 mg/L Kaolin solution was used to observe the turbidity changes and flux decline during filtration by a turbidity inspector (HANNA instruments, HI83414-Turbidity Free/Total chlorine). The values of turbidity and flux decline during the filtration with Kaolin solution were obtained per 30 minutes. Based on the 0.1mg/L Kaolin solution, the rejection rate was determined according to the following Eq. (3). All of experiments were conducted at room temperature and at 1 bar pressure.

$$\text{Rejection rate (\%)} = \left(C_0 - \frac{C_f}{C_0} \right) \times 100\% \qquad (3)$$

Where C_0 is initial turbidity values of 0.1mg/L Kaolin solution and C_f is the filtrate turbidity values.
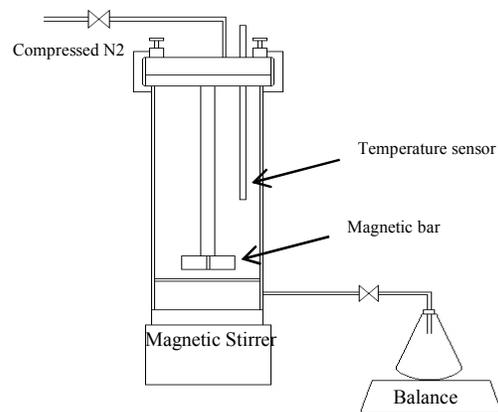

Fig. 1 Schematic diagram of a dead-end-cell device.[25]

GO elution test of PVdF/GO hybrid membranes during filtration

In order to confirm the no elution of GO from PVdF/GO hybrid membrane during long time operation the ultraviolet-Visible (UV-Vis) spectra of GO solution and filtrated water were investigated by UV-Vis spectrometer (SHIMADZU, UV-1650PC). GO solutions from 100 ppb to 1 ppm were used and the samples of water filtrated by PGNM02 were measured in 7 days filtration with dead-end cell device. Distilled water was used for feed at 1 bar pressure, and working operation time was 8 hours per day.

Results and discussion

Morphology and structure of synthesized GO and PVdF/GO hybrid nanofiber membranes

The synthesized GO was analyzed by FT-IR (Fig. 2). From Fig. 2, it was clearly observed that a peak appeared at 1630 cm^{-1} for the stretching vibration of remaining sp^2 character of C=C bond. The peak in the range of 3000-3700 cm^{-1} is attributed to the -OH stretching vibration. The peak at 1720 cm^{-1} is corresponding to the carboxyl group (C=O stretching vibration); 1050 cm^{-1} peak is the vibrational absorption peak for the C-O-C group. This shows that under our experimental conditions, the synthesized GO possesses many hydrophilic functional groups including -OH, -COOH, -C=O, -CH(O)CH-.
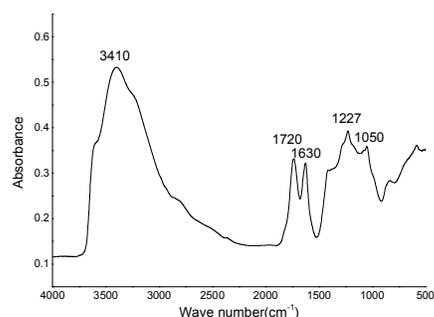

Fig. 2 FT-IR spectra of synthesized GO.

The STEM analysis was carried out to examine the surface morphology of synthetic GO. The winkle shape of the GO unique features was observed from the STEM images (Fig. 3 (e)). Further, it was shown that the GO sheets were composed of a multi-layer, which was expected that the GO layers were not completely exfoliated during the sample preparation process due to the relatively short time of ultrasonic dispersion. Thus, it could be expected that the GO would be introduced between the nanofiber in a multilayer structure, not less than 1nm of single layer structure.

The surface morphology of the neat PVdF nanofiber membrane and PVdF/GO hybrid nanofiber membranes was observed by SEM analysis. The Fig. 4 (a)-(e) images exhibit the surface morphology of nano-sized fibers with network-like porous structures. Then the average diameter of nanofiber was measured about 600~700nm. However, a two-dimensional structure of GO couldn't be observed for all of PGNM samples. But it was found that the colour of PGNM samples was gradually changed from white to brownish colour with increase of the GO contents. In order to confirm the existence of GO in the nanofiber the EDS was taken and the results showed the small amount of oxygen atom peaks (1.0 to 1.7%) due to the small amount of GO in nanofiber (Fig. 5).
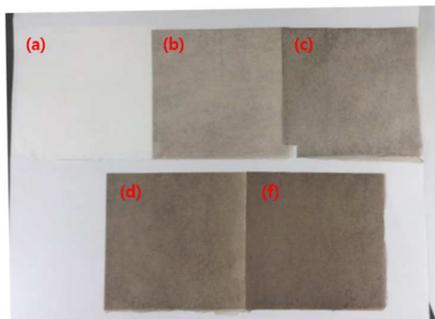
Fig. 3 Optical images of prepared nanofiber membranes; (a) PNM, (b) PGNM01, (c) PGNM02, (d) PGNM03, and (f) PGNM04.
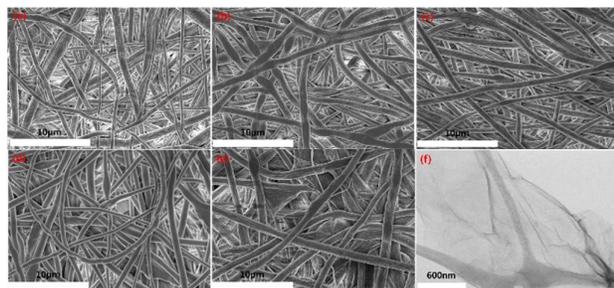

Fig. 4 STEM, and SEM images of prepared nanofiber membrane; (a) PNM, (b) PGNM01, (c) PGNM02, (d) PGNM03, (e) PGNM04, and (f) GO.
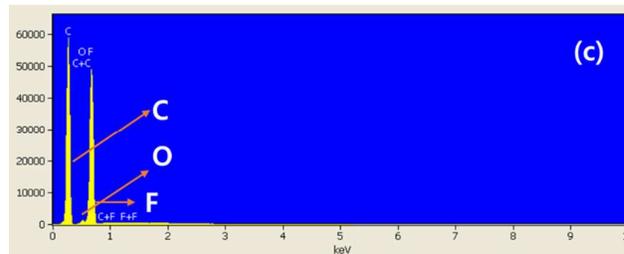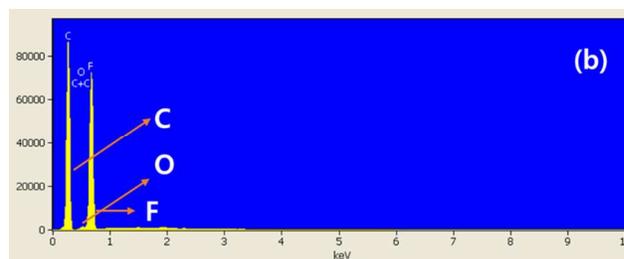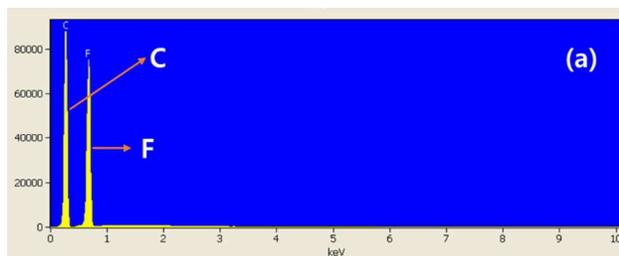
Fig. 5 EDS images of prepared nanofiber membranes; (a) PNM, (b) PGNM02, (c) PGNM04.

In order to make sure the existence of GO in the nanofiber membrane, Raman spectroscopy analysis was also carried out because this technique has been known as an efficient and quick method for determining the structure of graphene derivatives.

The Raman spectra in Fig. 6 show the D-band peak at ~1,352cm^{-1} and G-band peaks at ~1,601cm^{-1} in all of GO sheets and PGNM samples unlikely PNM samples. It is well known that the G-band corresponds to the first-order scattering of the E_{2g} mode observed for sp2 carbon domains, and the pronounced D band is associated with structural defects, amorphous carbon, or edges that can break the symmetry and selection rule.[16] As PGNMs also clearly exhibit the D- and G-band peaks. From the Raman spectroscopy results it could be concluded that GO was successfully incorporated with the PVdF nanofiber membrane.
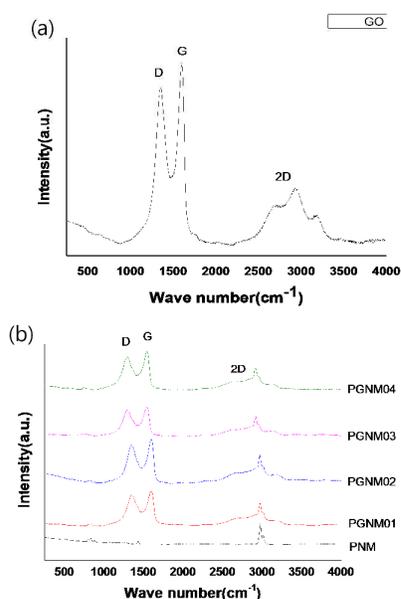
Fig. 6 Raman spectra of synthesized GO (a) and prepared nanofiber membranes (b).

Pore size and porosity analysis of PVdF/GO hybrid nanofiber membrane

It was observed that neat PVdF membrane had a bubble point of 0.4 μm and mean pore size of 0.26 μm. With increasing the content of GO in PVdF nanofiber membranes, the pore size of PGNMs gradually decreased. The largest pore size of PGNM04 containing 0.4 wt% of GO was tested to be ~0.2 μm. The pore properties of a series of membrane samples are summarized in Table 2. Although the membrane pore sizes somewhat decreased as a function of GO content, overall porosities of the membranes were measured about 35%, then the thickness was a range of 55~65 micrometer. It was speculated that the GO, a two-dimensional material, did not like other nano-fillers such as a nano-clay which affected the overall porosity of membranes.

Table 2 The pore-properties of prepared nanofiber membranes

Sample code	Biggest pore Diameter (nm)	Smallest pore Diameter (nm)	Avg. pore Diameter (nm)	Porosity (%)	Thickness (μm)
PNM	402.7	144.9	259.2	35	55~64
PGNM01	316.5	135.2	218.8	38	54~62
PGNM02	256.4	133.4	203.5	35	55~65
PGNM03	241.2	132.9	185.0	34	57~62
PGNM04	200.6	118.6	167.1	32	58~61

Mechanical properties of PVdF/GO hybrid nanofiber membranes

Fig. 7 shows the mechanical properties of various hybrid nanofiber membranes as a function of GO content. The tensile strength was measured as mechanical properties. As the amount of GO in

nanofiber membrane increased, the tensile strength gradually increased. This is presumably caused by a strong hydrogen bond interaction between the GO and PVdF nanofiber. Thus, all of samples exhibited enhanced mechanical properties higher than 280 kgf/cm^2. These results could be explained by the high number of complex physical bonds in the nanofiber itself.
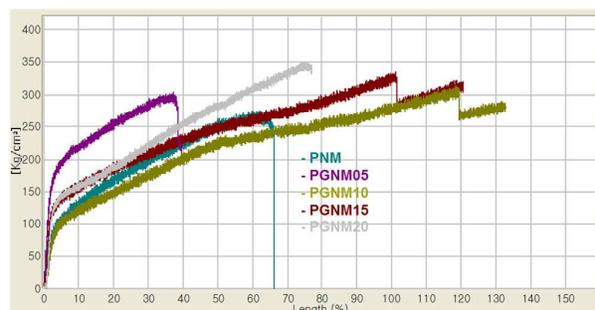
Fig. 7 Stress-strain curve of prepared nanofiber membranes.

Contact angle analysis of PVdF/GO hybrid nanofiber membranes

As GO possesses hydrophilic carboxyl, hydroxyl, and epoxide groups, it was speculated that the hydrophobic PVdF could exhibit hydrophilic property upon introduction of small amount of GO. With systematic increase of the GO content in the nanofiber membrane, the water flux was obviously improved and the contact angle of composite membranes gradually decreased from 70° to 40° which are shown in Fig. 8.
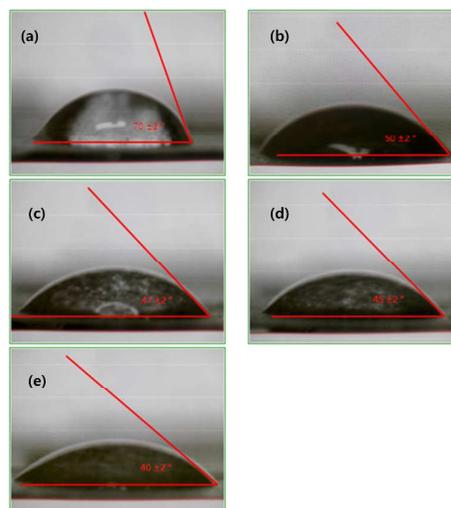

Fig. 8 Contact angle results of prepared nanofiber membranes; (a) PNMs, (b) PGNM01, (c) PGNM02, (d) PGNM03, and (e) PGNM04.

Pure water flux of PVdF/GO hybrid nanofiber membranes

According to other researches, it was known that water molecules could be easily drawn to the inside of membrane with hydrophilic surface, hence the flux of a membrane can be increased by enhancing hydrophilicity of the membrane.[12] The pure water flux results were shown in Fig. 9. Although the PVdF membrane has the largest pore-diameter among all samples, the pure water flux was very low due to the

hydrophobic nature. Under the 1 bar pressure condition, the water flux value of neat PVdF membrane was lower than 200 kg/m^{2}hr. However, when adding GO into PVdF nanofiber, all of the PVdF/GO hybrid nanofiber membranes showed 3 times higher values of pure water flux than that of neat PVdF membrane due to its hydrophilic nature. Meanwhile, PGNM02 sample had the highest value of water flux among all of the samples. However, the water flux values of PGNM04 were lower than PGNM02 and PGNM03 despite of having the lowest contact angles (Fig. 7). This result is in accord with the pore-properties of PGNMs and it is expected that the membrane pores is gradually blocked as an aggregation of GO.
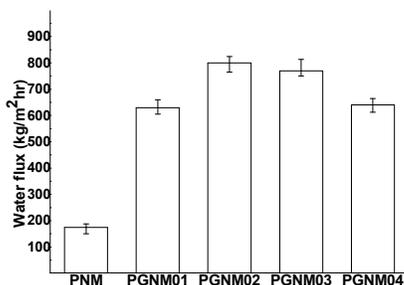

Fig. 9 Pure water flux results of prepared nanofiber membranes at 1 bar pressure**.**

Turbidity change and flux decline results of PVdF/GO hybrid nanofiber membranes

For the rejection of turbidity test, 0.1 mg/L Kaolin solution (160 NTU) was used, where standard distill water showed a turbidity of 0.16 NTU. Filtrate rejection rate and flux decline results of our membranes were shown in Table 3 and Fig. 10, respectively.

Table 3 Rejection rate with 0.1mg/L Kaolin solution at 1 bar pressure

| Sample code	After 30min Rejection (%)	60min (%)	120min (%)	180min (%)
PNM	99.89	99.90	99.89	99.89
PGNM01	99.90	99.90	99.90	99.90
PGNM02	99.90	99.89	99.89	99.90
PGNM03	99.90	99.90	99.90	99.89
PGNM04	99.90	99.89	99.90	99.90
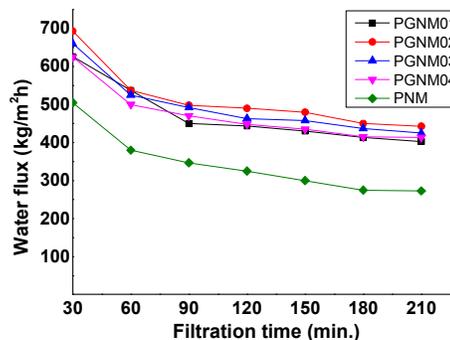
Fig. 10 Flux decline results during filtration with 0.1mg/L kaolin solution at 1 bar pressure.

During filtration with the kaolin solution, it was expected that the pore of membrane could be gradually blocked, resulting in decrease of the flux. As the neat PVdF nanofiber membrane was hydrophobic, it could be easily polluted by kaolin grains compared to PGNM samples. The flux was obviously declined in 90 min during filtration. The rejection rate of all samples was measured 99.9% during filtration tests with 0.1mg/L Kaolin feed solution. But the flux decline with 0.1mg/L Kaolin feed solution was improved with increase of GO in the nanofiber membrane, indicating the PVdF/GO hybrid nanofiber membrane could lowed the membrane fouling which has known the one of general problems with polymeric membrane. It can be concluded that the PVdF/GO hybrid nanofiber membrane can be used for the water treatment application as a microfiltration membrane.

GO Elution test of PVdF/GO hybrid nanofiber membranes during filtration

From the Fig. 11, it was observed that GO showed maximum absorption peak at ~237 nm attributable to π-π* transition of the atomic C-C bonds and shoulder peak at ~300 nm due to n-π* transitions of aromatic C-C bonds.[26] The filtrated water did not show the absorption peaks of both ~237 nm and ~300 nm, thus, it was confirmed that the GO in the nanofiber matrix wasn't eluted.
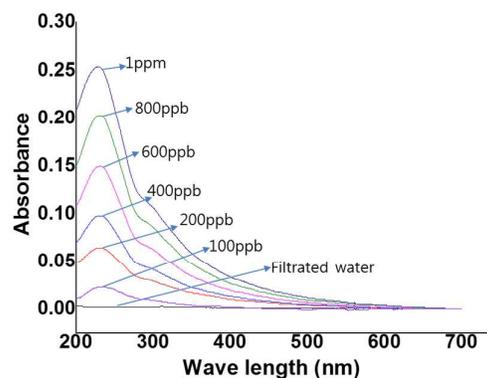
Fig. 11 UV-vis spectra results of various concentrated GO and filtrate of PGNM02 during filtration for 7day at 1 bar pressure.

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Conclusions

In this study, we focused on the preparation of porous PVdF/GO hybrid nanofiber membranes (PGNMs) for possible water-treatment applications. The formation of PGNMs was completed via the electrospinning method using a solution containing a mixture of PVdF powder (20 wt%) and exfoliated graphene oxide (0.1 to 0.4 wt%) in dimethyformamide (64 wt%) and acetone (16wt%). The resulting PGNMs improved mechanical property upon thermal treatment. The pore diameter of PGNMs was systematically controlled by simply increasing the number of PGNMs layers. The prepared membrane and nanomaterials (GO) were characterized by SEM, FT-IR, UV-Vis spectra, Raman analysis, and tensometer. These results showed that the pore-diameter was controlled by 0.2 micron with narrow distribution. Based on contact angle tests, these prepared PVdF/GO hybrid nanofiber membranes exhibited hydrophilic characteristics. In addition, the PGNMs showed high pure water flux results up to 3 times and outstanding flux decline with 0.1mg/L Kaolin solutions compared to pure PVdF nanofiber membrane. At this point, it is expected that the antifouling ability of membranes can be improved by adding GO. Based on the results of GO elution test, it was confirmed that the GO in the nanofiber matrix wasn't eluted. It was concluded that the PVdF/GO hybrid nanofiber membranes can be utilized for water-treatment.

Acknowledgements

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