NOVEL COMPOSITE POLYACRYLONITRILE (PAN) ELECTROSPUN FIBROUS MEMBRANE FOR HIGH-PERFORMANCE WATER FILTRATION

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In this current study we have fabricated nonwoven filter membrane of polyacrylonitrile (PAN) that consists of antifouling and antibacterial capacity. Bleaching powder (BP) was incorporated through PAN fiber during electrospinning using blend solution of BP nanoparticles (NPs) and PAN. The morphology and composition of the composite BP/PAN fibers were observed by field scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS). The obtained results revealed that sufficient amount of BP NPs were effectively loaded on/into PAN fibers. The presence of BP on/into PAN fibers could significantly increase the hydrophilicity of PAN membrane which indicated that as-fabricated membrane can be used not only for bacterial destruction but also for introducing antifouling activity on the membrane. Significant increase in hydrophilicity of composite membrane compared to the pristine PAN membrane and excellent antibacterial activity of BP loaded PAN fibers indicated that this composite membrane will be a potential water filter media to provide pure drinking water.

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1. Introduction

Drinking water contaminated with pathogens kills millions of people every year, particularly in under developed countries [1]. People, in these countries, are commonly using chemical disinfectants, mainly chlorine (from bleaching powder), for drinking water treatment [2]. However, excess of chlorine in water is not only suspected to create unpleasant odor for drinking but also create carcinogenic byproducts when organic matter is present in water [3]. Furthermore, harmful particulates (either bleaching powder particles which are mainly used for chlorination of water or other foreign particles) taken with drinking water may cause the serious health problem. Therefore, searching of eco-friendly technique to fabricate functional water filter membrane which can remove pathogens and particulates impurities from water is potential for the people of under developed countries.

Most water filtration applications have one common purpose- to protect against harmful waterborne contaminants whose dimension is nano to micro size [4, 5]. Therefore, materials used for this propose should have small pore diameter with sufficient porosity. Electrospun nonwoven fabrics possess several unique properties that make them good candidate for the filtration,

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separation, and cleaning applications as they have large specific surface area, high porous structure with nano/micro size range [6-9]. The potential of electrospun fibers for filtration proposes has been reported in literature by showing separation of tiny particles[10]. However, there are still many problems to be solved, such as the decline of the flux caused by membrane fouling which affects the performance significantly [11, 12]. Fabrication of functional electrospun membrane with sufficient hydrophilicity and capacity to generate gaseous bubbles continuously on the surface of membrane to reduce organic and inorganic fouling of the membrane is potential in water treatment application.

The concept of introducing BP (which can produce Cl_2 gas) on/into the chemically stable polymeric electrospun membrane for water filtration paves the new revolution in water treatment. Here, our hypothesis is to incorporate sufficient amount of commercially available BP particles through the electrospun PAN fibers using single step process. PAN is mostly chosen for the preparation of fibrous filter media owing to the chemical stability and excellent weatherability [13, 14]. To date, although different electrospun membrane of PAN and its composite were fabricated, no effort has been given to the development of BP incorporated antifouling membrane with excellent antibacterial activity of either PAN or any other polymeric fibers. Therefore, the main object of this study is to investigate cost effective multifunctional membrane processing technique and discusses structure property relationship of as-synthesized nanofibers for expand membrane applications and improve membrane performance for water filtration.

2. Experimental

2.1. Materials and methods

Polyacrylonitrile (PAN) with an average molecular weight (Mw) of 150,000 was purchased from Sigma-Aldich; 99.5% N,N-dimethylformamide (DMF) was obtain from Samchun, Korea (Cas No. 68-12-2); and bleaching powder [calcium hypochlorite ($Ca(OCl)_2$)] was purchased from Alfa Aesar, England (Lot: 10114246). Extremely small size BP particle were obtained by using mechanical grinder.

2.2. Fabrication of nanofibrous membrances

A 12 wt% PAN solution was prepared in DMF solvent using magnetic stirrer followed by addition of different amounts (0, 25, 40 wt%) of BP. The homogenous blend solution was obtained by further magnetic stirring followed by ultrasonication. Polymer solution was fed with a plastic syringe of a 25 ml through the metal capillary (nozzle) having di = 0.21 mm (21 G) attached to a 1-D robot-system that moves laterally controlled by LabVIEW 9.0 program (National Instrument) Fig. 1 [15]. The feeding rate via a controllable syringe pump was maintained at 0.5 ml/h. Electrospinning process was carried out at a electric voltage of 15 kV and the spinneret to collector distances of 18 cm, at ambient temperature of 25°C and humidity of 40%, and different electrospun mats were collected as a mat on the polyethylene sheet coated on rotating drum. After vacuum dried for 20 h, the fiber mats were used for further analysis. The following name conventions will be used from here onwards: NM-0, NM-1, and NM-2, referring to PAN fiber containing 0, 25, 40 wt% BP, respectively.

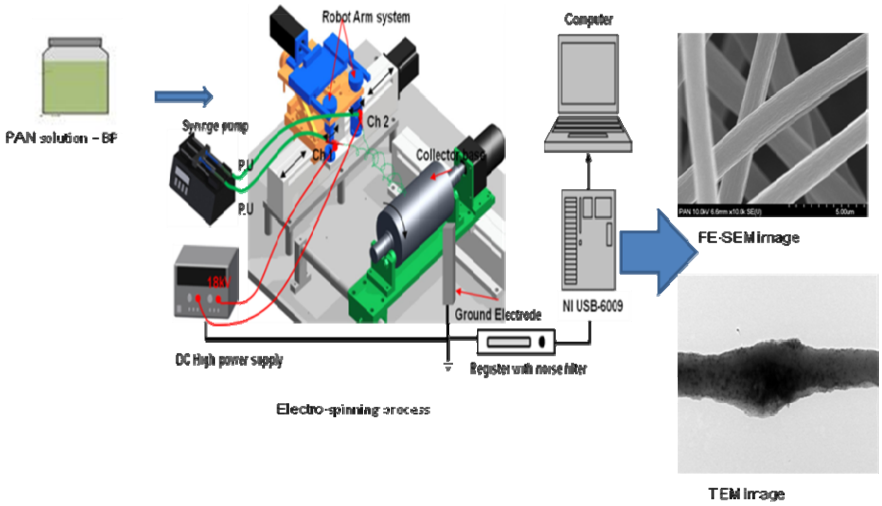

Fig. 1. Schematic diagram of fabrication of BP/PAN composite fibers

2.3. Characterization of electrospun fibers and measurements

The surface morphology of different electrospun fibers was analyzed by field emission spectroscopy (FE-SEM, S-7400, Hitachi, Japan) and transmission electron microscopy (Bio-TEM, H-7650, Hitachi). The elemental composition of the fibers was analyzed using EDS connected to the FE-SEM. The wettability of the electrospun mats was measured with deionized water contact angle measurements using a contact angle meter (GBX, Digidrop, France). Deionized water was automatically dropped (drop diameter 6 μm) onto the mat after 0, 1, 3, 9 seconds, respectively.

2.4. Antibacterial test.

For bacterial inactivation test, one colony of *Escherichia coli* (*E. coli*) was taken out from the original stock in an agar plate and was cultured lysogeny broth (LB) medium at 500 μl. This bacterial solution was incubated at 35±0.1˚C. The working suspensions were prepared by adding 200 μl of inoculated LB medium to a 100 ml sterilized distilled water in a beaker and antibacterial experiment was carried out in a sterilized 50 ml centrifuge tube containing *E. coli* suspension (20 ml) and different membranes. At this time, the centrifuge tubes are completely plugged to seal chlorine gas in water and then are maintained at a 60 rpm rate speed by incubated shaker (SI-300R, Jelo. tech. made in korea). The initial bacterial concentration was maintained at 10^4 CFU/ml with different mats (4×4 cm^2) in centrifuge tube and the tests were performed at 37℃ temperature for 72 h. At given 12 h intervals, 1 ml of the suspension was collected and serial dilution in distilled water was carried out. To count the bacterial colonies, ready-to-use Petrifilm (3M Petrifilm, USA) and prepared agar plates were used. After incubation for 24 h, the number of bacteria colonies was counted using a colony counter.

3. Results and discussion

The morphologies of PAN fibers containing different amount of BP particles are shown in Fig. 2 (FE-SEM images). In NM-0 (pristine PAN) electrospun mat (Fig.2a), the fibers appear continuous with smooth surface. The average fiber diameter of pristine.

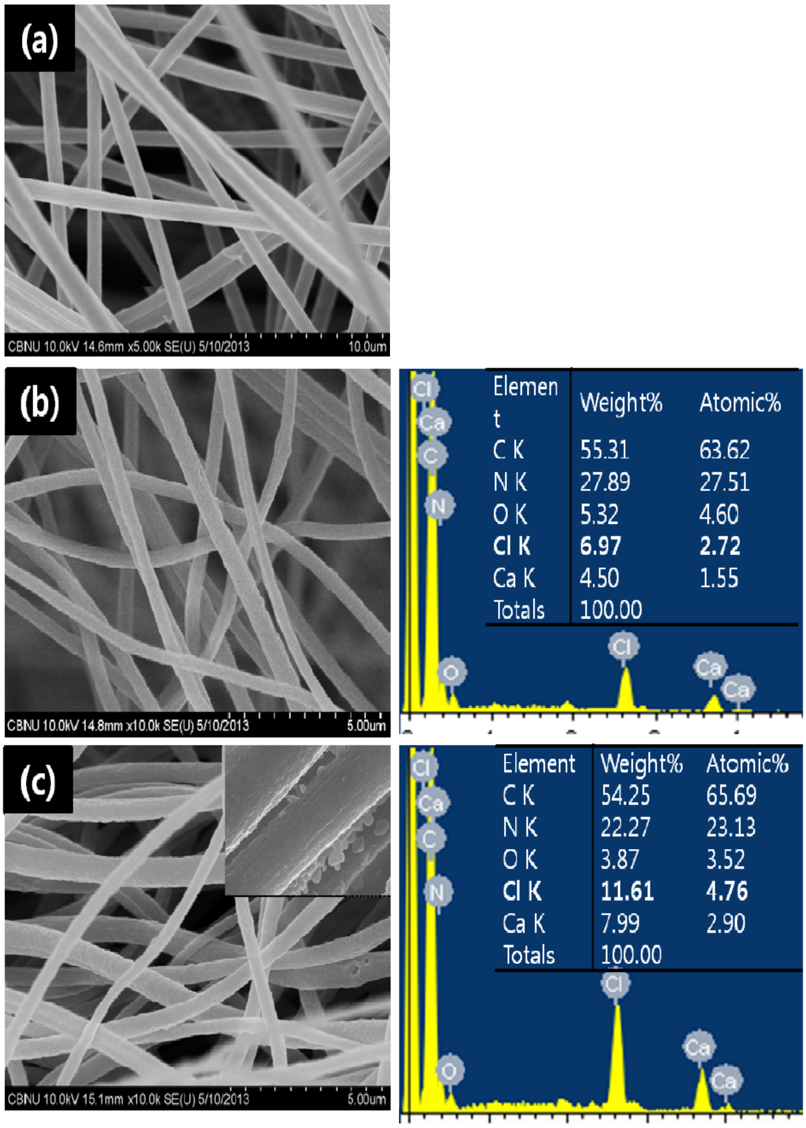

Fig. 2. FE-SEM images of NM-0 (a), NM-1 (b), and NM-2 (c) membranes and their corresponding EDS

PAN fibers was 1032 nm. However, increasing amount of BP in PAN solution could decrease the fiber diameter. The average fiber diameter of NM-1 and NM-2 fibers was 443 and 496 nm, respectively. Furthermore, presence of BP NPs in PAN solution leads the deposition of BP NPs on the surface of PAN fibers and formed non-smooth fibrous surface (Fig. 2c). The cause of the smallest diameter nanofibers in NM-1 mat is probably due to the increase in conductivity of polymer solution caused by BP [16, 17]. However, excess amount of BP hinders the spinability of polymer solution due to the agglomeration of BP particles. Inset of Fig. 2c clearly revealed that sufficient amount of BP are also present on the surface of PAN fibers. The presence of BP NPs on/into PAN fibers was evaluated by EDS spectra. Figure 2b and c indicate the successful incorporation of BP NPs through the electrospun PAN fibers. The morphology of NM-1 and NM-2 fiber was further investigated using TEM images (Fig. 3). Inset of Fig. 3 shows that NM-1 fiber has smooth surface with sufficient amount of BP particles into the fibers. However, 40 wt% BP powder containing PAN (NM-2) fibers had sufficient agglomerated BP particles on the surface of the fibers.

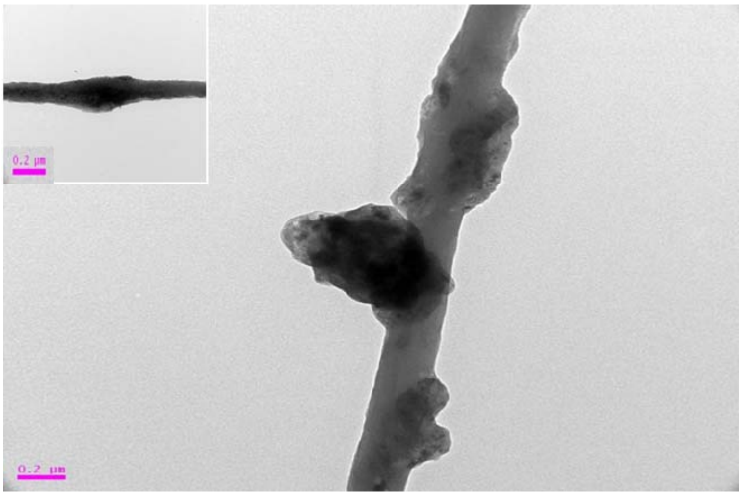

Fig. 3. TEM image of NM-2 fiber (inset is TEM image of NM-1 fiber)

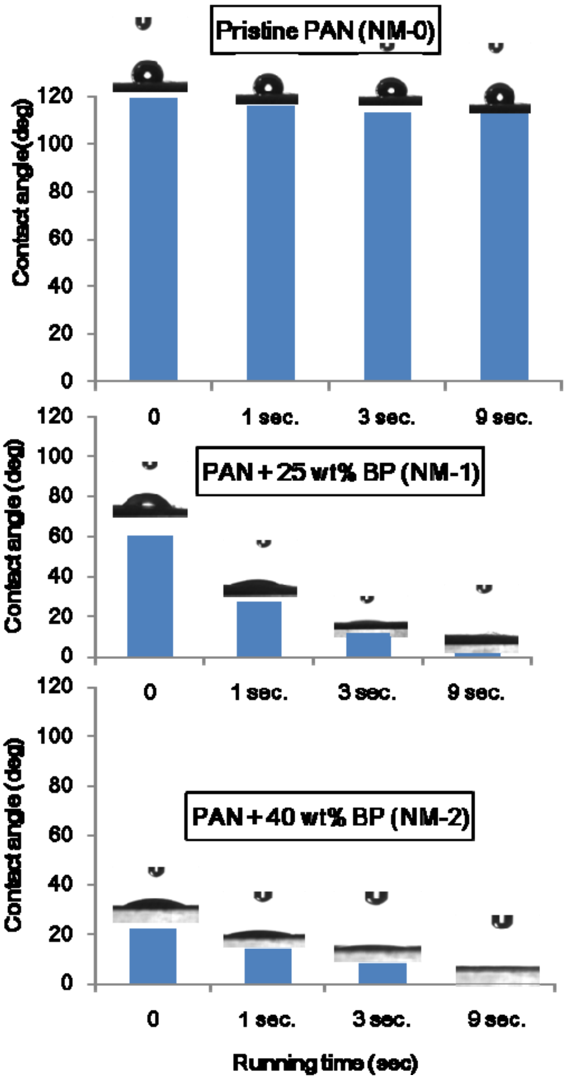

Fig. 4. Water contact angles of different membranes during different time interval

The contact angles (CA) measurements of the pristine and BP/PAN composite mats are shown in Fig.3. CA indicates the wettability of a membrane surface, and higher CA (more hydrophobic) tends to have higher tendency of fouling [18]. Therefore, resent membrane technology has focused on the enhancement of hydrophilicity (low CA) of nanomembranes. The pristine PAN fibrous membrane showed a hydrophobic surface whereas composite membranes showed that their hydrophilicity increases with the amount of BP in PAN fibers. Since, BP has great affinity to water, the time dependent CA measurement showed that CA in composite membranes is significantly decreased with increasing time. Figure 4 clearly shows that the CA of pristine PAN membrane is almost constant up to 9 sec. However, there is pronounced decreased in CA of composite membranes. The time depended CA measurement indicates that 40 wt% BP powder containing PAN membrane (NM-2) has the highest hydrophilicity. The highest hydrophilicity of NM-2 membrane is related to the interaction of BP with water. The solubility of BP in water is 21 g/100 mL and it easily react with water. Therefore, there is no doubt that the hydrophilicity of PAN membrane is significantly increased with increasing BP concentration.

The sufficient hydrophilicity of membrane can increase the rate of filtration. However, such membranes still suffering from bio-fouling and particle fouling. Therefore, introduction of solid substance through the fibers which can generate gaseous bubbles continuously is highly potential in water filtration. These bubbles can easily push the filtrate materials deposited on the pore of the membrane and increase the filter efficiency of the membrane. When bleaching powder is added to water, it converted into different species as given in the following equations.

(a) $Ca(OCl)_2 \longrightarrow Ca^{++} + Cl^- + OCl^-$

(b) $OCl^- + H_2O \longrightarrow HClO + OH^-$

(c) $2HClO\ (aq) + 2H^+ + 2e^- \rightleftarrows Cl_2\ (g) + 2H_2O$

Hypochlorous acid (HOCl) is the active constituent of BP that actually does the disinfection of pollutant water [19]. The antibacterial activity of composite PAN fibers is shown in Fig. 5. It clearly shows that the antibacterial activity of PAN fibers is dramatically changed when BP is incorporated through it. Moreover, NM-1 and NM-2 mat shows the almost same antibacterial activity. It revealed that the dissolution of BP to produce active constituent (HOCl) is almost similar whether the fibers contain less or more amount of BP. We believe that the BP particles deposited on the surface of fiber dissolve in water first and those particles which incorporated through the fibers should slowly dissolve which could provide active constituents for long time.

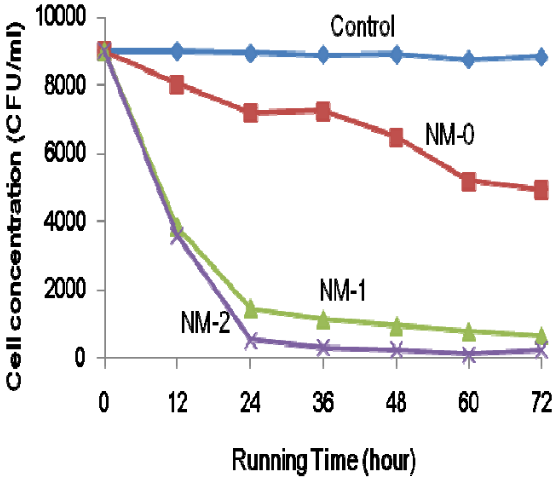

Fig. 5. Time dependent antibacterial activity of different membranes against Escherichia coli

BP is strong bleaching agent in aqueous medium and may cause the destruction of polymer fibers when composite PAN membrane is used for water filtration. Therefore, we have chosen the most chemically inert polymer PAN [20]. The effect of BP on PAN morphology was examined by taking FE-SEM image of fibers after one week water treatment. Figure 6 revealed that there is no pronounced change on fiber structure. We observed some pores on the surface of fiber which is probably either due to the dissolution of BP particles which were attached on the surface of fibers or evolution of gaseous bubbles from those BP particles which were incorporated inside the fibers.

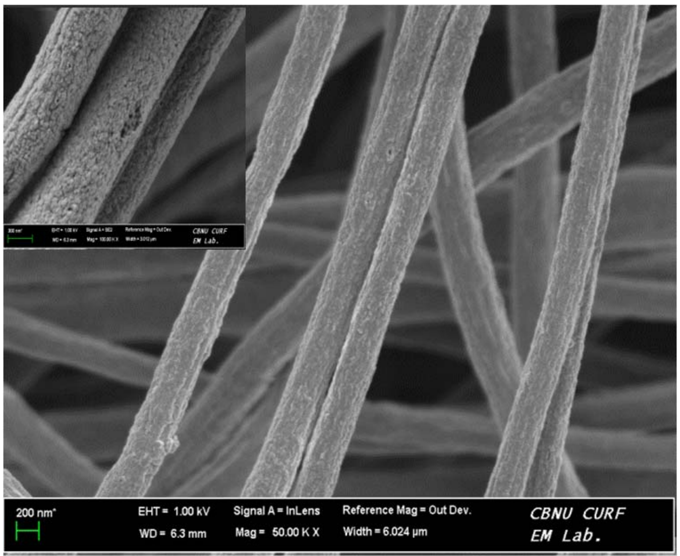

Fig. 6. FE-SEM image of NM-2 fibers after one weak water treatment (inset shows the some porous structure on the surface of fiber)

4. Conclusion

In this study, the fabrication of electrospun BP/PAN composite fibrous membrane and its antibacterial activity with antifouling capacity have been successfully demonstrated. The morphology and composition of the electrospun BP/PAN fibers were observed by FE-SEM, TEM and EDS which showed that sufficient amount of BP could be uploaded through the electrospun PAN fibers. It was found that the electrospun PAN fibers containing 25 and 40 wt% BP have great potentially to destruct the bacteria present in water. Furthermore, significant improvement in hydrophilicity of PAN fibers caused by BP can increase the filter efficiency and antifouling activity of the membrane. Therefore, as-fabricated composite BP/PAN fibrous membrane may be a potential candidate for the industrial water filtration application in future.

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