



Novel functionalized carbon nanotubes for improving the surface properties and performance of polyethersulfone (PES) membrane

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ABSTRACT

Amine functionalized Multi-walled carbon nanotubes (F-MWCNTs)/polyethersulfone (PES) membranes were prepared using phase inversion induced by immersion precipitation. Crude MWCNTs were chemically treated using strong acids ($\text{H}_2\text{SO}_4/\text{HNO}_3$) and 1,3-phenylenediamine (mPDA) to produce the functional amine groups ($-\text{NH}_2$) on their surfaces. F-MWCNTs with different concentration were blended in the casting solution containing PES, polyvinylpyrrolidone (PVP) and dimethylacetamide (DMAC). Pure water was used as non-solvent. The FTIR spectra indicated that the amine functional groups were produced on the surface of MWCNTs. The membranes prepared with different concentrations of F-MWCNTs were characterized using contact angle, field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and permeation tests. The surface hydrophilicity of membranes was significantly improved by addition of F-MWCNTs in the casting solution. An increment in the porosity, pore size and surface roughness of the membranes was observed by increasing F-MWCNTs content up to 1 wt.%. Further addition of F-MWCNTs caused a reduction in porosity and roughness of formed membrane. The membranes prepared with 0.5 and 1 wt.% of F-MWCNTs showed higher performance than neat membrane. Addition of F-MWCNTs in the casting solution improved the BSA rejection and antifouling properties of PES membrane.

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1. Introduction

Polyethersulfone (PES) is classified as a transparent amorphous and high-T_g polymer, which has high mechanical, thermal and chemical resistances. These properties are adequate factors to wide application of PES in manufacturing asymmetric membranes with different pore sizes in surfaces [1–4]. Due to the low hydrophilic properties of PES among other membrane materials such as polyacrylonitrile, cellulose acetate, polyamide, polyamide-imide, PES membrane is known as high fouling membrane for aqueous filtration [1–5]. Therefore, many investigations have been done to change the surface properties of this hydrophobic membrane [6–8]. Methods such as blending, surface graft polymerization, chemical grafting, and radiation induced grafting have been developed in attempts to increase the surface hydrophilicity of membranes [9–12]. In addition, organic–inorganic hybrid membranes have been favored recently as next generation of membranes [13,14]. Inorganic fillers and additives especially nano-sized materials such as zeolite, titanium dioxide, and silica were also embedded in polymeric membranes to

improve their performances because of their enhanced properties, such as high perm-selectivity, higher hydrophilicity, and enhanced fouling resistance [15–17].

Carbon nanotubes (CNTs) have gained more attention as one of these additives recently. In some literatures, the increments in special parameters like modulus and tensile strength, water flux and permeability, and rejection have been studied because of adding CNTs to polymeric membranes [16–19]. However, the efficient utilization of CNTs in composite applications depends on the ability to disperse the CNTs homogeneously throughout the matrix and the compatibility between CNTs and the matrix. These two factors are important in the utilization of fillers in polymer composites as well as CNTs [20,21].

The main problem of using pristine CNTs is their insolubility in solvents and weak affinities for most polymers [22,23]. Thus, surface functionalization is carried out in order to improve their dispersion capability and performance [21,24,25]. Surface oxidation and introduction of hydrophilic functional groups into the surface of the CNTs can also be helpful to obtain better dispersion of carbon nanomaterials into relevant matrices [26]. Amine group has a high reactivity, a wealth of chemistry and can react with many chemicals such as polymers [27–29].

In this research, novel functionalized MWCNTs (F-MWCNTs) containing amine groups were fabricated and blended with polyethersulfone

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(PES) casting solution for improving the surface properties and performance of ultrafiltration membranes. The conventional method to functionalize CNTs with amine groups is generally a process involving a reaction, toxic coupling reagents (SOCl_2), but in this study we prefer to use phenyldiamine directly. It is predicted that the amine F-MWCNTs are able to improve the hydrophilicity of PES membranes. The influences of F-MWCNT concentrations in the casting solution on the membrane morphology and performance were investigated. Moreover, in this paper the changes in PES membrane surface composition, hydrophilicity and antifouling properties were discussed with addition of F-MWCNTs in the casting solution.

2. Experimental

2.1. Materials

Polyethersulfone (PES Ultrason E6020P with $M_w = 58,000$ g/mol) as membrane polymer and N,N-dimethylacetamide (DMAC) as solvent were supplied from BASF. Multiwall Carbon nanotubes (O.D. \times I.D. \times L 5 nm \times 1.3–2.0 nm \times 50 μm) manufactured by CVD method were purchased from Sigma-Aldrich. Polyvinylpyrrolidone (PVP, with $M_w = 25,000$ g/mol), nitric acid 65% (HNO_3), Sulfuric acid 96% (H_2SO_4), 1,3-phenylenediamine (mPDA), N,N-dimethylformamide (DMF), tetrahydrofuran (THF) and Bovin Serum Albumin powder (BSA, $M_w \sim 66$ kDa) with were obtained from Merck.

2.2. Functionalization of MWCNTs

MWCNTs were first treated with a mixed acid solution containing sulfuric acid (H_2SO_4) and nitric acid (HNO_3). 100 mg of pristine MWCNTs was added to 150 ml $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture (3:1 by volume ratio). This solution was refluxed under magnetic stirring at 90 °C for 1 h. The carboxylated MWCNTs were filtered with a 0.2 μm cellulose acetate microfiltration membrane, washed with distilled water until pH increased to natural. The carboxylated MWCNTs were then dried in a vacuum drying oven at 100 °C for 1 h before further treatment.

For amine functionalization of carboxylated MWCNTs, 100 mg of carboxylated MWCNTs was added to solution of 20 g mPDA dissolved in DMF. The solution was stirred for 96 h at 70 °C with magnetic

stirrer and then filtered with a 0.2 μm cellulose acetate microfiltration membrane. The resulting powder was washed with tetrahydrofuran (THF) to remove excess mPDA. As final stage, amine functionalized MWCNTs (F-MWCNTs) were dried in a vacuum drying oven at 80 °C for 6 h. Procedure for carboxylic and amine functionalization, and mechanism of amine functionalization of MWCNTs (b) are shown in Fig. 1.

2.3. Characterization of F-MWCNTs

The FT-IR spectra used to investigate the changes in the chemical composition of F-MWCNTs. Results for the pristine, carboxylic and amine functionalized MWCNTs were recorded using Bruker-IFS 48 FT-IR spectrometer (Ettlingen, Germany) with horizontal. Samples of 1 mg of the Pristine CNT, carboxylic and amine functionalized MWCNTs were prepared with 300 mg of KBr to obtain translucent sample disks. 32 scans were taken with 4 cm^{-1} resolution between 400 cm^{-1} and 4000 cm^{-1} . The morphology of unmodified and modified MWCNTs was directly observed by field emission scanning electron microscopy (FESEM, Hitachi-S4160, Japan).

2.4. Preparation of PES/F-MWCNTs blend membranes

The flat sheet membranes were prepared by phase inversion via immersion precipitation technique. The blend homogeneous solutions were prepared by dissolving the 16 wt.% PES polymer at different concentrations of F-MWCNTs (0–2 wt.%) in DMAC as solvent at the presence of 4 wt.% PVP as pore former at around 25 °C with magnetic stirrer at 200 rpm for 8 h. The homogeneous polymer solution was kept stagnant for the removal of bubbles. The compositions of casting solution are shown in Table 1. The solution was sprinkled and cast on polyester non-woven fabric using a home-made casting knife with 75 μ thickness. This was immediately moved to the non-solvent bath for immersion at room temperature without any evaporation. The non-solvent was only water. The prepared membranes were washed and stored at 25 °C distilled water for 1 day to completely leach out the residual solvents and additives. As the final stage, the membranes were dried by placing between two sheets of

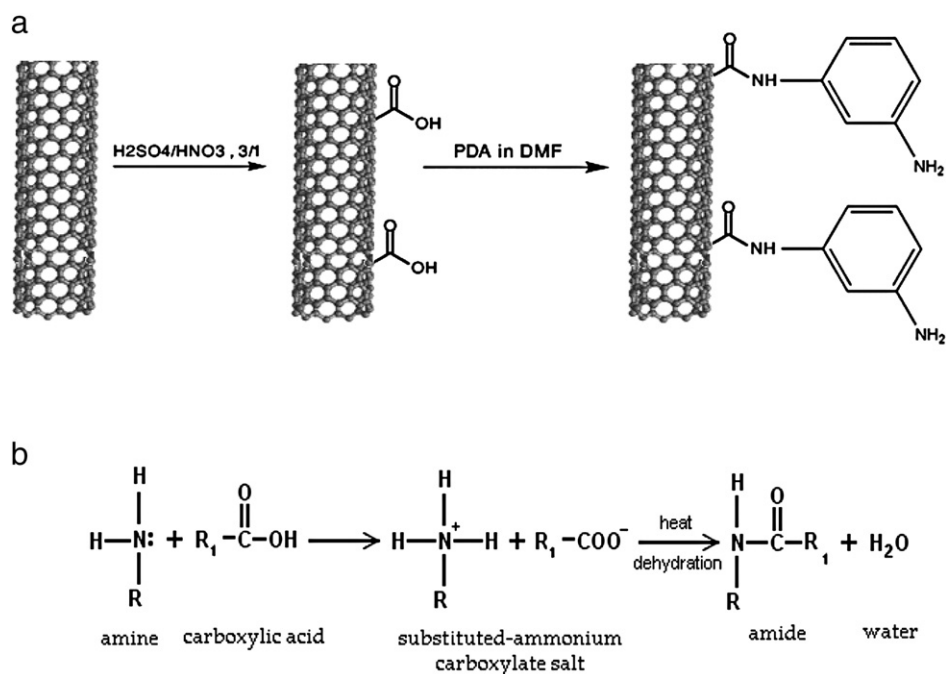


Fig. 1. Procedure for carboxylic and amine functionalization of MWCNTs (a) and mechanism of amine functionalization of MWCNTs (b).

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