ARTICLE

Preparation of Amphiphilic Polymer-Functionalized Carbon Nanotubes for Low-Protein-Adsorption Surfaces and Protein-Resistant Membranes

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ABSTRACT Multiwalled carbon nanotubes functionalized with poly(sulfone) (PSF) and poly(sulfobetaine methacrylate) (PSBMA) (MWNT-PSF/PSBMA) have been prepared through sequential atom transfer radical polymerization. The structure of MWNT-PSF/PSBMA hybrid has been characterized with FTIR, Raman spectroscopy, and high-resolution transmission electron microscopy. Incorporation of PSBMA chains to MWNTs introduces amphiphilic and protein-resistant properties to MWNT-PSF/PSBMA. Addition of 1 wt % MWNT-PSF/PSBMA to PSF films significantly improves their protein-resistant characteristic, as the composite films show a 4.4% of protein adsorption compared to poly(styrene) Petri dishes. The PSF/MWNT-PSF/PSBMA composite has been applied to prepare antifouling ultrafiltration membranes for protein separation. This work demonstrates an effective and convenient approach to prepare low-protein-adsorption surfaces and antifouling membranes.

KEYWORDS: carbon nanotubes • atom transfer radical polymerization • protein adsorption • antifouling membranes

INTRODUCTION

Developments of surfaces resisting to nonspecific protein adsorption are critical for many biorelated applications. Protein-adsorption-resistance is also an important feature of ultrafiltration membranes for protein concentration and fractionation. Poly(ethylene glycol) (PEG) (1, 2), carbohydrate-derived side-chain polyethers (3), phosphorylcholine-based materials (4−6), zwitterionic sulfobetaine polymers (7−9), and carboxybetaine polymers (10) have shown their ability to resist protein adsorption. Using these materials, protein-resistant surfaces have been obtained through formation of self-assembled monolayers (11−14), surface modifications (15−18), surface grafting copolymerization (19, 20), and physical coatings (21, 22). Most of the reported methods need special molecule designs and complicated synthesis routes. Another approach to prepare protein-resistant surfaces is coating the protein-resistant materials on substrates (21, 22). The drawbacks of this method are the need of large amounts of protein-resistant materials and the unsatisfied physical and mechanical properties of the coated layers. On the other hand, addition of amphiphilic copolymers possessing protein-resistant segments to hydrophobic polymer matrix also introduces protein-resistant properties to the resulted polymeric films and membranes (23−25). However, the degrees of protein-adsorption-reduction reported to this kind of films/membranes are not high. Hence, new materials and methods that are able to create protein-resistant surfaces easily, effectively, and economically are of high interest.

Chemical modification of carbon nanotubes (CNTs) brings chemical functionalities and dissolution properties to CNTs, so as to extend the application scopes of CNTs (26−30). Polymer-functionalized MWNTs have been used as functional modifiers for the preparation of polymer nanocomposites possessing enhanced mechanical properties and electrical conductivities (31−34). For example, sulfonated-CNTs have been demonstrated as effective additives for proton-exchange-membranes. The addition of only 0.05 wt % sulfonated-CNTs to Nafion membranes could significantly increase their proton conductivitie (35, 36). Very small amounts of CNTs are enough to significantly enhance the properties of matrix polymers.

Functionalization of CNTs with the matrix polymer of the as-prepared polymer/CNT nanocomposites is an ideal approach to preparation of high-quality nanocomposites (37, 38). As poly(sulfone) (PSF) is known for having high toughness, thermal stability, and biocompatibility and a wide range of applications in biomedical materials and separation membranes, it is of interest to use PSF-functionalized-MWNTs (MWNT-PSF) in preparation of PSF/MWNT nanocomposites. On the other hand, incorporation of protein-resistant polymeric segments to MWNT-PSF could introduce amphiphilic and protein-resistant properties to the functionalized MWNTs. Therefore, in this work low-protein-adsorption surfaces and protein-resistant membranes have been prepared using amphiphilic-polymer-functionalized multiwalled CNTs (MWNTs). PSF chains have been incorporated

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Received for review August 31, 2010 and accepted November 4, 2010

DOI: 10.1021/am100811q

2010 American Chemical Society

Published on Web 11/19/2010

to MWNT surfaces through the chemistry of atom transfer radical polymerization (ATRP) (39). Further functionalization of MWNT-PSF has been carried out through surface-initiated ATRP using sulfobetaine methacrylate (SBMA) as a monomer. The obtained amphiphilic-polymer-functionalized-MWNTs have been utilized as modifiers for preparation of PSF/MWNT nanocomposite films and membranes. The PSF/MWNT nanocomposite films, which contain only 1 wt % of functionalized-MWNTs, have demonstrated low-protein-adsorption characteristics (about 4.4% fibrinogen adsorption compared to the polystyrene Petri dish). The ultrafiltration membranes made of the PSF/MWNT nanocomposites have also shown antifouling features examined with a BSA ultrafiltration experiment.

EXPERIMENTAL SECTION

Materials. PSF, which possesses a number-averaged molecular weight of 33 500 Da, is received from Amoco Performance Inc. USA. The as-received PSF was dissolved in chloroform and precipitated from excess methanol for purification prior to use. Reagent grade chemicals of chlorotrimethylsilane (98%, Alfa Chemical), paraformaldehyde (Showa Chemical Co., Japan), and tin(IV) chloride (99.995%, Aldrich) were used in PSF chloromethylation. Copper(I) chloride (CuCl, 99.995%, Aldrich), 2,2′-dipyridyl (99%, Aldrich), poly(ethylene glycol) methacrylate (PEGMA) (average molecular weight of about 526 g mol^{-1}, Aldrich), SBMA (Monomer-Polymer and Dajac Laboratories, Inc., U.S.A.), and N-isopropylacrylamide (NIPAAm, 97%, Aldrich) for CNT modification were used as received. MWNT with average diameters of 10−50 nm and length of 1−25 μm was obtained from Carbon Nanotube Co., Ltd., Incheon, Korea. The preparation method of poly(styrene)/PNIPAAm-modified MWNT (MWNT-PS/PNIPAAm) was reported previously (39). HPLC-grade chloroform and N,N-dimethylformamide (DMF) from TEDIA Chem. Co. were dried with calcium hydride and potassium hydroxide, respectively, prior to use as solvents in reactions.

Characterization. Raman spectra were obtained using a Renishaw InVia Raman spectrometer employing a He−Ne laser of 1 mW radiating on the sample operating at 632.8 nm. Fourier transform infrared (FTIR) spectra were obtained through attenuated total reflectance (ATR) method using a Perkin-Elmer Spectrum One FTIR equipped with a multiple internal reflectance apparatus and a ZnSe prism as an internal reflection element. High-resolution transmission electron microscopy (HR-TEM) was conducted with a JEOL JEM-2010 HR-TEM. Thermogravimetric analysis (TGA) was performed with an instrument from Thermal Analysis Incorporation (TA-TGA Q-500) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

Protein Adsorption Tests. PSF films on silicon wafers were prepared using a PSF solution in chloroform (0.1 wt %) and a spin-coating method (3000 r.p.m.). The surface-coated silicon wafer was then applied to protein adsorption tests. The adsorption of human fibrinogen on the silicon wafer surfaces was evaluated using the enzyme-linked immunosorbent assay (ELISA) according to the standard protocol (40).

Membrane Filtration Tests. The PSF-based ultrafiltration (UF) membranes were prepared by a wet phase inversion method. Polymer-functionalized MWNTs (1 wt % of PSF) and a pore-forming agent of poly(ethylene glycol) (PEG8000, PSF/PEG weight ratio = 5.7:1) was added to a 15 wt % PSF solution in dimethylacetamide. The obtained solutions were stirred for 24 h at 40 °C and were left 6 h to allow complete release of bubbles. After casting the solutions with a casting knife of 300 μm thickness on a glass plate, the plate was immediately immersed in a coagulation bath of double distilled water. UF membranes were obtained through phase inversion at 4 °C. The UF membranes were washed with deionized water for 24 h to completely remove the residual solvent and pore-forming agent. Water fluxes of the membranes were measured with a dead-end filtration cell. The effective membrane area is 7.0 cm^2. The permeating water was collected in a baker place on an electronic balance. After 120 min of filtration, the membranes were cleaned with deionized water for 20 min and then the water flux was measured again.

Chloromethylation of PSF. Preparation of chloromethylated PSF was carried out according to the reported method (41). PSF (8.0 g, 18 mmol) in 300 mL of dried chloroform was charged into a 1000-mL round-bottom flask with stirring. After addition of paraformaldehyde (5.4 g, 180 mmol), chlorotrimethylsilane (22.8 mL, 180 mmol), and tin(IV) chloride (0.8 mL, 7.2 mmol), the reaction system was kept at 55 °C for 72 h. The reaction mixture was precipitated in excess methanol and purified by repeating the dissolution−precipitation process for 3 time. The product was collected by filtration and dried under a vacuum at 30 °C overnight. Chloromethylated PSF in white powder was obtained (8.12 g). The degree of chloromethylation is 0.70, i.e., chloromethylated PSF possesses 0.70 chloromethyl group in each repeating unit of PSF chains. FTIR (KBr, cm^{-1}): 2967, 2868, 1583, 1486, 1235, 1105, 831, 750. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.8−7.8 ppm (aromatic protons), δ 4.5 ppm (-C$\underline{\boldsymbol{H}}_2$Cl), δ 1.6 ppm (-C$\underline{\boldsymbol{H}}_3$).

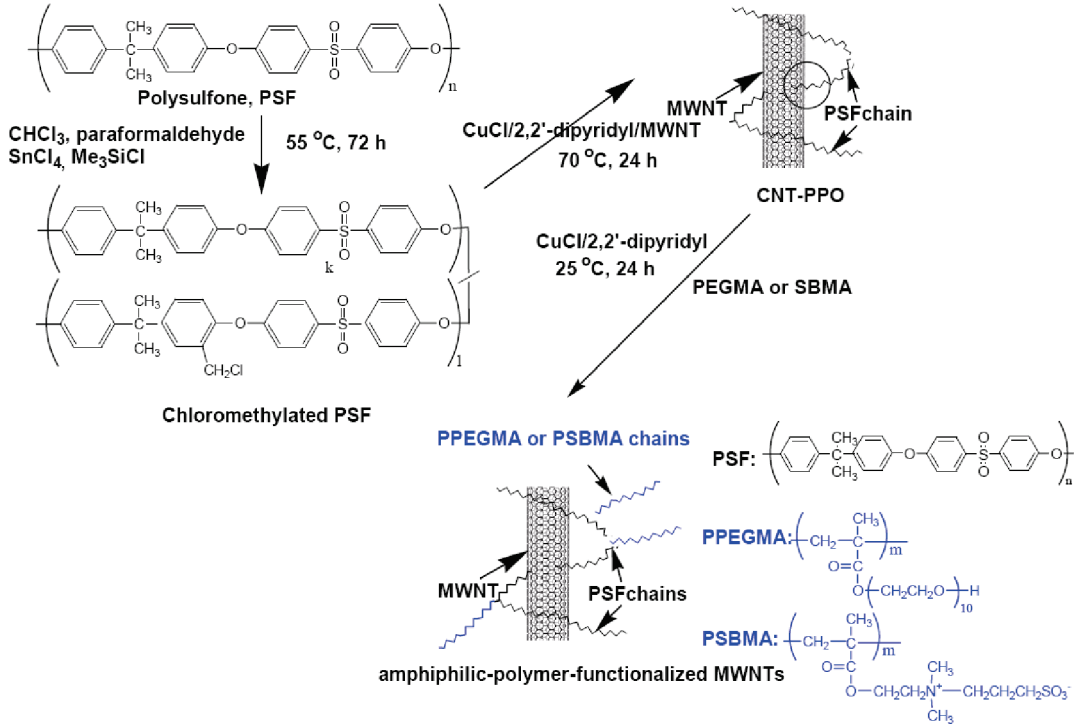
Preparation of PSF-Modified MWNT (MWNT-PSF). Chloromethylated PSF (0.5 g) was dissolved in 30 mL of chloroform. The solution was purged with argon gas flow for 15 min. After addition of MWNT (0.4 g), CuCl (0.13 g), dipyridyl (0.3 g), the reaction system was purged with argon for another 15 min. The reaction system was then degassed for 3 times and then reacted at 70 °C for 24 h. The reaction mixture was poured into excess tetrahydrofuran (THF). MWNTs were collected with filtration, washed with THF and hot water several times to remove the physically adsorbed compounds, and then dried under a vacuum to give the product of CNT-PSF (0.51 g).

Preparation of Amphiphilic-Polymer-Modified MWNTs. MWNT-PSF (0.4 g) was dissolved in 30 mL of methanol/water mixture (v/v 4:1). The solution was purged with argon gas flow for 15 min. After addition of SBMA (4 g), CuCl (0.05 g), and dipyridyl (0.3 g), the reaction system was purged with argon for another 15 min. The reaction system was then degassed for 3 times and then reacted at 25 °C for 24 h. The reaction mixture was poured into excess water. MWNTs were collected with filtration, washed with hot water for several times to remove the physically adsorbed compounds, and then dried under a vacuum to give the product of CNT-PSF/PSBMA (0.42 g). MWNT-PSF/PPEGMA was obtained using PEGMA as the monomer in the same manner.

RESULTS AND DISCUSSION

Preparation and Characterization of Amphiphilic-Polymer-Modified MWNTs. Chloromethyl groups have been introduced to the benzene rings of PSF chains through chloromethylation reaction. The incorporated −CH_2Cl groups could serve as initiating sites of ATRP (17) and are reactive toward MWNTs (15). Hence, the modified PSF chains which possesses −CH_2Cl groups could react with MWNTs. This reaction has been utilized in this work for preparation of PSF-modified MWNTs (MWNT-PSF, Scheme 1). After the reaction between PSF and MWNTs under ATRP conditions, PSF chains chemically bond to MWNT surfaces. The PSF chains attached on MWNTs still possess −CH_2Cl groups, which could serve as initiating sites for sequential ATRP for further functionalization of MWNTs. In the sequential ATRP, SBMA was utilized as a monomer. As a result, PSBMA chains have

Scheme 1. Preparation of Amphiphilic-Polymer-Modified MWNTs



been consequently incorporated to MWNT-PSF. Incorporation of PSBMA chains to MWNTs brings amphiphilic and protein-resistant properties to the obtained MWNT-PSF/PSBMA nanohybrid. In addition to MWNT-PSF/PSBMA, MWNT-PSF/PPEGMA was also prepared in the same manner using PEGMA as a macro-monomer.

MWNT-PSF/PSBMA nanohybrid has been characterized with FTIR, Raman spectrometry, TGA, and high-resolution TEM. Figure 1a shows the ATR-FTIR spectra of the samples. The PSF chains of MWNT-PSF is characterized with absorption peaks at 1495 (Ph), 1320 (sulfone group), and 1062 (C−O−C) cm^{-1} appearing in the spectrum of MWNT-PSF. The PSBMA chains of MWNT-PSF/PSBMA demonstrate absorption peaks at 1711 (C═O), 1464 (C−N), and 1170 ($-SO_3^-$) cm^{-1}. Figure 1b shows the Raman spectra of the samples. The neat MWNTs show a tangential band (G band) at about 1597 cm^{-1} and a disorder band (D Band) at around 1322 cm^{-1}. Compared to the neat MWNTs, MWNT-PSF shows an increase in D to G band intensity ratio (I_D/I_G) from 1.13 to 1.33. This change in the D/G ratio indicates that some sp^2-hybridized carbons of MWNTs convert to be sp^3-hybridized after PSF functionalization. This result gives evidence to support the success of bonding PSF chains to MWNT side walls. The modified MWNTs then serve as macroinitiators to initiate ATRP of SBMA. After the SBMA polymerization, the functionalized MWNTs (MWNT-PSF/PSBMA) exhibit a decrease in the intensity of the D band and an increase in the intensity of D′ band at about 1614 cm^{-1} (D′ band is directly affected by the disorder in nanotubes). The results correspond to the increase in intensity of sp^3-hybridized carbons. As shown in Figure 1c, neat MWNTs are thermally stable until 900 °C under nitrogen atmosphere. The organic portions of the polymer-functionalized MWNTs are relatively thermally unstable compared to pristine MWNTs. Hence, the weight losses of the polymer-functionalized MWNTs in the TGA thermograms have been attributed to the degradation of the polymer portions, i.e., PSF and PSBMA. The PSF portion of MWNT-PSF demonstrates a weight loss of about 15 wt % at 350−500 °C. Meanwhile, the PSBMA chains of MWNT-PSF/PSBMA contributes to its weight loss at about 250−300 °C. The weight fraction of PSBMA of MWNT-PSF/PSBMA has been calculated to be about 10 wt %. The amorphous polymer portions of the polymer-functionalized MWNTs could be directly observed with a high-resolution TEM. As it can be seen in Figure 1d, MWNT-PSF has a polymer layer of about 2.5 nm covered on the outer surfaces of MWNTs. The thickness of the amorphous layer increases to about 4 nm with incorporation of PSBMA. The high-resolution TEM micrographs provide direct evidence to the incorporation of polymers to MWNT surfaces.

Fabrication of Protein-Resistant Surface. MWNT-PSF/PSBMA and MWNT-PSF/PPEGMA have been utilized for preparation of PSF/MWNT nanocomposite films coated on silicon wafers. The PSF chains of the polymer-functionalized MWNTs provide compatibility between MWNTs and PSF matrix and help to anchor the polymer-functionalized MWNTs into the polymer matrix (23). A PSF/MWNT composite film possessing pristine MWNTs has also been prepared for comparison. The fraction of the pristine or polymer-functionalized MWNTs added to the PSF composite films is 1 wt %. The protein adsorption properties of the PSF film surfaces have been determined using fibrinogen and a direct ELISA method. Figure 2 shows the fibrinogen adsorption of the pristine PSF film and the PSF/MWNT nanocomposite films, using the signal intensity of the pristine PSF film surface as

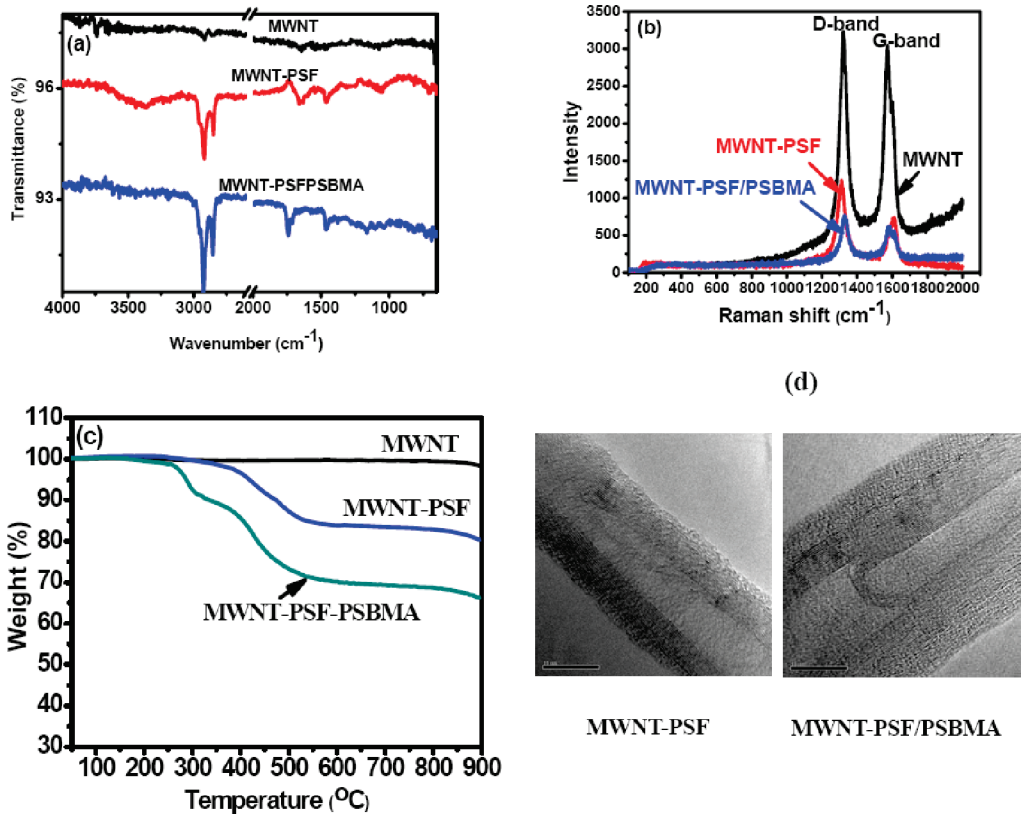


FIGURE 1. Characterization of amphiphilic-polymer-modified MWNTs: (a) ATR-FTIR spectra, (b) Raman spectra, (c) TGA thermograms, and (d) high-resolution TEM micrographs.

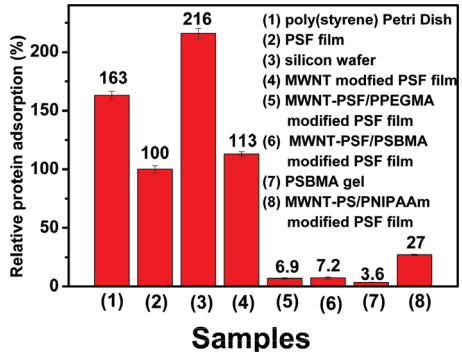


FIGURE 2. Fibrinogen adsorption of the pristine PSF film and the PSF/MWNT nanocomposite films coated on silicon wafers.

a basis (100%). Bare silicon wafer shows a 200% protein adsorption compared to the pristine PSF film. Meanwhile, addition of pristine MWNTs to PSF increases its fibrinogen adsorption, as PSF/MWNT composite film exhibits a 113% protein adsorption. Both MWNT-PSF/PSBMA and MWNT-PSF/PPEGMA nanocomposite film surfaces display relatively low fibrinogen adsorption (Figure 2). About 6.9−7.2% of fibrinogen adsorption, corresponding to about 4.4% protein absorption compared to the protein adsorption of PS Petri Dish, has been found to these two composite films. The fibrinogen adsorptions of MWNT-PSF/PSBMA and MWNT-PSF/PPEGMA composite films are as low as comparable to the protein amounts adsorbed on the PEG-coated surfaces and on the PSBMA film surfaces. As a result, only 1 wt % MWNT-PSF/PSBMA or MWNT-PSF/PPEGMA is effectively enough for preparation of protein-resistant PSF composite films, which display protein-resistant efficiency comparable to PEG and PSBMA surfaces.

PPEGMA and PSBMA grafted on substrate surfaces have been reported to reduce the fibrinogen adsorption of the substrates (8). Nevertheless, the preparation routes for the above-mentioned materials usually need special surface functionalization on the substrates and complicated reaction processes. Moreover, surface modification usually alters the surface morphology (such as pores and roughness) and properties of the substrates, subsequently sacrificing the performances of the products for practical applications. In this work, we demonstrate a convenient and effective approach to prepare low-protein-adsorption surfaces. Some obvious advantages of the method include simplicity of large-scale production, high compatibility to current polymer processing techniques, wide applicability to various polymers and substrates, use of very low amounts of protein-resistant materials, and low cost.

PPEGMA and PSBMA have been recognized as protein-resistant materials. Hence, the PPEGMA and PSBMA attached on MWNTs should provide the most contribution to the low-protein adsorptions of the PSF/MWNT composite film surfaces. Nevertheless, the interaction between proteins and the PSF/MWNT composite films should carry out at the film surfaces. Hence, MWNT-PSF/PSBMA (or MWNT-PSF/PPEGMA) should move toward the PSF/MWNT composite film surfaces to make the surfaces displaying low-protein-adsorption characteristics. Wang and Hobbie (42) reported that single-walled carbon nanotubes (SWNTs) could act as a

natural surfactant as well as an interface material in hydrophilic/hydrophobic interfaces. These features have also been found with MWNTs in our own tests. As a result, MWNTs themselves could serve as surfactants so as to migrate to the surfaces of the PSF/MWNT composite films. The pristine PSF film exhibits a smooth surface with a water contact angle of about 80°. MWNT bundles appear on the film surfaces of PSF and pristine PSF and MWNTs. This result demonstrates the ability of pristine MWNTs moving toward PSF film surface. The presence of MWNT bundles makes the PSF composite film surface become relatively hydrophobic with an increase in water contact angle to 88°. As a result, a 13% increase in the protein adsorption has been observed compared to the pristine PSF film. The surfactant characteristics of MWNTs make themselves an effective carrier of bringing PPEGMA or PSBMA chains to the PSF composite film surfaces. Moreover, the polymer chains anchored to MWNTs impart much amphiphilic characteristics to MWNT-PSF/PSBMA and MWNT-PSF/PPEGMA. In the preparation of PSF/MWNT composite films, MWNT-PSF/PSBMA and MWNT-PSF/PPEGMA therefore tend to move to the film surfaces. Carbon nanotube bundles also appear on the surfaces of MWNT-PSF/PSBMA-modified PSF film. Compared to pristine MWNTs, MWNT-PSF/PSBMA has higher compatibility to PSF matrix because of their anchored-PSF chains. As a result, the MWNT bundles at the surfaces of PSF composite films immerse in PSF matrix. The hydrophilic PSBMA chains of MWNT-PSF/PSBMA stand toward PSF/MWNT composite film surfaces, consequently increasing their surface hydrophilicity while lowering their water contact angle to 75°. On the other hand, we have also used poly(styrene) and poly(N-isopropylacryamide) (PNIPAAm) to modify MWNTs (MWNT-PS/PNIPAAm). Compared to MWNT-PSF/PSBMA, MWNT-PS/PNIPAAm possesses amphiphilic characteristics but not protein-resistant feature. Formation of PSF films with MWNT-PS/PNIPAAm also reduce their water contact angle to about 75°, which is close to the value found in MWNT-PSF/PSBMA-modified PSF composite films. This result indicates the migration of MWNT-PS/PNIPAAm toward PSF/MWNT-PS/PNIPAAm composite film surfaces. The fibrinogen adsorption of PSF/MWNT-PS/PNIPAAm composite film is 27% of the adsorption of the pristine PSF films. Some protein resistance has been found in PSF/MWNT-PS/PNIPAAm composite film because of the hydrophilicity of PNIPAAm. Nevertheless, its protein resistant performance is much lower compared to that of PSF/MWNT-PSF/PSBMA or PSF/MWNT-PSF/PPEGMA composite films. As a result, PPEGMA and PSBMA chains are still essential for fabrication of protein-resistant surfaces. The obtained results demonstrate an effective and convenient approach to prepare low-protein-adsorption surfaces. Nevertheless, the adhesion strength between the substrates and coated polymer layers as well as the incorporation of biodegradability (3) to the materials are worthy of further studies.

The protein-resistant abilities of PPEGMA and PSBMA chains have been correlated to the formation of hydration layers (43), as water expulsion from the surface and the protein is the first step to facilitate protein adsorption (44). As mentioned earlier, MWNT-PSF/PPEGMA and MWNT-PSF/PSBMA could migrate to the PSF film surfaces because of the amphiphilic property of MWNTs. Therefore, the PPEGMA and PSBMA chains contribute to the formation of hydration layer at the film surfaces. Moreover, some studies have demonstrated that the water molecules absorbed on CNTs tend to organize themselves into a hydrogen-bonded network (45−47). As a result, the MWCNT bundles at the PSF composite film surfaces help the formation of stable water layer near the film surfaces. The relatively stable water hydration layer could prevent the changes of surface behaviors and increase the protein-resistance of the film surfaces (44). On the other hand, MWNTs might cooperate the steric stabilization effect with the PPEGMA and PSBMA chains for protein-resistance (17, 47). The features discussed above could attribute to the decline of protein adsorption. Nevertheless, the reactions between the film surfaces and protein molecules are believed to be complicated and require more investigation for better understanding (18).

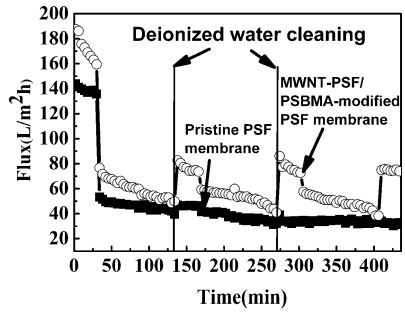


FIGURE 3. Water fluxes in membrane filtration tests using BSA solutions (mg mL^{-1}). MWNT-PSF/PSBMA-modified PSF membrane shows high water flux recovery due to its low protein adsorption.

Preparation of Antifouling Membrane. The above-mentioned materials and method are effective not only for preparation of low-protein-adsorption surfaces but also for fabrication of protein-resistant and low-fouling membranes. This kind of membranes is very useful for filtrations and bioseparations. MWNT-PSF/PSBMA (1 wt % related to PSF in the solution) has been added to the solution of PSF. Through the conventional solution-casting method, PSF/MWNT-PSF/PSBMA composite membranes have been prepared and applied to the ultrafiltration experiments on a Bovine serum albumin (BSA, 1.0 mg mL^{-1}) solution. The water fluxes in filtration decrease dramatically in the first 30 min operation because of protein molecules depositing or adsorbing on the membrane surfaces and inside the membrane pores. As shown in Figure 3, the PSF/MWNT-PSF/PSBMA composite membrane shows a relatively high flux compared to the pristine PSF membrane before and after BSA filtration experiments. The high initial water flux of the membrane comes from its relatively high hydrophilicity. The decreases in the membrane fluxes after filtration operation indicate the occurrence of membrane fouling. Membrane fouling appears on both pristine PSF membrane and the MWNT-PSF/PSBMA-modified PSF membrane, due to the adsorption of proteins to the membrane and pore surfaces (23). The proteins adsorbed on the pristine PSF membrane

that could not be removed by hydraulic cleaning result in the irreversible fouling of the membrane. On the other hand, the adsorbed proteins on the MWNT-PSF/PSBMA-modified PSF membrane could be removed with water cleaning. As a result, an increase in the water flux of the membrane with water cleaning has been observed. This result indicates that the amount of irreversible protein adsorption observed to PSF/MWNT-PSF/PSBMA composite membrane has been significantly reduced because of the presence of PSBMA chains. Hence, the flux of PSF/MWNT-PSF/PSBMA composite membrane can be recovered after water washing. The PSF/MWNT-PSF/PSBMA composite membrane shows a high water flux of about 90 L/(m^2 h) after three times of BSA solution ultrafiltrations. Meanwhile, the flux recovery has not been observed with pristine PSF membrane. It is noteworthy that the flux recovery ratios in the second run (J_{w2}/J_{w1}) and third run (J_{w3}/J_{w2}) are as high as 0.95 for PSF/MWNT-PSF/PSBMA composite membrane. The high recovery ratios indicate that the protein adsorption on PSF/MWNT-PSF/PSBMA composite membrane is reversible. The composite membrane shows antifouling features. Therefore, reuse of the membranes in filtration is possible. Nevertheless, membrane fouling could not be completely prevented even using the membranes with low-protein-adsorption surfaces.

CONCLUSION

Amphiphilic-copolymer-functionalized MWNTs (MWNT-PSF/PPEGMA and MWNT-PSF/PSBMA) have been prepared with ATRP techniques and have been applied for preparation of protein-resistant PSF-based nanocomposite films. The PSF-based nanocomposite films exhibit about 4.4% fibrinogen adsorption compared to that of the PS Petri dishes, and 3.6% compared to that of to the bare silicon wafer surfaces. The membrane made of PSF/MWNT-PSF/PSBMA nanocomposite also exhibits antifouling characteristics in BSA ultrafiltration experiments. The results demonstrate a convenient and effective approach to the preparation of low-protein-adsorption surfaces and antifouling membranes. Applications of the prepared nanocomposites for the marine-biofouling-resistant materials are of high potential and under further study.

Acknowledgment. Financial support on this work from the Ministry of Education and the National Science Council (NSC 99-2221-E-033-007-MY3) of Taiwan is highly appreciated.

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AM100811Q