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Separation Science and Technology

Publication details, including instructions for authors and subscription information:

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To cite this Article Kouwonou, Yao , Malaisamy, Ramamoorthy and Jones, Kimberly L.(2008) 'Modification of PES Membrane: Reduction of Biofouling and Improved Flux Recovery', *Separation Science and Technology*, 43: 16, 4099 – 4112

To link to this Article: DOI: 10.1080/01496390802414726

URL: <http://dx.doi.org/10.1080/01496390802414726>

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Modification of PES Membrane: Reduction of Biofouling and Improved Flux Recovery

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A 0.22 μm polyethersulfone microfiltration membrane was modified using acrylic acid irradiated with UV light. The degree of grafting (DG) was confirmed by FTIR spectroscopy, which varied from 21 to 568 $\mu\text{g}/\text{cm}^2$ for differing irradiation times and initial monomer concentrations. The contact angle of the modified membranes was at least 10° less than the unmodified PES membrane. Modification filled the pores with copolymer, and decreased the permeability of the membrane. However, following the filtration of *E. coli*, and membrane cleaning, the flux recovery was 100% for the modified membranes and only 50% for the unmodified membranes. Thus, the modification helped in showing reversible biofouling and higher flux recovery.

Keywords: Membrane biofouling, flux recovery, microfiltration, membrane surface modification

INTRODUCTION

Microfiltration and ultrafiltration membranes are being used increasingly to purify drinking water, to treat wastewater prior to discharge, and to reclaim wastewater to increase existing potable water resources (1,2). Microfiltration membranes are suitable for pretreatment of water with relatively strong biological activity or colloidal content, such as secondary effluent from wastewater treatment plants. However, membrane fouling continues to

Received 2 December 2007; accepted 16 May 2008.

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decrease overall system performance, consequently increasing operation and maintenance costs associated with membrane-based water treatment technologies. Fouling can be caused by suspended solids, colloids, metal oxides, scales, biological slime (biofouling), and organics oil and grease (3). Frequent cleaning and backwashing, often with chemicals, can somewhat reduce fouling but over time, fouling becomes irreversible.

Biofouling is particularly hard to control; as long as nutrients are available, bacteria will multiply, excrete extracellular substances, and form biofilms that cause fouling (4). Biofouling is affected by operational conditions such as feed water quality, temperature, pH, length of filtration cycle, and crossflow velocity. The chemical and physical characteristics of the membrane polymer can also influence biofouling. For example, surface roughness, hydrophobic interaction, pore size, pore distribution, and the charge density can all affect biofouling. For example, Knoell (1999) performed water flux and bacterial adhesion (without any filtration) experiments using polysulfone containing sulfonated polyether-ethersulfone/polyethersulfone block copolymer microfiltration membranes. They showed that while the water flux is inversely correlated with surface hydrophobicity and polysulfone content, the cell attachment is positively correlated with the pore geometry and hydrophobicity (5). Also, it is generally acknowledged that hydrophilic surfaces are less susceptible to fouling (6,7).

Membrane modification to discourage biofilm attachment and growth is one method to reduce biofouling. Modification techniques can be physical, chemical, or a combination. The choice of the specific type of surface modification depends on the chemical structure of the support membrane, the desired characteristics of the modified surface. In this study, graft-polymerization on polyethersulfone membranes was initiated without a photoinitiator. Photo-grafting is defined as the copolymerization of a monomer on a substrate polymer by the influence or initiation of UV light. Photo-grafting can be completed with or without a photoinitiator. This method has the following advantages: mild reaction conditions, ability to absorb UV light without affecting the bulk polymer, and permanent alteration of the membrane surface with facile control of the chemistry. Thus, this technique is particularly useful for modifying and functionalizing polymeric materials. The mechanism for the observed photochemical reaction of polyethersulfone membranes with acrylic acid monomers is shown elsewhere (8).

After using photografting techniques to modify membranes, several researchers (8–13) have reported a reduction in both reversible and irreversible fouling of inorganic, organic and biological substances. Kim et al. (2002) modified thin-film composite (TFC) membranes with TiO_2 nanoparticles and demonstrated that the modified membranes prevented

biofouling (14). Backpulsing combined with surface graft-polymerization was used by Ma et al., (2001) to successfully reduce biofouling of polypropylene (PP) and cellulose membranes (10). Hilal et al. (2004, 2005) proposed that biofouling by *E. coli* could be reduced by photo-grafting quaternary-2-(dimethylamino)ethylmethacrylate (qDMAEM) and 2-acrylamidomethyl-1-propane sulfonic acid (AMPS) onto a PVDF membrane. The PVDF membrane modified by qDMAEM exhibited no growth of *E. coli*, while *E. coli* colonies grew on the unmodified PVDF membrane (15,16).

Yu et al. (2006) used a sequential photoinduced graft polymerization of acrylic acid onto a polypropylene hollow fiber microporous membranes. The pure water flux (PWF) of these membranes increased as the degree of grafting increased and the pH decreased (17). The modified membranes also showed higher operating flux and greater flux recovery.

The goal of this study was to modify commercially available polyethersulfone membranes using UV assisted graft polymerization to reduce biofouling and to elucidate the mechanisms by which the modified surfaces resist biofouling. Specifically, attempts are made to link membrane surface properties to biofouling reduction. Acrylic acid was chosen as the graft monomer.

MATERIALS AND METHODS

Materials

Polyethersulfone (PES) membranes with pore size of $0.22\text{ }\mu\text{m}$ (GE Osmotics) were used as the base material. The membrane sheet obtained was cut into circular coupons of 44.5 mm diameter prior to modification. Polyethersulfone is very photo sensitive, has good resistance to oxidants, possesses strong mechanical properties, heat distortion, aging resistance, and environmental endurance. Acrylic acid (AA) was purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without purification. Acrylic acid reduced organic fouling (NOM, proteins) but has not been evaluated for biofouling reduction (12,13). We also selected it as it is a low molecular weight and is negatively charged over a wide pH range. *E. coli* suspension stock was diluted using PBS buffer to a practical level concentration of 10^6 cells/mL (*E. coli* 33–5612 Microbiologics, St. Cloud, MN) (18). A UV irradiation chamber was custom manufactured (SPDI Inc., FL) and equipped with lamps (made in Germany) with an intensity of $28 \pm 2\text{ mW/cm}^2$ at a wavelength of 300 nm from a distance of 40 cm from the lamp. Milli-Q water ($18.2\text{ M}\Omega\cdot\text{cm}$) was employed to prepare acrylic acid solutions, *E. coli* feed dilutions and pure water flux measurements.

METHODS

Surface Modification

Each membrane coupon was initially soaked in water for 12 hours to remove any chemicals or particles attached on the surface during production. The membrane was then air dried at 20°C and placed in an air oven for 12 hours at 38 ± 2°C. The membrane was then removed from the oven and weighed to determine the dry weight. The dry membrane was then impregnated with AA solution in a petri dish. The membrane was then placed in the UV reactor with the active side facing up and exposed to UV radiation under nitrogen. The modified membrane was then shaken in water for 4 hours at 250 rm^{-1} in order to remove excess acrylic acid and then placed in 0.1 M NaOH on a shaker for 30 min to neutralize the unreacted acrylic acid and to remove any homopolymer formed. Afterwards, the modified membrane was rinsed with pressurized water and shaken in water for 1 hour to remove the excess NaOH from the membrane (15). The modified membrane was then air-dried at room temperature and placed in the oven for 12 hours before determining the dried weight.

Membrane Characterization

Degree of Grafting (DG)

The extent of the modification is shown by the degree of grafting (DG). The degree of grafting is the amount of the polymer grafted on the membrane. DG can be expressed as the percentage of weight increase (10), the number of moles of monomer grafted (8), and spectroscopic analysis (19,20). In this study, the degree of grafting was normalized to the membrane area and calculated using the following formula,

$$DG = \frac{W_1 - W_0}{A} \quad (1)$$

expressed in $\mu\text{g}/\text{cm}^2$ (15). “ W_0 ” is the weight of the unmodified membrane, “ W_1 ” is the weight of the membrane after modification and “ A ” is the area of the membrane. The weight measurements were made using a balance with ±0.0001 g of accuracy.

FTIR-SEM-Contact Angle Analyses

Surface chemical functionality of the unmodified and modified PES membranes was obtained using an IR spectrometer (Nicolet Magna

560, Nicolet Instrument Corp., Madison, WI). Thirty-two scans were performed at a resolution of 4 cm^{-1} at an incident angle of 45° after mounting the membrane facing an ATR germanium crystal. The IR penetration depth for this incident angle is $0.1\text{--}1\text{ }\mu\text{m}$.

Surface morphologies of the unmodified and modified membranes were obtained by SEM (JEOL HSM 636lv). The membrane samples were frozen in liquid nitrogen and sputter-coated with gold at a thickness of 5 nm before being scanned.

Hydrophobicity was characterized using a contact angle instrument. (Phoenix 150, Surface & Electro-Optics Corporation, South Korea, supplied by Scientific Gear LLC, VA). Air/water contact angle was measured by the sessile drop method on a dry membrane immediately after leaving a drop as is used elsewhere using other systems (17). The values of the left and right were recorded and averaged.

Permeate Flux Experiments

A dead-end stirred cell set up was used to study the membrane filtration performance. The system consisted of a filtration cell (Model 8050, Millipore Corp., Bedford, MA) with a total cell volume of 50 mL and a membrane effective area of 13.4 cm^2 . The stirred cell was connected to a 20 L stainless reservoir containing ultra pure water or 3 L reservoir containing *E. coli* suspension. The stainless steel reservoir was pressurized with dry nitrogen.

Filtration Protocol

All the membranes were hydraulically compacted at 276 kPa until steady state was reached. The pressure was then varied between 69 and 207 kPa to evaluate the permeability of the membrane. At each pressure, three flux measurements were obtained before lowering the pressure to 138 kPa for the clean water flux (J_o) measurement.

E. coli suspension (10^6 CFU/mL) was filtered and the flux measured (J_e). The membrane was then removed and placed in pure water for 12 hours in order to allow bacteria growth at room temperature. The membrane was then cleaned by soaking in ultra pure water and shaken for 30 min in a mechanical shaker, at 250 rm^{-1} in order to remove any weakly-adhered foulants. After water rinsing, the membrane was loaded into the stirred cell again to measure the flux, J_w and to evaluate reversible fouling. In order to disinfect and clean the strongly adhered bacteria

on the membrane surface the membrane was then shaken in sodium hypochlorite (NaOCl) solution (10 mg/L) for one hour. Then the membrane was rinsed with ultra pure water and the flux was measured to evaluate irreversible fouling, J_c .

RESULTS AND DISCUSSION

Degree of Grafting

The degree of AA grafting as a function of monomer concentration and irradiation time is shown in Fig. 1. At 4 minutes irradiation time (T_{irr}), the degree of grafting was $50 \pm 4 \mu\text{g}/\text{cm}^2$ using 100 mM acrylic acid. DG did not vary significantly when the AA concentration was raised to 300 mM. However when T_{irr} was extended to 8 minutes, DG increased substantially to over $150 \mu\text{g}/\text{cm}^2$ at 100 mM AA concentration and increased linearly to $568 \mu\text{g}/\text{cm}^2$ when the concentration was raised to 300 mM. The slope of the graph corresponding to 8 minutes T_{irr} is 10 times higher than that for 4 minutes, suggesting that polymerization was primarily dependent on the time of irradiation rather than the concentration of acrylic acid. We also understood that the concentration is sufficient for an 8-minute long reaction, as one might expect exhaustion of the monomer at longer reaction times.

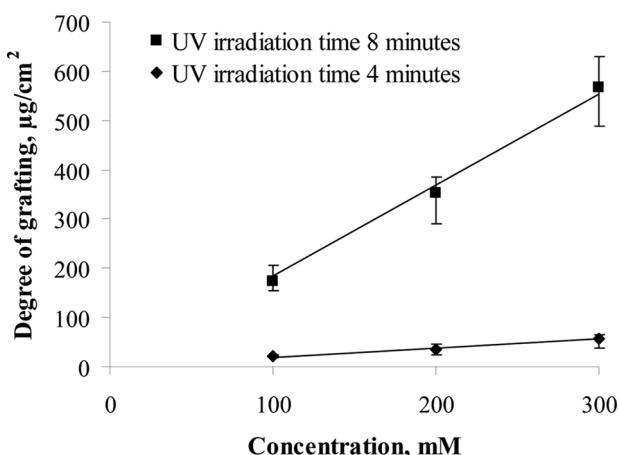


Figure 1. Effect of concentration of acrylic acid on the degree of grafting on 0.22 μm PES membranes.

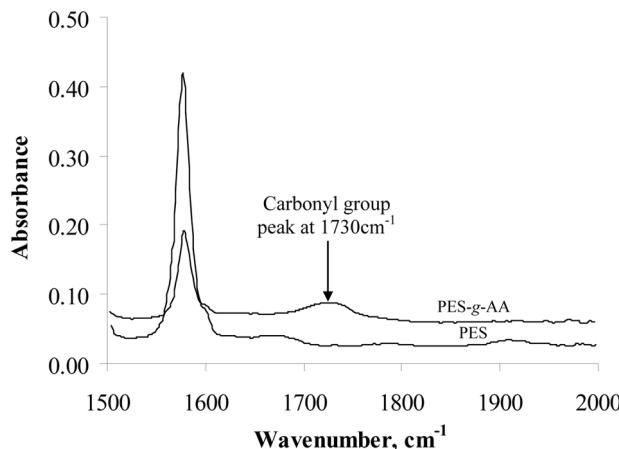


Figure 2. FTIR spectra of an unmodified and AA-modified PES membrane surface (Absorbance values of PES-g-AA spectrum are manually enhanced by 0.05 a.u.).

FTIR Spectroscopy

ATR-FTIR spectroscopy was performed in order to elucidate the surface chemistry of the modification. Representative spectra of an unmodified and a graft-modified (4 minutes T_{irr} , 100 mM AA) PES membrane surface were obtained and are shown in Fig. 2. The spectra of both membrane surfaces are similar at all wavenumbers except the presence of a new peak at $\sim 1730\text{ cm}^{-1}$ for the grafted membrane. This unique peak corresponds to the carbonyl functional group ($-\text{C}=\text{O}$) of the protonated carboxylic acid group of acrylic acid (21) and further confirms the modification of the surface.

SEM Morphology

The surface of the unmodified membranes and representative samples for modified membrane (4 minutes T_{irr} , 100 mM acrylic acid) were scanned using scanning electron microscopy (Fig. 3). The unmodified membrane surface has open pores as depicted in Figure 3(a) and sponge structure extending throughout the thickness as depicted in Fig. 3(b). The grafted AA filled the pores, as depicted in Figs. 3(c) and 3(d). It has been debated whether grafted monomers cover the surface, followed by pore filling, or whether pores are filled before the surface is covered. This is an

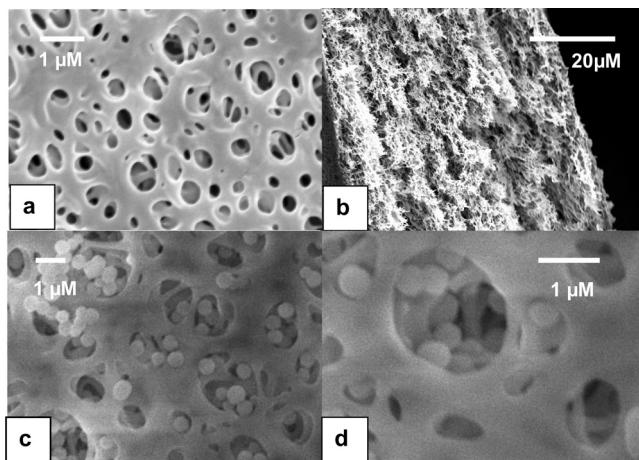


Figure 3. SEM micrographs of (a) top surface of an unmodified membrane at 15,000 \times magnification, (b) cross-section of an unmodified membrane at 1000 \times magnification, (c) top surface of a membrane modified with 100 mM of acrylic acid at 4 min at 10,000 \times magnification, (d) top surface of a membrane modified with 100 mM acrylic acid at 4 min at 20,000 \times magnification.

important consideration, as one may wish to have surface coverage only, or pore filling only. Our results indicate that pore size and shape play a key role in deciding the mechanism of coverage. If the pore size is large enough for the monomer to enter and fill the pore volume while allowing the copolymer chains to extend in and outwards from the pores, pore filling would occur first followed by surface polymerization or both mechanisms would occur simultaneously. Under the conditions of our study, the pore size is large enough for the AA to penetrate, so the dominant mechanism is likely pore filling followed by surface coverage.

Contact Angle Measurements

It has already been shown that one can manipulate the hydrophilicity of the membrane surface by modifying with acrylic acid (17). However, in order to identify whether the hydrophilicity can be manipulated in some controlled fashion, the contact angles of the modified membranes were measured by sessile drop method. The modified membranes (both at 4 minutes and 8 minutes) have contact angles as low as $44 \pm 1^\circ$ irrespective of the degree of grafting, whereas the unmodified membrane is at least $10 \pm 4^\circ$ higher, which suggests that the modification increased the

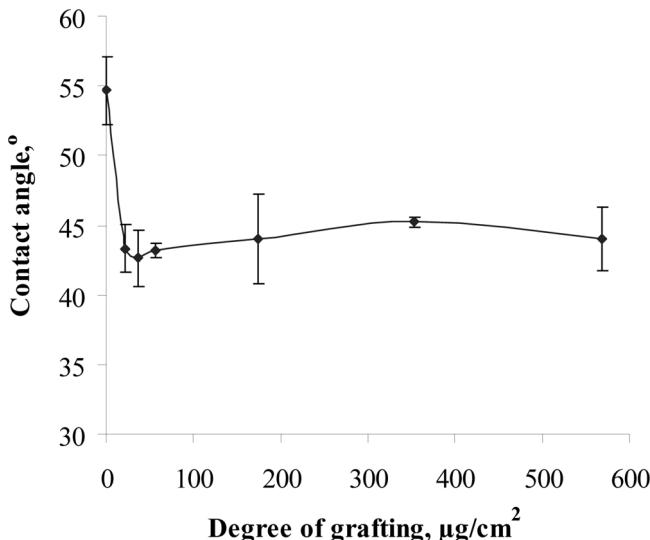


Figure 4. Air/water contact angle values of unmodified and modified membranes with various degrees of grafting by sessile drop method.

hydrophilicity of the PES (Fig. 4). The hydrophilicity does not correlate with the degree of grafting.

Permeability

The permeability values for the unmodified and modified membranes are shown in Table 1. The unmodified membrane has a permeability of 80 $\text{L}/(\text{m}^2 \cdot \text{h} \cdot \text{kPa})$; permeability of the 4 minute irradiated membranes reduced to about $34 \pm 2\%$ of the initial unmodified membrane permeability, irrespective of the concentration of the monomer. Membranes that were irradiated for 8 minutes were impermeable to water due to the pores becoming completely filled with copolymer.

Permeate Flux in Various Stages of Filtration

The filtration data for both unmodified and modified membranes are graphically represented in Fig. 5. Note that pure water flux declined from 11 to 3.5, 3.76, 3.9 $\text{L}/(\text{m}^2 \cdot \text{h})$ at 138 kPa after modification, and the flux of the *E. coli* suspension (J_e) further declined to 0.47, 0.08, 0.15, and

Table 1. Permeability of unmodified 0.22 μm PES membrane and membrane modified at 4 min irradiation

Membrane and preparation condition	Degree of grafting DG, $\mu\text{g}/\text{cm}^2$	Initial permeability, $\text{L}/(\text{m}^2 \cdot \text{h} \cdot \text{kPa})$
Unmodified PES 0.22 μm	n/a	79.7 ± 3.4
PES + 100 mM of acrylic acid	21 ± 4	25.8 ± 1.8
PES + 200 mM of acrylic acid	36 ± 10	27.4 ± 2.1
PES + 300 mM of acrylic acid	56 ± 15	29 ± 0.4

0.1 $\text{L}/(\text{m}^2 \cdot \text{h})$ for 0, 21, 36, and $56 \mu\text{g}/\text{cm}^2$ degrees of modification respectively. However the flux recovery (Figs. 5 and 6) significantly increased for the modified membranes. Only about 50% of the flux was recovered after hydraulic rinsing and chemical cleaning for the unmodified membrane, whereas the flux was completely recovered for all the modified membranes (Fig. 6). The flux after hydraulic cleaning (J_w) is higher than the original pure water flux. Since the membranes were subjected to much higher pressure than the operating pressure, during pre-compaction, there is no likelihood of loosely bound homopolymer or co-polymer

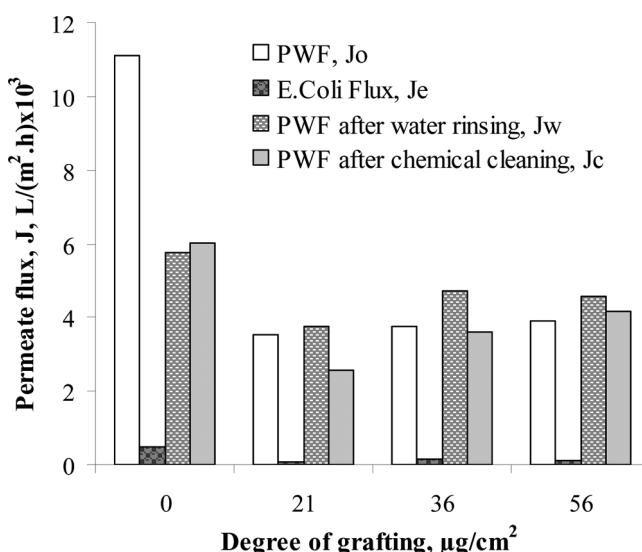


Figure 5. Permeate flux of unmodified and modified membranes at various stages of the study. J_o is the pure water flux (PWF), J_e is the *E. coli* flux, J_w is pure water flux after hydraulic cleaning, and J_c is pure water flux after chemical cleaning.

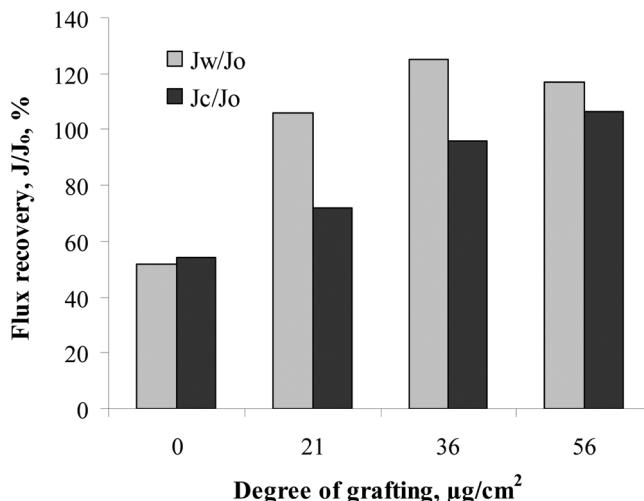


Figure 6. Flux recovery of modified and unmodified PES membranes. J_o is pure water flux (PWF), J_w is pure water flux after hydraulic cleaning, J_c is pure water flux after chemical cleaning.

remaining on the surface. Hence this increase in PWF after cleaning is attributed to a temporary enlargement or deformation of pores.

These results indicate that all of the biofouling is reversible in the modified membranes while the unmodified membranes exhibited both reversible and irreversible biofouling. For the unmodified membrane, the chemical cleaning has only a minor effect in recovering the flux (J_c). The chemical cleaning on the modified and hydraulically cleaned membranes has a slightly negative impact on the flux. Note that a very low concentration of NaOCl was used compared to $\sim 400 \text{ mg/L}$ used in practice. The lower concentration was effective and would not oxidize the surface of the membrane.

Note that the membranes grafted with acrylic acid in the range of 21 to $56 \mu\text{g}/\text{cm}^2$ did not exhibit irreversible biofouling and also had acceptable pure water flux. Hydrophilic surfaces discourage cell attachment (22), and the modified membranes have increased hydrophilicity, which may account for some of the decrease in cell attachment. In addition, acrylic acid modified membranes are expected to have negative surface charge (17) which also would repel the negatively charged *E. coli* cells by electrostatic repulsion and prevent adherence on the surface. Both mechanisms are likely to affect biofouling mechanism under the conditions of this study.

Although DG should increase hydrophilicity and surface charge, leading to less biofouling, there is an upper limit beyond which the increase in monomer attachment results in unacceptably low permeability due to pore blocking by the copolymer. In other words, DG values greater than $174\text{ }\mu\text{g}/\text{cm}^2$ resulted in very low membrane permeability.

CONCLUSIONS

UV assisted graft-polymerization was used to functionalize polyethersulfone membrane (PES) in the absence of photoinitiator and cross-linker. Acrylic acid at 100 mM concentration with UV irradiation times of 4 minutes at 300 nm were found to be sufficient to affect the polymerization with a reasonable degree of grafting on 0.22 μm PES membranes. The degree of grafting was more dependent on the time of irradiation than the initial concentration of the monomer, though a linear relationship exists between the monomer concentration and degree of grafting. Under the conditions of this study, pore filling dominates over surface coverage during the polymerization step. The permeate flux decreased upon modification as a result of pore filling. The *E. coli* flux declined for both modified and unmodified membranes. However the flux was recovered completely after hydraulic cleaning for all the modified membranes, whereas only 50% of the initial flux was recovered even after chemical cleaning for unmodified membranes, suggesting that the modified membranes were reversibly biofouled while the unmodified PES membranes were irreversibly biofouled. Based on the surface chemistry of the modification, both electrostatic interactions and hydrophilicity are considered to be the mechanisms that discourage cell attachment.

ACKNOWLEDGEMENT

This work was supported by the Nanobiotechnology Center (NBTC), an STC program of the National Science Foundation under Agreement No. ECS-9876771. This material is also based upon work partially supported by the Center of Advanced Materials for the Purification of Water with Systems (WaterCAMPWS), a National Science Foundation Science and Technology Center, under Award No. CTS-0120978.

The authors acknowledge the technical help from Dr. Peizhen Zhou, Dr. Jude Abanulo, Mrs. Lily Wan, and Mr. Kirk Finlay for SEM, FTIR, and *E. coli* culture preparation and assays respectively.

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