



Low fouling negatively charged hybrid ultrafiltration membranes for protein separation from sulfonated poly(arylene ether sulfone) block copolymer and functionalized multiwalled carbon nanotubes



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ABSTRACT

Low fouling negatively charged hybrid ultrafiltration membranes with adjustable charge density were fabricated from blends of poly(arylene ether sulfone) (PAES) block copolymer and the sulfonated copolymer (S-PAES) in combination with different fractions of sulfonic acid functionalized multiwalled carbon nanotubes (MWCNT-SO₃H) by non-solvent induced phase separation method. Porous hybrid membrane morphologies, structure and surface properties were characterized comprehensively using scanning electron microscopy, Fourier transform infrared spectroscopy in the attenuated total reflection mode, as well as contact angle and zeta potential measurements. Results confirmed that the fabricated membranes were hydrophilic and negatively charged in the studied pH range 3–10. The water permeabilities and increased protein fouling resistances of the membranes were dependent on the fraction of MWCNT-SO₃H in the membranes. The protein transmission as function of pH value and fraction of MWCNT-SO₃H was studied for two model proteins (bovine serum albumin and myoglobin) and found to be controlled by size exclusion and the content of MWCNT-SO₃H. The highest transmission of proteins at their isoelectric points was obtained for the membrane containing 2 wt% of MWCNT-SO₃H relative to total membrane polymer. The selectivity of the hybrid membranes for the separation of the binary protein mixture could be systematically increased by increasing surface charge density by increasing fraction of MWCNT-SO₃H. Consequently, the trade-off relationship between permeability and selectivity for conventional ultrafiltration membranes where separation is based on size exclusion solely could be overcome and performance be tuned by a small fraction of a functional additive.

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1. Introduction

The separation and purification of proteins is a prerequisite for specific utilizations of proteins in biotechnology, food, biomedical and pharmaceutical industries [1–4]. To obtain purified proteins, precipitation, ion-exchange chromatography, ultrafiltration, centrifugation, adsorption, membrane adsorber and electrophoretic membrane contactor have been used [1,2,4–7]. Among the aforementioned separation methods, ultrafiltration (UF) has been demonstrated as a straightforward, efficient, and scalable alternative for concentration and purification as well as separation of protein mixtures in model solutions and fermentation broths [2,8,9]. Polyamides, polyimides, polyacrylonitrile, polyvinylidene fluoride,

polysulfone and polyethersulfone are commonly used in the fabrication of UF membranes [10].

UF membranes from these polymers have often relatively low permeability and selectivity. Another major obstacle in UF processes is membrane fouling by protein solutions [2,8,9]. Two types of membrane fouling can occur: (i) reversible fouling and (ii) irreversible fouling [2,8,9,11]. The coating of block copolymer on the membrane surface, blending of hydrophobic polymer with a small fraction of functionalized copolymers, inorganic fillers or conductive polymers and the covalent grafting of functional hydrophilic polymers onto the hydrophobic membrane surface by polymerization using ultra-violet light or atom transfer radical polymerization have been explored to enhance the membranes hydrophilicity and antifouling ability [8,9,11–15]. However, the surface-coated layer is physically bound on the membranes surface and therefore it is relatively easily washed off. Grafting of polymers on the membranes surface is responsible for variations in barrier pore size

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and distribution leading to a decline of permeability of the modified membranes. Therefore, the incorporation of nanofillers into the polymer matrix for the fabrication of low fouling hybrid porous membranes has gained much attention in membrane science and technology. Zirconium oxide, titanium oxide, zeolite, highly dispersible polypyrrole, sulfonated polyaniline, graphene oxide and carbon nanotubes have been explored as nanofillers to fabricate low fouling porous hybrid membranes [8,9,14,16–20]. In particular, carbon nanotubes (CNT) have received tremendous attention. The unique characteristics of CNT make them premier choice for new composites. Single walled CNT (SWCNT) and functionalized multiwalled carbon nanotubes (MWCNT) have been used in the fabrication of low fouling porous membranes because of their high hydrophilicity and superior water binding capacity [14,16,19–21]. However, hybrid membranes derived from hydrophobic polymers and nanofillers have usually low selectivity during the UF of proteins mixture solution [8,14,17,21]. This problem could be solved by anchoring anionic or cationic groups in the barrier layer of porous membranes [2,16,22–25]. Mehta and Zydney have reported that the membrane performance in protein concentration and separation can be significantly improved by controlling the surface charge density because the charged UF membranes had better permeability and selectivity than unmodified membranes [23]. Recently, Kumar and Ulbricht have reported negatively charged UF membranes with adjustable charge density derived from sulfonated PAES/PAES block copolymer blends. The selectivity of the membranes towards lysozyme versus bovine serum albumin (BSA) was tunable with increasing density of sulfonic acid groups in the barrier layers [2]. Overall, the separation of proteins from their mixture solution is possible by exploiting repulsive electrostatic interactions. Hence, the combination of size and charge based selectivity will be helpful for improving the separation performance of membranes in UF processes. The transport of proteins across charged UF membranes is also dependent on type and strength of electrostatic interactions between the membrane and protein molecules which can be modulated by solution pH relative to the isoelectric point of the protein [2,16,25,26]. Thus, selective separation of proteins using charged UF membranes is, in principle, possible at a controlled pH.

The purpose of this study was to expand the scope compared to a previous study on membranes from sulfonated PAES/PAES block copolymer blends via the non-solvent induced phase separation method (“phase inversion”) method [2] by the integration of sulfonic acid functionalized multiwalled carbon nanotubes (MWCNT-SO₃H). The filler MWCNT-SO₃H was used to modulate the charge density in the barrier layer of the hybrid membranes and to explore other effects onto membrane performance. The fabricated membranes have been characterized comprehensively and then used in UF studies with the model proteins BSA and myoglobin at varied solution pH and constant applied transmembrane pressure.

2. Experimental section

2.1. Materials

Disodium hydrogenphosphate was obtained from Acros Organics. 4-Aminobenzenesulfonic acid, and toluene were purchased from Sigma–Aldrich. Sodium dihydrogenphosphate monohydrate, thionyl chloride (SOCl₂), tetrahydrofuran (THF) and N-methyl pyrrolidone (NMP) were obtained from Merck Chemical Co. Bovine serum albumin (BSA) was purchased from Gerbu Biotechnik, GmbH, Germany, and myoglobin (Mb) was purchased from Sigma–Aldrich. Carboxylated multiwalled carbon nanotubes (MWCNT-COOH) (purity >95%, –COOH content 3.86 wt%, average diameter 9.5 nm and length <1 µm) were purchased from Nanocyl, Belgium. Other

solvents and reagents were commercially grade and used as received. Deionized (DI) water and water purified with a Milli-Q system (Millipore) were used in this study.

2.2. Synthesis of unmodified and sulfonated poly(arylene ether sulfone) block copolymer

The synthesis of PAES by aromatic nucleophilic substitution (S_NAr) polycondensation reaction and the subsequent sulfonation under conditions where chain scission could be minimized were performed as described before [2,27]. The multiblock copolymers PAES and S-PAES had high molecular weights (weight-average molar mass M_{w} : >145 kg mol^{−1} and number-average molar mass M_n : >70 kg mol^{−1}). The degree of sulfonation for S-PAES block copolymer was 54%.

2.3. Preparation of sulfonic acid functionalized multiwalled carbon nanotubes

The sulfonic acid groups on the multiwalled carbon nanotubes were anchored via amide linkage formation by reaction between activated MWCNT-COOH and 4-aminobenzenesulfonic acid (Scheme 1) [28]. Initially, MWCNT-COOH were treated with 1 M aqueous HCl solution for 24 h at RT to remove the metallic impurities and washed several times with DI water until pH = 7 was reached. MWCNT-COOH was then dried in vacuum oven at 60 °C for 8 h to remove the adsorbed water. Thereafter, 1 g MWCNT-COOH was dispersed into 100 ml of thionyl chloride under nitrogen atmosphere and then the temperature was raised to 70 °C with constant stirring at 200 rpm. After 24 h, excess thionyl chloride was removed by distillation, and the solid black product was kept in vacuum oven at 70 °C for 12 h to remove residual traces of thionyl chloride from activated MWCNT (MWCNT-COCl). Thereafter, MWCNT-COCl was dispersed into THF and subsequently excess of 4-aminobenzenesulfonic acid solution in slightly basic aqueous medium (pH ~ 9) was added drop wise into the solution. The mixture was then refluxed at 60 °C for 24 h. The resulting sulfonic acid functionalized MWCNT (MWCNT-SO₃H) was filtered using 0.22 µm Teflon membrane. Thereafter, the product was washed several times with DI water and finally dried in vacuum oven at 60 °C for 24 h. The functionalization with sulfonic acid groups on the MWCNT was confirmed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) (cf. Section 2.4; see Supporting information, Fig. S1). The fiber morphology after functionalization was finer than for the original material. A peak for sulphur in the EDX spectrum which was not present in the original material confirmed the introduction of sulfonic acid groups on the MWCNT.

2.4. Membrane preparation and characterization

PAES/S-PAES and PAES/S-PAES/MWCNT-SO₃H hybrid membranes were prepared by non-solvent induced phase separation (NIPS) method [2,8,16]. The 20 wt% blend polymer solutions were prepared by dissolving PAES and S-PAES block copolymers (1:1) in NMP with a constant stirring at RT for 24 h and homogeneous solutions were obtained. The solutions were filtered and left at RT for 6 h to remove the air bubbles. Thereafter, varied fractions of MWCNT-SO₃H (1–4 wt%; cf. Table 1) relative to the total amount of block copolymers were added into the solutions. The casting solutions were further stirred at 40 °C for 24 h to achieve a better dispersion of MWCNT-SO₃H in the casting solutions.

The viscosities of the casting solutions were measured using Anton Paar Rheometer Physica MCR301 instrument and the details are given in Supporting Information; Section S1.

The solutions were cast onto a clean glass plate using a casting knife with gap height of 300 µm. After 30 s, the glass plate with the

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