Integrated antimicrobial and antifouling ultrafiltration membrane by surface grafting PEO and N-chloramine functional groups

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Abstract Ultrafiltration membranes with integrated antimicrobial and antifouling properties were fabricated using an engineering thermoplastic (carboxylated cardopoly(aryl ether ketone), PEK-COOH). Different molecular weights of PEO (Mw: 120, 350, 550) were grafted to the PEK-COOH membrane surface via EDC/NHS methodology. N-chloramine modified membranes then were prepared by simple exposure to dilute sodium hypochlorite solution. The surface grafting processes were all performed in water (i.e. without organic solvent). With this surface modification, the hydrophilicity of membranes improved significantly and the pure water flux increased compared to the unmodified PEK-COOH membrane. Furthermore, the PEO and N-chloramine modified membranes were resistant not only to both protein adsorption and bacterial adhesion, but also to microbial proliferation. The results of this work suggest that PEO and N-chloramine modified membranes are promising as fouling-resistant membranes.

Keywords Membrane, Surface grafting, antimicrobial, antifouling

1 Introduction

Ultrafiltration (UF) is widely used in various separation processes, such as food and dairy processing[1], protein separation[2], wastewater treatment[3], reverse osmosis pretreatment[4, 5]. However, most of the materials used to fabricate ultrafiltration membrane, such as polyethersulfone (PES), polysulfone (PSf) and poly(vinylidene fluoride) (PVDF) are susceptible to fouling by proteins and microbes. Over time, the fouling of membrane surfaces by proteins and microbes can facilitate biofilm formation, which decreases the membrane performance and lifetime. As a result, UF membranes can be expensive. Two methods have traditionally been used to prevent fouling and biofilm formation. One of these strategies is the hydrophilic modification of membranes, which inhibits the adhesion of protein and bacterial on membrane surface[6, 7]. The second strategy is the use of antimicrobial materials, which can prevent the proliferation of microbes on membrane surfaces. Despite their popularity, these two strategies both have significant drawbacks. Hydrophilic modification does not to inhibit microbial proliferation, whereas the antimicrobial strategy does nothing to remove the dead microorganisms from the membrane surface. Thus, it is crucial to develop antimicrobial and antifouling membranes that can both resist microbial attachment and inhibit the proliferation of microbes.

The hydrophilicity of PES, PSf and PVDF membranes has been improved through redox initiated grafting, plasma treatment or UV treatment. However, those processes are usually detrimental to membrane and are difficult to control. Surface chemical grafting[8-13] also has been widely used to increase the hydrophilicity of membrane surfaces. However, it is relatively difficult to introduce hydrophilic groups to the surface of PES, PSf and PVDF under mild conditions by chemical surface grafting. Fortunately, cardo poly(aryl ether ketone) containing carboxyl (PEK-COOH) (Fig. 1) has been reported[14, 15]. PEK-COOH is an engineering thermoplastic that has excellent properties such as

good thermoxidative stability, excellent mechanical properties, and a high glass transition temperature. It also possesses outstanding membrane formation property[14, 15]. Furthermore, the presence of the carboxyl group (-COOH) in functionalized cardo poly(aryl ether ketone) makes it easy to obtain hydrophilic membranes by the surface chemical grafting functional groups. It has been shown that methoxypolyethylene glycol (PEO) has excellent antifouling properties due to its resistance to biomacromolecules[16-18]. However, there are still some difficulties associated with the use of PEO materials in membrane fabrication, such as crystallinity and poor mechanical properties. Fortunately, those difficulties can be easily overcome through the grafting of PEO to the surface of a membrane that has already been prepared.

Several antimicrobial agents, such as silver nanoparticles[19, 20], chitosan[21, 22], quaternary ammonium compounds[23, 24] and N-halamine compounds[25-28] have been used in the preparation of antifouling membranes. Of these agents, compounds containing the N-halamine functional group have received a great deal of attention. N-chloramines, a class of N-halamine, can easily be obtained through the reaction between $RR'NH$ and dilute sodium hypochlorite solution. N-chloramines are stable both in air and in water. Furthermore, N-chloramines are known to be effective against a broad spectrum of microorganisms and they can be renewed by a simple process[29].

In this study, novel renewable antibiofouling membranes integrating both antimicrobial and antifouling properties are reported. First, PEO-NH₂ with different molecular weights (Mw: 120, 350, 550) were grafted to the membrane surface through EDC/NHS methodology to modify the hydrophilicity of the membrane surface. Then, immersion of the modified membrane in dilute sodium hypochlorite solution results in incorporation of N-chloramine functional group, which can kill microbes on membrane surfaces (as shown in Fig. 1). Systematic investigation of protein fouling, bacterial fouling and proliferation, and biofilm formation then was applied to examine the membrane performances. The antimicrobial and antifouling properties of the membrane, along with its renewability make it an excellent candidate for use in various separation processes.

2 Materials and methods

2.1 Materials

PEK-COOH was prepared as previously reported[15]. Methoxypolyethylene glycol amine (PEO-NH₂, Mw: 120, 350, 550) was synthesized as reported[30, 31]. Bovine serum albumin (BSA, pI 4.8, Mw 67 kDa) was purchased from Sino-American Biotechnology Co., Ltd. *E. coli* MG1655 (ATCC 47076) was obtained from the Coli Genetic Stock Center (CGSC), and *Staphylococcus aureus* (*S. aureus*, ATCC 6538) was obtained from Dingguo Biotechnology Co., Ltd. All other chemicals were reagent grade and used as received.

2.2 Membrane preparation

The PEK-COOH ultrafiltration membrane was prepared through the phase inversion method. A solution of 17% PEK-COOH in Dimethylacetamide (DMAc) was cast onto clean glass plates using a casting knife with a 150 μ m gate gape. Immediately after casting, the film on the glass was immersed in deionized water, which led to rapid membrane formation. Then, the membranes were washed with deionized water and stored in deionized water until use.

2.3 Preparation of PEO and N-chloramine modified membranes

PEK-COOH ultrafiltration membranes were activated by submersion in a solution of 100 mM N-hydroxysuccinimide (NHS) and 200 mM 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC) in MES buffer (50 mM, pH 5.5) for 4 h. After washing the activated membranes with deionized water to remove unreacted NHS and EDC, the membranes were immersed in a 50 mM methoxypolyethylene glycol amine (PEO-NH₂, Mw: 120, 350, 550) solution for 24 h at room

temperature. Next, the modified membranes were washed with deionized water to remove any adsorbed PEO-NH₂. The modified membranes were then immersed in dilute sodium hypochlorite solution (0.5% in 0.1 M phosphate buffer, pH 7) for 0.5 h. Then, the membrane was washed with deionized water, and the washing water was tested with potassium iodide/starch to confirm that free chlorine had been completely removed from the surface of the membrane. The surface grafting procedure for the incorporation of PEO-NH₂ and N-chloramine functional groups is shown in Fig. 1.

Fig. 1 The process of the surface grafting of PEO-NH₂ and N-chloramine functional group onto carboxyl membrane

2.4 Characterization of PEO and N-chloramine modified membranes

The chemical composition of PEO-grafted membranes was characterized through attenuated total reflectance infrared analysis (ATR-IR, Bio-Rad digilab Division FST-80 spectrometer). The surface composition of the PEO and N-chloramine modified membranes was also characterized by X-ray photoelectron spectroscopy (XPS). XPS analysis was performed using a Thermo ESCAL 250 spectrometer with a monochromated Mg K α X-ray source (1253.6 eV photons). The survey scans were taken in the range of 0-1200 eV at a take-off angle of 90°. The binding energy (BE) scale is standardized by setting the peak maximum in the C 1s spectrum to 284.6 eV. A high-resolution C 1s spectrum was fitted using Shirley background subtraction. The hydrophilicity of the membranes was evaluated through static contact angle measurements using contact angle goniometer (JC2000C Contact Angle Meter, Powerach Co., Shanghai, China). Distilled water (2 μ l) was dropped onto the membrane surfaces, and the contact angles of the drops were measured in triplicate at room temperature to obtain the average contact angle. Adhesion of bacteria and biofilm formation on the PEK-COOH membranes and PEO and N-chloramine modified membranes were evaluated using a scanning electron microscope (SEM, XL 30 ESEM FEG, FEI Company). All samples were sputtered with gold prior to SEM measurement.

2.5 Ultrafiltration experiments

Ultrafiltration experiments were completed as previously reported [18]. Generally, all membranes were tested using a cross-flow filtration cell, and the effective membrane area was 23.7 cm². First, each membrane was compacted at 0.2 MPa for 1 h. Then, the operation pressure was set to 0.1 MPa for 1 h to obtain the pure water flux J (L/(m²h)), which was calculated using the following equation:

$$J = \frac{V}{A \Delta t}$$

where V is the volume of permeated water (L), A is the membrane area (m²), and Δt is the permeation time (h).

The rejection of BSA (R) was calculated according to the feed and the permeate concentration via analysis of absorption at 280 nm using a UV spectrophotometer according to the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

where C_p and C_f (mg/ml) refer to the concentration of BSA in permeate and feed solutions, respectively. Both pure water flux and rejection of BSA were measured in triplicate.

2.6 Static protein adsorption experiments

Both the PEK-COOH membrane and the PEO and N-chloramine modified membranes (1 cm × 1 cm) first were washed three times with deionized water, and then were immersed in 2 ml of 1 mg/ml FITC-labeled BSA solution at room temperature for 8 h to facilitate protein surface adsorption. After the incubation period, the membranes were rinsed gently with deionized water to remove any BSA loosely bound to the membrane surface. Finally, membrane surface fluorescence was observed using a confocal fluorescence microscope.

2.7 Bacteria surface adhesion test

E. coli K12 and *S. aureus* were cultured and washed as reported[32]. After the final wash, *E. coli K12* and *S. aureus* suspensions in PBS were diluted to reach 10^8 CFU/ml for the membrane surface adhesion test. All membranes were immersed in 2 ml of the *E. coli K12* or *S. aureus* suspensions. The incubation was carried out at 37 °C for 6 h. The suspension of the bacteria was removed, and the membrane samples were washed with PBS three times to remove any loosely bound bacteria. Then, All membranes were treated with glutaraldehyde (3 vol%) and aqueous solutions of ethanol as reported¹¹. Finally, adhered bacterial cells on membrane surfaces were observed by SEM.

2.8 Antibacterial efficacy

The bactericidal properties of the antimicrobial membranes were evaluated through *E. coli* (gram-negative bacteria) and *S. aureus* (gram-positive bacteria). *E. coli* and *S. aureus* resuspended in PBS (approximately 10^6 CFU/ml). The “sandwich” system for antibacterial tests was followed. Generally, small pieces (1 cm×1 cm) of PEK-COOH membranes were sterilized for 30 min on both sides through exposure to UV light. Ten microliters of bacterial suspension (approximately 10^6 CFU/ml) was dropped onto the membrane surface, and then another identical membrane was placed on the first membrane surface. These “sandwiches” were held in place by sterile weights to ensure adequate contact with the bacteria. After contact times of 30 min, the sandwich was transferred to sterile centrifuge tubes containing 2 ml of 0.2 mol/L sodium thiosulfate to quench any active free chlorine. The mixture then was shaken vigorously for 20 min. An aliquot of the solution was serially diluted, and 100 µl of each dilution was placed onto a LB nutrient agar plate. Bacterial colonies were counted after incubation at 37 °C for 24 h.

2.9 Biofilm evaluation

S. aureus was selected to observe biofilm formation on the membrane surfaces. Generally, the membranes (2 cm²) were putted on the bottom of a 24-well plate. The *S. aureus* suspension (2 ml, approximately 10^8 CFU/ml) was added to the surface of membranes, respectively. The membranes were remained in the bacterial suspension for 2 h. Then, the membranes were removed and washed gently with sterilize water for three times. After removing the loosely attached bacterial, all the membranes were placed in LB medium and then they were cultured at 37 °C for 24 h. Finally, the membranes were treated with glutaraldehyde and ethanol as described above and the biofilm on the membrane surfaces was observed through SEM.

3 Results and discussion

3.1 Construction of PEO and N-chloramine modified membranes

For the covalent grafting PEO to membrane surface, the carboxylic groups on PEK-COOH served as functional handles. PEO-modified membranes were obtained using NHS as the activator and EDC as the coupling agent. After a reaction time of 4 h, the membrane that had been activated by EDC and NHS was washed and dried for ATR-IR. Two new peaks at 1740 and 1775 cm^{-1} were found, which were assigned to the C=O stretches of newly attached succinimide group. After immersing the activated membranes in 50 mM PEO-NH₂ (Mw: 120, 350, 550) for 24 h, the absorption peak at 1740 and 1775 cm^{-1} disappeared, and the absorptions of both the amide C=O stretch of at 1651 cm^{-1} and the C-H stretch at 2875 cm^{-1} characteristic of PEO increased, indicating that the PEO segments had been successfully grafted to the membrane surface.

Fig. 2 ATR-IR spectra of the PEK-COOH membrane, activated membrane and grafted membranes

The chemical composition of PEO-grafted membrane surfaces were characterized by XPS analysis. As shown in Fig. 3, PEK-COOH membrane had no nitrogen content while the signals for nitrogen were observed for the PEO-grafted membranes. This observation further indicates that PEO was successful grafted onto the membrane surfaces as PEO-NH₂ was the only source of nitrogen. The results of the analysis of the surface compositions of PEK-COOH membrane and PEO-grafted membranes are summarized in Table 1. The XPS analysis of the membranes demonstrates that the C–O content of the prepared membranes increased as the molecule weight increased from 120 to 550, further indicating that the PEK-COOH membrane was successfully modified. Both ATR-IR and XPS analysis confirm that PEO-NH₂ was grafted successfully to the membrane surface and that amide bonds were introduced. The presence of the amide bond makes it is possible to easily functional the membrane surface with N-chloramine functional groups through expose to diluted sodium hypochlorite solutions. XPS analysis of the newly modified membrane revealed the N 1s peak located at 399.2 eV remained, while a new peak that corresponded to the electronic binding energy of Cl 2p appeared at 201.0 eV, indicating that the chlorination process was successful (Fig. 3). The similar results were also found for membranes modified by PEO with molecule weight for 120 and 350.

Table 1 Surface elemental atomic percentage of PEK-COOH membrane and PEO-grafted membranes

Membranes	Surface elemental (%)		
	C	O	N
PEK-COOH	82.10	17.90	
PEO-120	77.54	18.84	3.62
PEO-350	77.03	19.41	3.56
PEO-550	75.76	21.21	3.03

Fig. 3 XPS wide scans of PEK-COOH membrane and modified membranes

3.2 Characterization of PEO and N-chloramine modified membranes

The hydrophilicity of membrane surface plays important roles in membrane properties. To evaluate the hydrophilicity of membrane surface, the water contact angle was measured. The results of the measurements are shown in Fig. 4. The data show that the contact angle of membranes decreased. The contact angle was decreased to 68° when the molecular weight of PEO was 350 and 550, indicating that modified membranes can exhibit remarkable hydrophilicity. The decrease in the water contact angle can be assigned to the increased surface coverage of hydrophilic PEO domains on the hydrophobic PEK-COOH membrane.

Fig. 4 Static water contact angles of PEK-COOH membrane and PEO-grafted membranes

The rejection of BSA and the pure water flux of the PEO with different molecular weights and N-chloramine modified membranes are plotted in Fig. 5. It can be concluded that the modification on the membrane surfaces had a little impact on BSA rejection, suggesting that the grafting process is mild and does not decrease the membrane performance. The pure water flux was also observed to increase when PEO was grafted to the surface of the PEK-COOH membranes, which is consistent with the results of contact angle experiment. When the molecular weight of grafted PEO was 550, the water flux was as high as $141.4 \text{ L/m}^2\text{h}$ which was approximately 50% higher than that for the unmodified PEK-COOH membrane ($95.7 \text{ L/m}^2\text{h}$). One possible reason for this level of water flux was the presence of hydrophilic groups on the outer surface of the membrane.

Fig. 5 Pure water flux and rejection for BSA of membrane with PEK-COOH membrane and PEO-grafted membranes

3.3 Protein adsorption on the modified membranes

The nonspecific attachment of proteins on membrane surfaces is believed to be the major cause of the membrane fouling. The inherent hydrophobicity and electronegativity of PEK-COOH membrane increases the likelihood of proteins on membrane surfaces and pore walls during the membrane separation process. Therefore, improving the hydrophilicity and electronegativity of membrane surface could effectively solve the problem of membrane fouling. PEO and its derivatives have excellent antifouling properties due to its resistance to biomacromolecules as reported[33-35]. Thus, PEO segments were introduced to the membrane surface in this study. BSA labelled by fluorescein isothiocyanate (FITC-BSA) was used to evaluate the antifouling properties of PEO modified membranes as shown in Fig. 6. The PEK-COOH membrane exhibited high protein attachment, likely due to its hydrophobicity. Significant quantitative decreases in BSA adsorption were observed on modified membranes compared to the PEK-COOH membrane. No protein adsorption was observed on the membrane surface modified by PEO with molecular weights of 350 and 550. The improved antifouling property should be attributed to the increased hydrophilicity and the reduced electronegativity of membrane surface. The results suggested that PEO segments play important roles on inhibiting the protein adsorption as reported by many other studies[17, 36].

Fig.6 FITC-BSA adsorption on the surfaces of PEK-COOH membrane and modified membranes. a,

PEK-COOH; b, PEO-120-Cl; c, PEO-350-Cl; d, PEO-550-Cl.

3.4 Bacteria surface adhesion on the PEO-modified membranes

The bacterial fouling of membrane surfaces can lead to biofilm formation, making it a major factor in membrane performance and lifetime[37]. To test the ability of PEO-modified membranes to resist bacterial fouling, *E. coli* and *S. aureus* (gram-negative and gram-positive, respectively) were used to evaluate the attachment performance on PEO-modified membranes surfaces. PEK-COOH membrane was used as the control. The results of the bacteria adhesion test on PEO-modified membranes are shown in Fig. 7. The unmodified PEK-COOH membrane showed a significant bacterial attachment after 6 h incubation in the bacterial media as shown in Fig. 7. This observation could be ascribed to hydrophobicity of the PEK-COOH membrane, which enhances the interaction between the membrane surface and bacteria. Significant decreases in the attachment of both *E. coli* and *S. aureus* were found for PEO-modified membrane surfaces. The adhesion amount of both *E. coli* and *S. aureus* on the membrane surfaces also clearly decreases when the Mw of PEO increases. The results are attributed to the grafting of PEO segments to membrane surface[38]. First, PEO can form a hydration layer on membrane surface through bonding with water molecules, which works as an effective barrier for protein and bacterial attachment[39]. Second, the mobility of PEO chain can introduce a large excluded volume and steric repulsion to reduce protein and bacterial attachment due to its flexible configuration[16].

Fig. 7 SEM images of *E. coli* and *S. aureus* attachment on the surfaces of the PEK-COOH membrane and PEO-grafted membranes.

3.5 Antimicrobial efficacy

Although the PEO-modified membranes reduce the attachment of bacteria, there are still some bacteria remained and proliferated on the membrane surface, resulting in fouling of the membrane over time. Thus, the antibacterial N-chloramine functionalized group was introduced to membrane surface. The antimicrobial activities of PEO and N-chloramine modified membranes were investigated through “sandwich” systems. The membranes were evaluated with *E. coli* K12 and *S. aureus*, representing gram-negative and gram-positive bacteria, respectively. The results are summarized in Fig. 8. The N-chloramine functionalized membrane was found to provided 100% reduction of both *E. coli* and *S. aureus* within 30 min of contact time, indicating that N-chloramine functionalized membranes have excellent antibacterial properties.

Fig. 8 Biocidal test results of PEK-COOH and PEO and N-chloramine functional group modified membranes

The antibacterial properties of membranes usually decreased or lost completely during the separating process. As a result, the renewability of the antibacterial properties is important for more widespread implementation of antibacterial membranes. It is thought that the biocidal property of N-chloramine is due to the transfer of active chlorine from the N-chloramine groups to microorganisms in aqueous solution, which also results in the conversion of the N-chloramine groups to amide groups[40]. Thus, the renewability of the N-chloramine functionalized ultrafiltration membrane was evaluated. First, the N-chloramine membrane was quenched by immersion in 0.3% sodium thiosulfate aqueous solution at room temperature for 0.5 h, which resulted in the disappearance of Cl 2p peak in XPS. Next, the quenched membrane was exposed to sodium hypochlorite solution again. Analysis of the membrane again by XPS showed that the Cl 2p peak in XPS appeared again, indicating that the N-chloramine functionalized membrane is renewable (Fig. 9).

Fig. 9 XPS wide scans of N-Chloramine modified membranes

3.6 Bacterial biofilm formation

To further investigate the antibacterial and antifouling properties of the PEO and N-chloramine modified membranes, *S. aureus* was selected as a model bacteria to study biofilm formation. PEK-COOH was selected as a control. First, all the membranes were exposed to *S. aureus* for 2 h. Next, loosely attached *S. aureus* on membrane surface were washed away. Finally, all of the membranes were cultured in LB medium for 24 h. The results are shown in Fig. 10. It is clear to see the high bacterial

growth on the PEK-COOH membrane, whereas bacteria are hardly visible on the PEO and the N-chloramine modified membranes after 24 h in LB culture (Fig. 10 (1)). Furthermore, while biofilm formation was observed on PEK-COOH membrane surface, there was almost no presence of *S. aureus* on modified membranes (Fig. 10 (2)). The results are attributed to both the hydrophilic modification and the antimicrobial modification, which not only inhibits the adhesion of protein and bacterial on membrane surface but also prevents the proliferation of microbes on membrane surfaces. From the results, it can be concluded that the addition of PEO and N-chloramine functional groups to the PEK-COOH membranes greatly enhanced their antimicrobial and antifouling abilities.

Fig. 10 (1) Bacterial growth of *S. aureus* on different membranes after 24 h in LB medium. (2) Biofilm formation by *S. aureus*. a, PEK-COOH membrane; b, PEO-120-Cl; c, PEK-350-Cl; d, PEK-550-Cl.

4 Conclusions

Herein, we reported an approach to fabricating membranes with PEO segment and N-chloramine functional groups that exhibit both antimicrobial and antifouling properties. Different molecular weights of PEO were introduced to the PEK-COOH membrane surface via EDC/NHS methodology. The results revealed that the PEO-grafted membranes increased significantly compared to that of the unmodified PEK-COOH membrane. PEO-grafted membranes were also found to resist both protein adsorption and bacterial adhesion. Furthermore, the modified membranes showed high efficiency in biocidal efficiency. As a result, the PEO-grafted and N-chloramine functionalized membranes have the potential to be used as antifouling membranes with broad applicability.

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