



Tuning the ultrafiltration properties of anti-fouling thin-layer hydrogel polyethersulfone composite membranes by suited crosslinker monomers and photo-grafting conditions

Polina Dobromirova Peeva, Thorsten Pieper, Mathias Ulbricht*

Lehrstuhl für Technische Chemie II, Universität Duisburg-Essen, 45117 Essen, Germany

ARTICLE INFO

Article history:

Received 7 April 2010

Received in revised form 4 July 2010

Accepted 8 July 2010

Available online 15 July 2010

Keywords:

Anti-fouling

Ultrafiltration

Photo-grafting

Crosslinking

ABSTRACT

Anti-fouling composite membranes were prepared via photo-initiated “grafting-from” of the hydrophilic monomer poly(ethylene glycol) methacrylate on commercial polyethersulfone ultrafiltration membranes. A fine adjustment of the sieving properties of the modified membranes could be achieved by addition of suited crosslinker monomers in appropriate ratio to the reaction mixture. In this study, two crosslinkers were used: N,N'-methylene bisacrylamide (MBAA) and pentaerythritol triallyl ether (PETAE). Systematic variations of UV intensity and UV irradiation time in combination with varied monomer mixtures have been performed. The resulting membranes have been characterized with respect to degree of functionalization, contact angle and zeta potential as well as water flux and protein ultrafiltration performance with bovine serum albumin and myoglobin, yielding data for solute rejection and permeability loss due to membrane fouling. A minimum degree of functionalization was necessary to achieve fouling resistance, and especially in this range, the effects of the two crosslinker monomers were largely different. Crosslinking with the “two-armed” MBAA yielded denser hydrogel layers on the porous base membrane and, consequently, enhanced protein rejection with increasing crosslinker ratio. In contrast, on the same membrane pore size, hydrogel layers crosslinked with the “three-armed” PETAE yielded a more open barrier structure and the protein rejection decreased with increasing crosslinker ratio. Overall, this study delivered fundamental results for the preparation of high performance composite membranes with enhanced selectivity and anti-fouling properties for ultrafiltration.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Membranes for ultrafiltration (UF) are frequently used in the industry as an easy and efficient tool for the preparation of quality products. In the recent decade, they became increasingly important, especially in the biotechnology and food industry for the concentration and separation of fermentation and food products yielding high purity and yield [1,2]. Most of the filtered products belong to the classes of proteins or other biopolymers. The major problems during their filtration are the flux decline and loss of selectivity due to membrane fouling.

Polysulfone (PS) and polyethersulfone (PES) are often used for the preparation of UF membranes due to their mechanical, chemical and thermal stability [1,3]. However, these materials are strongly affected by fouling during filtration, mostly due to their relatively hydrophobic character. By reducing the hydrophobicity, the non-

specific binding of product or other components on the membrane surface can be lowered. To minimize fouling, surface modification via physical (preadsorption) and chemical methods (plasma treatment, ultraviolet (UV) or high-energy irradiation) is already well established [3–5]. Among the various strategies, “grafting-from”, i.e., the heterogeneous graft copolymerization of suited functional polymers, is the most versatile approach [3]. Photo-initiated functionalizations of polymeric membranes can be very selective and efficient in combination with low cost for industrial implementation [6]. Aromatic polysulfones can be directly activated by UV irradiation to form radicals as initiator for “grafting-from” functionalizations of membranes [7,8]. Ulbricht et al. [8–10] grafted via UV initiation acrylic acid (AA) and various acrylates or methacrylates having polyethylenglycol (PEG), carboxyl, sulfopropyl, dimethylaminoethyl or trimethylammoniummethyl side groups onto PS, PES or polyacrylonitrile (PAN) UF membranes and studied the resulting membrane hydrophilicity and surface charge and the consequences for membrane performance. The anti-fouling properties of grafted layers from a wide variety of hydrophilic agents had already been investigated. The research group of Belfort has analysed the effects of different monomers, such as 2-hydroxyethyl

* Corresponding author. Tel.: +49 201 1833151; fax: +49 201 1833147.

E-mail addresses: mathias.ulbricht@uni-due.de, mathias.ulbricht@uni-essen.de (M. Ulbricht).

methacrylate, AA, N-vinyl-2-pyrrolidinone (NVP) and many more [7,11–14], using UV assisted “grafting-from” modification of PES membranes. According to hydrophilicity, static protein adsorption and filtration measurements, an increased fouling resistance to bovine serum albumin (BSA) compared to unmodified PES or regenerated cellulose membranes was found. Susanto and Ulbricht [15] compared the fouling behaviour of PES membranes which had been photo-grafted with the zwitterionic N,N-dimethyl-N-2-(methacryloyloxyethyl)-N-(3-sulfopropyl) ammonium betaine and the hydrophilic poly(ethylene glycol) methacrylate (PEGMA) and found better performance of the polyPEGMA modified membranes.

Among the hydrophilic monomers applied for surface hydrophilization, PEGMA has already been comprehensively studied. Uchida et al. [16] grafted PEGMA monomers with varied PEG chain lengths onto polyethylene terephthalate film. The modified surfaces exhibited strong hydrophilic properties and a surface charge of nearly zero. Similar results were achieved by Susanto et al. [17] when modifying PES UF membranes with polyPEGMA chains via UV irradiation. In this study the prepared low-fouling PES-based UF membranes were analysed with respect to water permeability, hydrophilicity, surface charge, and solute rejection, and fouling studies were also performed. The new membranes showed higher rejection and fouling resistance to sugarcane juice polysaccharides and BSA. Lui et al. used UV/ozone treatment [18] or interfacial polymerization [19] to graft PEG onto PES membrane surface. The successfully prepared modified membranes showed improved hydrophilicity and reduced protein adsorption. PEG monomers are also of great interest in the preparation of bulk hydrogels for the further application on membranes as anti-fouling coatings [20,21].

The reason why PEGs are fouling resistant to proteins are their kosmotropic properties. Kosmotropes stabilize the native protein structure due to their high hydration [22,23]. However, the water structure near to these species has the most important role. The formation of “structured” or “tightly bound” water close to the surface is responsible for their low interactions with protein molecules [24,25]. Vogler [26] discussed the attractive or repulsive forces between surfaces immersed in water. The water structure close to a more hydrophobic surface is disturbed, i.e., the water is “less dense” with an open hydrogen-bonded network; in this case, the interactions between this and another surface (including that of a macromolecule) are attractive and replacement of water at the hydrophobic surface by adsorbed solute is enhanced. Close to hydrophilic and kosmotropic surfaces the water structure is similar to the bulk water structure; repulsive forces between this surface and another hydrophilic surface or solute are observed.

Therefore, thin-film composite membranes with grafted anti-fouling layers made of kosmotropic polymer hydrogels, e.g., polyPEGMA, are very promising materials and it would be even more attractive if the sieving properties of the hydrogel could also be adjusted during “grafting-from” [15]. Indeed, it had been found that “grafting-from” using mixtures of PEGMA and N,N'-methylene bisacrylamide (MBAA) reduced the hydraulic permeability and shifted the sieving curve to smaller molecular weights [15]. It is well known that the “mesh” structure of bulk hydrogels can be manipulated by, among other factors, the content of bi- or multifunctional crosslinker monomers in the reaction mixture used for *in situ* radical polymerization [27]. Fänger et al. [28] used the bifunctional MBAA to crosslink poly(N-isopropylacrylamide) for the preparation of hydrogels with adjustable mesh size, as indicated by different “cut-off” values for biomacromolecules. Wu et al. [29] synthesized films of crosslinked NVP/MBAA and analyzed their structure, water sorption and transport properties. The results showed that higher crosslinker content in the prepolymerization mixture led to tighter structures, less water uptake and lower water

permeability. Application of “three-armed” crosslinker monomers has also already been studied. For instance, hydrophilization of self prepared PES membranes was performed via a thermally induced surface crosslinking polymerization with poly(ethylene glycol) diacrylate (PEGDA) and trifunctional trimethylolpropane trimethacrylate (TMPTMA) [30]. By adding TMPTMA to the PEGDA solution, the crosslinking process was accelerated due to the higher amount of double bonds in TMPTMA. The anti-fouling ability and permeability could be well adjusted.

Aim of this study was the preparation of anti-fouling membranes with excellent sieving properties for the use in concentration and fractionation steps of macromolecular mixtures, e.g., proteins or other biopolymers, in UF processes. In the present work, PES UF membranes were functionalized with PEGMA by UV induced graft polymerization to obtain thin-layer hydrogel composite membranes. The synthesized hydrogel layers were *in situ* crosslinked via addition of the crosslinker monomers MBAA or pentaerythritol triallyl ether (PETAE) to control the sieving properties of the new composite membranes. These monomers were chosen because they provide relatively short distance (number of atoms) between the potential crosslinking points (carbon-carbon double bonds) in the molecule and they are soluble in water. Since the UV irradiation dose is the driving force for this surface-initiated polymerization [17], the UV irradiation time at same UV intensity (i.e., the UV irradiation dose) was varied in order to achieve varied hydrogel layer thickness. Very good anti-fouling properties for protein solutions were achieved beyond certain UV dose. Most important, it will be demonstrated that the UF sieving properties can be easily tuned by the simultaneous variation of the UV dose and crosslinker type and amount.

2. Experimental

2.1. Materials and analyses

Commercial PES flat sheet membranes with nominal molecular weight cut-off (MWCO) of 10 and 50 kDa (named PES 50 and PES 10, respectively) from Sartorius-Stedim, Germany, were used in this study. Prior to use, all the membranes were cut to circular samples with diameter of 44 mm, washed in ethanol (p.a.; from VWR, Germany) for 1 h to remove preservatives and soaked overnight in 0.01 M Na₃N (Sigma-Aldrich, USA) solution in ultrapure water. Poly(ethylene glycol) 400 monomethacrylate (PEGMA 400) (number indicates the molecular weight of the PEG in g/mol) was purchased from Polysciences Inc., USA. “Two-armed” crosslinker MBAA and “three-armed” PETAE were supplied from Sigma-Aldrich, USA. The terminus “arms” indicates the maximum number of crosslinking points per molecule in a hydrogel network. The molecular structures of these two crosslinkers are shown in Fig. 1.

The proteins BSA, Fraction VH (Gerbu, Germany), and myoglobin from skeletal muscle (Sigma-Aldrich, USA) were used in test solutions with concentration of 1 g/l in 0.01 M phosphate buffer (potassium dihydrogen phosphate, KH₂PO₄, and disodium hydrogen phosphate dihydrate, Na₂HPO₄·2H₂O, from Fluka Chemie AG, Germany). An ionic strength of 0.01 M was chosen “to provide significant electrostatic interactions while maintaining protein stability” [31]. The pH value for these solutions was chosen near to their isoelectric points [32] (pH for the BSA solution was set at 5 and for the myoglobin solution at 7) in order to achieve a maximum in protein transmission and fouling behaviour [31,33,34]. Prior use, these test solutions were filtered through a 0.22 μm cellulose acetate microfiltration membrane (Sartorius-Stedim, Germany) to remove undissolved components. Water purified with a Milli-Q system from Millipore (USA) was used in all the experiments. Nitrogen pure gas was from Messer Griesheim GmbH, Germany.

Download English Version:

<https://daneshyari.com/en/article/636281>

Download Persian Version:

<https://daneshyari.com/article/636281>

[Daneshyari.com](https://daneshyari.com)