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Surface modification of polypropylene microfiltration membrane via entrapment of an amphiphilic alkyl oligoethyleneglycolether

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ABSTRACT

For surface hydrophilic and antifouling modification of polypropylene (PP) microfiltration membrane, the novel method for entrapment of the amphiphilic modifier octaethyleneglycol monooctadecylether ($C_{18}E_8$) was investigated in detail. The effects of the modification conditions on PP membrane and polymer structure were characterized by gas flow/pore dewetting, nitrogen adsorption/BET analysis, scanning electron microscopy and X-ray diffraction; surface properties were evaluated by ATR-FTIR spectroscopy and static water contact angle; filtration performance as well as antifouling property were investigated by water flux measurement, trans-membrane zeta potential, static and dynamic protein adsorption experiments. Furthermore, a stability study of the modified membrane was performed to offer a comprehensive understanding of this physical entrapment strategy. It can be concluded that both outer surface and inner pore walls of PP membrane were covered with oligoethylene glycol after entrapment modification by $C_{18}E_8$, with only very slight changes of membrane pore and polymer structures. Correspondingly, PP membrane surface hydrophilicity and antifouling performance were evidently improved. It was also found that the entrapped modifier has a tendency to leach out of the PP membrane in water at room temperature. However, after 8 weeks changes became very small, and the modified PP membrane surface still exhibited significant hydrophilicity and antifouling properties.

1. Introduction

Entrapment, the definition derived from a two-liquid process deposition accomplished by surface physical interpenetration network (SPIN), is a functionalization strategy to incorporate modifying species into the polymer surface region utilizing its reversible swelling property [1–3]. Early studies had been performed with polymethyl methacrylate, polystyrene, polyvinyl acetate or polyethylene terephthalate as substrates, via swelling in solutions of, for instance, poly(ethylene oxide–propylene oxide) (PEO–PPO) block copolymers or poly(ethyleneglycol) (PEG) in acetone or 80–82% trifluoroacetic acid/water mutual solvent and subsequent deswelling in water. In the past decade, entrapment of PEG into some polymer substrates which are lacking the desired surface functionality, such as poly(lactic acid) (PLA), has been used especially in the field of tissue engineering [3–5].

Polypropylene (PP) microfiltration membranes are intensively investigated with respect to introducing functional groups or layers into the polymer surface in order to overcome limitations in applications for separations or in the biomedical field, which are due to their low surface energy [6]. Surface modifications aiming at increasing the hydrophilicity and antifouling properties or the biocompatibility of PP membrane surfaces can be classified into physical (non-covalent) and chemical (covalent) methods. Wetting of the pores of PP membranes with polar solvents, e.g., isopropanol, can temporarily increase hydrophilicity. Adsorption of various substances, especially amphiphilic polymers, from solutions in the pores has also been used, but the hydrophilization is also not stable [7]. One more sophisticated example to introduce a functional “skin” is to deposit Langmuir–Blodgett layers onto PP membrane surface [8], however this method is complicated to realize. In contrast, chemical grafting is more popular because of the high efficiency and the stability of the modification. One group of methods is based on the pre-treatment of PP membrane with high-energy irradiation, e.g., plasma or UV, to generate reactive groups, and then chemically graft functional moieties [9,10]. The resulting covalent functionalization can be stable, but often undesired degradations of chemical or pore structure are observed. An alternative, more selective and less degrading strategy, mainly developed by Ulbricht et al., is to adsorb a photo-initiator on or into the membrane surface, and perform a subsequent UV initiated graft copolymerization to yield tethered polymer chains on the PP membrane surface [11,12]. It had been demonstrated that such “grafting-from” functionalization can be better controlled by

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entrapping the photo-initiator in the surface layer of the PP membrane pores (via swelling the PP in an initiator solution in an apolar solvent and then immobilizing it by deswelling the PP in a polar solvent), rather than by an adsorption process [13]. However, no work had been done to investigate the entrapment efficiency directly. Furthermore, it can be imagined that the membrane surface properties could be changed by the entrapment procedure itself.

Therefore, this study had three main aims, (i) to investigate the non-covalent modification of PP with hydrophilic moieties via surface entrapping (Scheme 1), (ii) to study the effects of entrapping modification onto the bulk and surface structure of porous PP membranes, and (iii) to evaluate the effects on surface and pore hydrophilicity and modification stability.

Considering the apolar base polymer PP, the two-liquid entrapment method under the conditions used in previous work [1–5] is not appropriate for hydrophilic modification of PP surfaces. However, using as the modifier amphiphilic substances instead of PEG should offer the opportunity to find one common solvent for both the PP membrane and this modifier in the first step of swelling/embedment. Moreover, vacuum drying instead of solvent replacement to extract the swelling solvent has the advantage of avoiding the leaching of the nascent immobilized modifier from the polymer substrate in the second step of deswelling/entrapment.

It is important to clarify the difference between our method and the so-called "PP surface modification by entrapment functionalization" of Bergbreiter et al. [14]. Their work was focused on the preparation of functionalized polyolefin films by blending with functional polymers in certain common solvents, but not by a post-modification of the polyolefine surface. Therefore, it would be more accurate to describe this approach as "blending" (accompanied by surface segregation) rather than "entrapment".

In this paper, octaethyleneglycol monooctadecylether was selected as amphiphilic modifier, and suitable modification conditions were established. It was expected that the results with this substance could then also be applied to amphiphilic macromolecules as surface modifier. The resulting modified PP membranes were characterized with respect to polymer and membrane pore structures, outer and inner surface properties, water permeability as well as static protein adsorption and membrane fouling under microfiltration conditions. In addition, the stability of the modified PP membranes was investigated. The results enable a comprehensive understanding of this novel entrapment method.

2. Experimental

2.1. Materials

Flat-sheet polypropylene microfiltration membranes (PP 2EHF) with a nominal pore diameter of 0.2 μm and a porosity of 70% were purchased from Membrana GmbH, Germany. Octaethyleneglycol monooctadecylether ($C_{18}E_8$), disodium hydrogenphosphate dihydrate, potassium dihydrogenphosphate, and trichloroacetic acid were from Fluka. 1,2-Dichloroethane (99.8+%, extra pure) carbon tetrachloride, xylene, 1,2,3,4-tetrahydronaphthalene, and Ponceau S were from Acros. 5-Sulfosalicylic acid was from Serva, acetic acid from Fischer, 1N KCl from Bernd Kraft GmbH, potassium hydroxide from Merck, sodium hydroxide from Roth, 1N HCl from Waldeck and HCl (conc.) from Riedel de Haen, and the Pierce BCA Protein Assay kit was purchased from Thermo Science. Bovine serum albumin (BSA), fraction V (fatty acid free), was from ICN Biomedicals, Inc. Ultrapure water from a Milli-Q system (Millipore Inc.) with a 18.2 MΩ resistivity was used in all experiments.

2.2. Surface entrapment of amphiphilic molecules

The PP membrane samples with a thickness of 190 μm, a diameter of 25 mm and hence volume of ca. 0.1 cm^3, were pre-treated with acetone to elute residual solvent from manufacturing, dried and weighed. Then, samples were immersed into a 25 g/L solution of $C_{18}E_8$ in 1,2-dichloroethane at room temperature for 20 h. Then, the swollen membrane was taken out and immersed into water for 20 min to achieve a hydrophilic/hydrophobic orientation of $C_{18}E_8$ in the membrane interface of water/1,2-dichloroethane. Subsequently, the solvent was removed by vacuum drying at 45 °C for 48 h. Thereafter, the modified sample was washed with water at room temperature for 2.5 h to elute the only adsorbed or coated $C_{18}E_8$ from the membrane. Then, gravimetry of the dried sample was performed in order to measure the weight gain by modification.

2.3. Characterizations

2.3.1. Membrane structure

Pore size distributions of membranes in the dry state were determined by the wetting fluid displacement technique with Capillary Flow Porometer CFP-34RTG8A-X-6-L4 (PMI Inc., Ithaca, NY, USA) as described in detail before [15]. Membrane surface area and morphology were characterized by BET specific surface area analyzer SA 3100 (Beckmann-Coulter GmbH, Krefeld, Germany) and scanning electron microscopy (SEM; Quantas 400 FEG, France), respectively.

X-ray diffraction was carried out using a STOE transmission diffractometer STADIP (2003-10, STOE & Cie GmbH, Germany) with a Cu Kα (λ = 0.1542 nm) generator at 50 kV and 30 mA.

Attenuated total reflection Fourier transform infrared (*ATR-FTIR*) spectra of the original and modified PP membranes were obtained using a Varian 3100 spectrometer (USA), equipped with a MCT detector and an ATR unit with a Ge crystal (60°). A total of 64 scans were performed at a resolution of ±4 cm^{-1}.

Trans-membrane streaming potential was measured using the system described in [15], at 25 °C with circulated electrolyte solution (0.001 M KCl, pH adjusted with 1 M KOH or HCl) by using a trans-membrane pressure difference of less than 1 bar. For each pH value, the potential was recorded at various trans-membrane pressures, and zeta potential was calculated from Smoluchowski equation [16].

2.3.2. Contact angle

Static water contact angles were measured by the sessile drop method with a contact angle goniometer (OCA 15 Plus, Dataphysics GmbH, Filderstadt, Germany) equipped with a video camera and an image analysis system. 7 drops of 5 μl water were injected onto PP membrane surface and the obtained values were averaged to acquire the contact angle of the membrane. In addition, the change in shape and, hence, contact angle of every water drop was recorded every 30 s and this process monitored for 20 min.

2.3.3. Water flux

The filtration experiments were performed at room temperature in a 25 mm diameter dead ended stirred ultrafiltration cell (10 ml, Amicon Model 8010, Millipore), with an additional feed reservoir connected to a nitrogen gas tank. The active membrane area was 3.14 cm^2. Initially the stirred cell and feed reservoir were filled with water. The unmodified PP membranes were prewetted with ethanol and the modified membranes were prewetted by water, each for 5 min to completely fill the pores, and then pressurized at ca. 4.1 kPa/cm^2 for 50 min till the water flux became stable (this indicated that in case of unmodified PP membranes, the water had completely replaced the ethanol from the pores). Then