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Polysulfone membranes clicked with poly (ethylene glycol) of high density and uniformity for oil/water emulsion purification: Effects of tethered hydrogel microstructure

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ABSTRACT

Hydrogel-tethered polysulfone (PSF) membranes have been synthesized by grafting propargyl-poly (ethylene glycol) (pro-PEG) onto azide-functionalized PSF membrane surfaces via the copper (I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction, and then used for oil/water emulsion purification. Three pro-PEGs (120, 750 and 1300 g/moL) and two PSF-azi membranes with different degrees of azide functionality were used to obtain a series of PSF-g-PEG membranes. The membranes were characterized in detail by FTIR, XPS, FESEM and the contact angle method. The click reaction was demonstrated to be effective, and PEG was densely and highly uniformly grafted on the membrane surfaces including the pore walls. A higher hydrodynamic thickness of the PEG layer leads to a lower contact angle. The grafting density has more impact on membrane properties than the PEG molecular weight. The membrane grafted with low-molecular weight PEG at high grafting density shows a better combination of antifouling performance and permeance. The best performance was 120 L m^{-2} h^{-1} emulsion flux with complete oil rejection and over 95% flux recovery in cycled fouling-rinsing tests. It is suggested that high grafting density should be pursued with strict control on the chain length to obtain good emulsion filtration membranes.

1. Introduction

A large amount of oily wastewater is emitted into the environment every day by industrial sources. From the estimates by OTM & Douglas-Westwood, 241 million barrels of produced water associated with oil and gas operations are globally generated every day, and by 2020 their generation is expected to grow to 292 million barrels [1]. Because of the complex composition and high oil content, oily wastewater has become one of the most serious types of water pollution [2–4]. Traditional remediation techniques include chemical emulsification, gravity settling, centrifugal settling, heat treatment, and electrostatic coalescence. These methods have been proven to efficiently remove free oil (in the form of large droplets in wastewater), but is inefficient to treat emulsified oil droplets (less than 20 μm in size) and dissolved oil. Traditional methods also suffer from other limitations, such as high cost (centrifugal settling and heat treatment), use of toxic chemicals and secondary pollution (chemical emulsification), and space limitations (gravity settling). Therefore, alternative methods are needed for oil/water emulsion wastewater treatment [5–7].

In recent years, membrane filtration has shown promise as a clean technology for oil/water emulsion treatment [3]. Membrane technology has many advantages such as high oil removal efficiency, low energy cost, small footprint, compact design, and minimal chemical addition [6,8,9]. Very recently, membrane technologies have been applied in oilfields and are playing an increasingly important role in refinery industries across the world.

As a novel technology, membrane filtration is still far away from being optimized for oil/water emulsion treatment. The biggest challenge is still that of membrane fouling [10,11]. Fouling is adsorption or accumulation of certain components of produced water on the membrane surface (external fouling) or in the membrane pores (internal fouling) that eventually causes flux decline, thus hindering the widespread application of membrane technology [10]. Many physical cleaning methods such as backwashing, air sparging, vibration, etc. are effective at dealing with reversible fouling but less effective for irreversible fouling. Chemical cleaning technologies using harsh conditions often damage the membranes and hence shorten their lifespan. In addition, internal fouling often cannot be completely eliminated even after substantial chemical or hydrodynamic cleaning. Consequently, the

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study of membrane materials with excellent antifouling properties remain active [12,13].

Many investigations have demonstrated that increasing the membrane surface hydrophilicity can significantly decrease membrane fouling [14–16]. A variety of surface modification methods, including blending with amphiphilic additives [17–19], surface coating [20–22] and surface grafting [23–26], are used to increase the fouling resistance of membranes. Early efforts on membrane materials used for oily wastewater treatment focus on synthesis of amphiphilic polymers as additives blended into membrane materials. Mayes et al. synthesized UF membranes incorporating the amphiphilic comb copolymer additive polyacrylonitrile-graft-poly (ethylene oxide) (PAN-g-PEO). The resulted membranes exhibit high resistance to irreversible fouling. Although comb copolymer modified membranes showed significantly better fouling resistance in oil/water emulsion treatment [11], the long-term fouling resistance of the membrane and the compatibility of the copolymer with the bulk material still remain as questions to answer for this technique. Several studies have applied surface coatings to enhance the membrane antifouling performance in oil/water emulsion filtration. Freeman et al. used PEG-cross-linked chitosan on polysulfone ultrafiltration (UF) membranes to increase their fouling resistance. The obtained hydrogel-coated membranes exhibited excellent performance in oil-in-water purification [10]. Although coating is a convenient method to increase fouling resistance, the reported membranes had low permeance. This happens because good antifouling performance requires a coating layer, which is usually thick when produced by a traditional dip-coating method. In addition, the chemical stability of the coating layer in the oil may also be questionable. Surface grafting has attracted more attention than surface coating, because more permanent surface modification can be achieved and more diverse chemistry and functionalities can be incorporated. Despite the current success in using surface grafting for membrane surface modification, the microstructure of the grafting layer needs to be tailored to obtain the advantages of surface grafting. For example, sufficient fouling resistance of modified membrane surface can only be assured by a fairly high grafting density. On the other hand, excessive grafting can result in membranes with low flux due to swelling of the grafting chains during filtration.

Many reports, including our previous work [25,27–29], have proved that surface grafting based on click chemistry can be used to tune the microstructure of the grafting layer more precisely than other chemistries. Using copper (I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction on membrane modification, we have successfully synthesized a series of nanoporous polysulfone (PSF) membranes with high grafting density. The membranes were demonstrated to have molecular sieving capacity and good antifouling properties when filtrating oil/water emulsions.

In this work, in order to optimize the membrane performance in real oily waste water emulsion filtration, the CuAAC reaction was conducted to graft propargyl poly (ethylene glycols) (pro-PEGs) with different molecular weights (120, 750 and 1300 g/moL) onto PSF membrane surface having different functional degree of azide groups (see Fig. 1). Two azide-functionalized PSF membranes were prepared and defined as PSF-azi0.17 and PSF-azi0.45 based on the functionality degree of azide per repeating unit of PSF. In that case, a series of PSF-g-PEG membranes having different grafting densities and grafting chain length were obtained and defined as $PSF_{0.17}$-g-PEG120, $PSF_{0.17}$-g-PEG750, $PSF_{0.17}$-g-PEG1300, $PSF_{0.45}$-g-PEG120 $PSF_{0.45}$-g-PEG750 and $PSF_{0.45}$-g-PEG1300. Two oil/water emulsion samples, soybean oil/water emulsion and real oilfield oil/water emulsion from a north oilfield of China were used to test the membrane in this work. The effects of the microstructure of the grafted polymer layer including graft chain length and graft density on the membrane performance filtrating oil/water emulsions were systematically studied with the aid of a thorough characterization of membrane materials by FTIR, XPS, FESEM and the contact angle method. We attempted to relate the key factors describing membrane structures to the membrane performance in oil/water emulsion filtration. These factors include mean pore diameter, grafting density, grafting chain length and hydrodynamic thickness of the grafted layer.

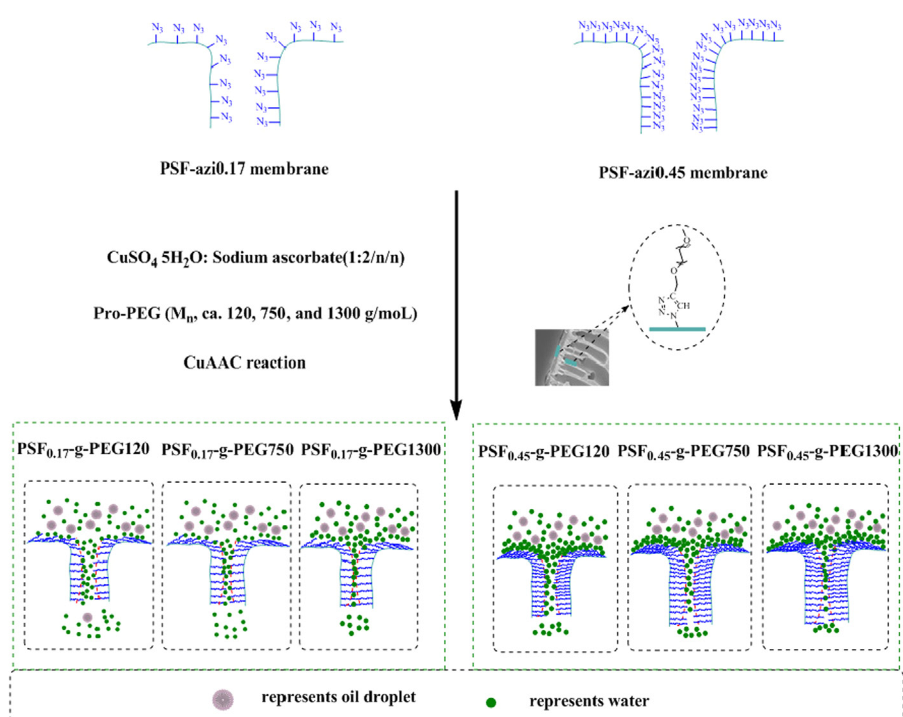

Fig. 1. Graft polymerization of PEG onto PSF membrane surface via the CuAAC reaction for oil/water emulsion treatment.