Advanced Block Copolymer Membranes for Oily Industrial Wastewater Treatment

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Abstract

Tremendous amounts of oily wastewater are produced daily from industrial processes, including petrochemical, textile, leather, and steel processing. This wastewater is a huge challenge to the environment and industry uses multiple approaches to separate the water from oil including oil-absorbing materials, gravity separation, flocculation, and coagulation. However, these concepts are ineffective in separating oily water emulsions where the oil droplets are smaller than 20 µm in size and do not perform well upon incorporating chemicals or using an electric field. Membrane filtration is one of the best strategies to handle such emulsions, especially the surfactant-stabilized ones, as they yield highly pure water permeate via simple filtration process and they can be cleaned re-used for multiple times at large-industrial scales. This presentation will give an overview of novel polystyrene-based copolymer membranes developed and tested at Qatar University in collaboration with the University of Southern Mississippi. The newly developed membranes display substantial enhancement in separating oil from water in tight emulsions while demonstrating remarkably high resistance to fouling over five runs in comparison to the commercial membranes that get fouled within only two emulsion runs. The presentation will outline the membranes' oil rejection efficiency, chemical, morphological, and mechanical stability after cycles of cleaning and reuse. Finally, the membranes were tested using synthetic oily water and real-field samples and testing protocols from the oil & gas companies in Qatar.

Keywords: Ultrafiltration; Block Copolymers composite membranes; Oil/water separation; Roll to Roll; Fouling resistance

1 Introduction

1.1 Membrane Separation

A significant breakthrough in membrane science would have profound economic and environmental impacts that ripple from increasing chemical production efficiency. Membrane separation is predominantly based on a size-sieving mechanism. Membrane performance is dictated by size, size distribution, porosity, pore geometry and the surface chemistry of pore walls. All membranes have an inherent tradeoff between membrane permeability (i.e., how fast molecules pass through a membrane material) and selectivity (i.e., to what extent the desired molecules are separated from the rest). For size-sieving based membrane filtration, pore size distribution directly determines the rejection rate of solutes present in a feed solution and thus membrane selectivity. To completely separate a mixture of solutes, membrane pores must be smaller than the smallest solute that is to be retained, and larger than the solutes to separate. Currently, the dominant technology for nano-filtration (pore size < 1 nm) and ultrafiltration (1 nm < pore size < 100 nm) is based on polymeric membranes made by phase inversion. Such membranes suffer from poor selectivity due to irregular pore openings and tortuous pore structure through the membrane. Such ill-defined pore structures impair both selectivity and fouling properties, causing a performance drop over the membrane's lifetime (Banerjee et al., 2010, Rana et al., 2010, Krishna et al., 2008). Surface modification with hydrophilic polymers (i.e. polyethylene-glycol (PEG) and zwitterion containing copolymers) onto polymer membranes have played an important role in improving membrane fouling performance (Li et al., 2015). Membrane fouling solutions remain urgently needed and are highly sought after. Despite their poor selectivity and fouling tendencies, polymeric membranes continue to dominate the market due to low material and manufacturing cost.

1.2 Self-assembled Isoporous Membranes

Block copolymers (BCPs) consist of two chemically distinct polymers that are covalently linked at one end. The unfavorable block-block interactions in tandem with the inherent, due to long-chain nature of the BCPs, entropic factor results in the separation of blocks into highly uniform microdomains with the size scale ranging from a few to tens of nanometers depending on the chain lengths used (Bates et al. 1990, Bates et al. 2017). The unique capability of BCPs to self-assemble into uniform microdomains has spurred researchers to investigate the possibility to use them in membrane filtration (Jackson et al., 2010, Xu et al., 2003, Yang et al., 2006). Two routes have been used to incorporate the ordered BCP domains into porous membranes. The composite BCP membrane approach involves-a composite membrane consisting of an isoporous BCP membrane layer (>80 nm) which serves as a sieve sits on top of a thick layer (~100 μm) of macroporous material serving as mechanical support (Yang et al. 2010). It has been demonstrated that the composite membrane shows high flux and selectivity for separating viruses from healthy cells (Yang et al., 2006, Yang et al., 2008). However, poor mechanical integrity of thin porous BCP films limits the maximum of allowable pressure for separation (2 bar) (Yang et al., 2008). In an alternative way to generate isoporous membranes, the BCP self-assembly has been combined with non-solvent phase inversion process (Peinemann et al., 2007; Wang et al., 2013). A brief description of the membrane fabrication process is as follows. After the BCP film is cast from solution, polymer concentration gradient is formed in the membrane due to solvent evaporation. The top layer of the membrane is high in polymer concentration while the bottom layer of the membrane is low in polymer concentration. Thus, the BCP chains in the top of the membrane would pass the disorder to order transition and form an ordered domain, while the BCP chains in the bottom of the membrane are still in the disordered state, which later become macroporous pores through the phase inversion.

1.3 Challenges for Isoporous Polymeric Membranes

Using the isoporous structure from BCP self-assembly is not an entirely new concept, yet through the past ten years of research the path to commercialization has yet to be realized. Two key factors limit using isoporous membranes manufactured by phase inversion. First, tight processing restrictions are required to order the top domain, which complicates the membrane manufacture process. Too short drying time results in no pore formation, while too long drying time make pores too wide. Additionally, phase inversion process is limited with respect to high molecular weight BCPs (>100 kDa) since ordered microdomains near the disorder to order transition are required while in solution. Smaller pore size (5 nm) requires lower molecular weight BCP (i.e. < 20 kDa), which do not tend to order in dilute solutions, limiting their use in the BCP based asymmetric membranes (Sutisna et al., 2016). Secondly, phase inversion of bulk BCP membranes consume large quantities of expensive block copolymers and thus are not ready for mass production despite the improvement in separation efficiency. Current homopolymer filtration membranes are based on low-cost polysulfone, polyethersulfone (PES), polyvinylidene fluoride (PVDF), and similar polymeric materials. Those commodity polymers are easy to synthesize in an industrial scale (> tons). While the cost of the block copolymer remains high.

1.4 Oil and Water Separation

The “crude oil” from the oil wells contain oil, gas, produced water and solid particulates. In the oil and gas extraction processes, the first step is to transfer this mixture to primary gravity separators to produce well defined layers of gas, oil and water. Thereafter, the separator outputs three major components: crude oil, process water (emulsion) and gas. There are many techniques for the separation of emulsions, yet all show major disadvantages. Membrane filtration is one of the best methods for large-scale separation of oily wastewaters. Their use in industry is encouraged due to many processing factors, such as simplicity washing, recyclability of throughput material in cross-flow membrane assemblies, and highly pure permeate. There is a significant difference in membrane properties depending on their surface properties. Thus, hydrophobic and hydrophilic membranes are prepared in various ways to provide better fouling resistance.

There are four membrane separation processes in water and wastewater treatment, namely, microfiltration (MF), ultrafiltration (UF), nano-filtration (NF), and reverse osmosis (RO). Based on membrane structure and function they can additionally be divided into a) Symmetric (MF/UF), b) Asymmetric (MF/UF), c) Thin film composite (RO/NF), and d) Skinned (MF/UF) (Nunes, 2006; Strathmann, 2001). Of specific interest in this study is the multilayer composite or thin film membrane and its typical structure. The composite membrane consists of very thin top filtration layer with a thickness typically less than 100 nm sitting on a top of porous support and backing polymer layer or layers. By having such structure, one can have the best of both worlds for flux, selectivity and cost.

1.5 Knowledge Gap and Advantage of our Approach

Non-solvent induced phase separation (NIPS) is the predominate method of manufacturing membranes, producing a thick network of interconnected pores (Peinemann et al., 2007). Selectivity and permeability of NIPS membranes are acceptable, but the reason this manufacturing method has been so widely adopted is that it is inexpensive, and these membranes can be produced substantially cheaper than better performing membranes. Block copolymer (BCP) membranes have been studied for years due to their ability to phase separate into highly regular pores and have been shown to have increased permeability and selectivity compared with NIPS membranes (Abetz, 2014, Nunes, 2016). Sadly, block-copolymer synthesis cost has been hindering the marketability of such membranes. Our work bridges the technological gap, i.e., superior block copolymer-based membranes can be made in a manner that their cost will become comparable with that of traditional NIPS membranes.

2 Methodology and Results

2.1 Membrane Preparation Methods

Various annealing methods were tested to fabricate a range of BCP membranes for oil-water separation in this work. Cold zone annealing (CZA), a dynamic and roll-to-roll compatible method for continuous membrane production, and UV etching were chiefly selected to synthesize BCP membranes. Asymmetric membranes comprised of a 100 nm thick nanoporous selective thin film layer with vertically oriented nano-pores, and templated by block copolymer self-assembly. A conventional PES microfiltration membrane provides mechanical support. In one piece of work, we used the CZA technique to fabricate thin-film membranes based on the PS-b-PMMA (57k-b-25k) block copolymer system. The BCP samples were mixed with different percentages of the PMMA (25 kDa) homopolymer. PMMA was able to swell only the PMMA blocks in the BCP and therefore help to achieve higher extents of phase separation between the two blocks. This method enabled us to control the cylinder size, therefore the pore size, by blending different percent of the homopolymers with a great degree of tune ability as shown in Figure 1. The membranes obtained have a thickness of around 100 nm and fabricated using zone annealing at 210°C with a speed of 10 µm/s.

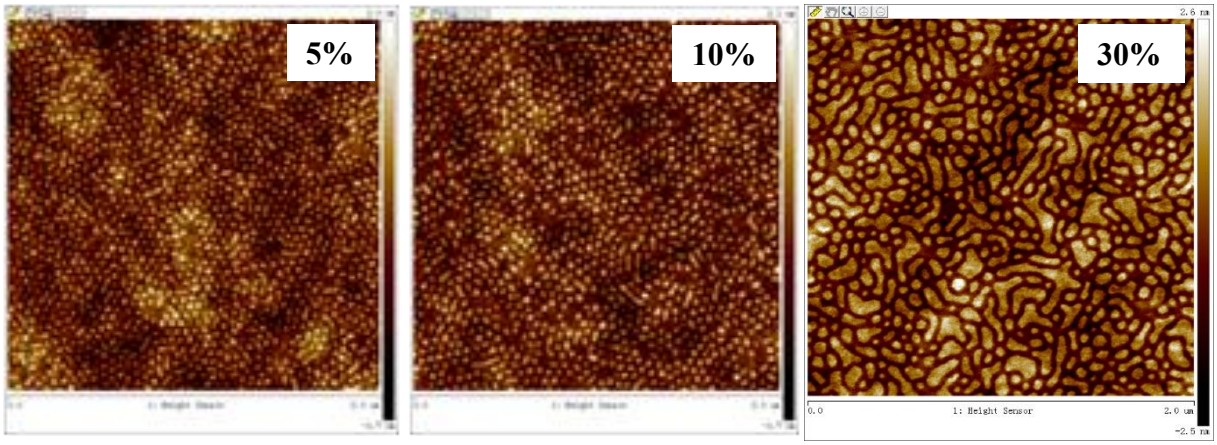

Fig. 1: Membranes based on PS-b-PMMA (57k-b-25k) swollen with different percentage of the PMMA homopolymer (25 kDa)

2.2 Membrane Filtration Efficiency

A bench scale setup incorporating an Amicon Ultrafiltration stirred cell (50 mL capacity, membrane diameter of 44.5 mm, actual filtration area 13.5 cm^2) was applied for testing flat sheet BCP membranes at pressures ranging from 1 to 5 bar. The filtration cell was placed on a magnetic stirring plate to ensure homogeneity of the produced water feed. The filtered water was collected in a glass beaker placed on a digital balance to weigh the permeate. The membrane water flux was then monitored.

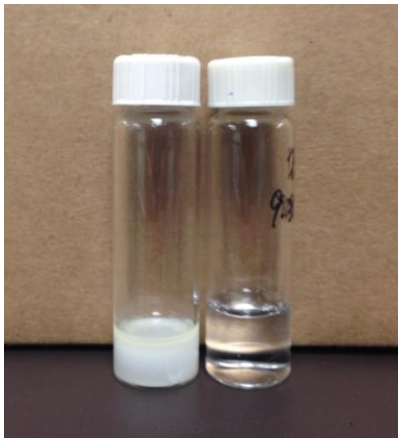

Fig. 2: Oil/water separation performance exhibited by fabricated BCP membranes

3 Conclusion

A wide range of nano-porous BCP membranes were synthesized and tested for effective separation of oil from produced water in this project. Various solvent annealing processes were assessed for directing self-assembly on BCP layer fabrication on conventional microfiltration membranes serving as a support layer. BCP membrane are being tested for their oil-water separation performance with promising results. Well-ordered BCP membranes displays high potential for upscaling and subsequent application in large scale produced water treatment.

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