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Enhanced abrasion resistant PVDF/nanoclay hollow fibre composite membranes for water treatment

Chi Yan Lai, Andrew Groth, Stephen Gray, Mikel Duke *

Institute for Sustainability and Innovation, College of Engineering and Science, Victoria University, P.O. Box 14428, Melbourne, Victoria 8001, Australia

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ABSTRACT

Seawater pretreatment with microfiltration and ultrafiltration is technically and economically feasible with advantages over conventional granular media filtration. Current membranes have short lifespans and wear irreversibly over time, especially in the presence of abrasive particles in seawater. Novel polyvinylidene fluoride (PVDF)/nanoclay hollow fibre membranes were fabricated by non-solvent induced phase separation (NIPS) to study the improvement of membrane physical endurance. Loss on ignition testing has shown high nanoclay retention was achieved at low initial nanoclay loading. Despite showing lower pure water permeability, the incorporation of nanoclay shifted the PVDF crystalline phase from α-phase to β-phase and improved the membrane structure as well as mechanical properties in terms of stiffness and flexibility. Tensile strength increased from 3.8 MPa to 4.3 MPa with 5.08 wt% Cloisite® 30B loading while break extension increased from 175% to 229% with 5.08 wt% Nanomer® I.44P nanoclay loading. An accelerated abrasion test revealed the membrane with an initial 5.08% loading of Nanomer® I.44P had improved abrasion resistance, lasting three times longer than the control membrane with no nanoclay addition. PVDF membranes containing commercial nanoparticles are therefore promising for improved abrasion resistance in water treatment applications.

1. Introduction

In order for a seawater desalination plant to run efficiently, seawater pretreatment is essential to remove the suspended solids including particulates, debris, silt, microorganisms and colloids before the seawater passes through the reverse osmosis (RO) system. Conventionally, seawater pretreatment is achieved by granular media filtration following coagulation and flocculation. With the recent advances in membrane technology, pretreatment with microfiltration (MF) and ultrafiltration (UF) has become more popular over the past decade. Examples of seawater desalination plants that have adopted UF pretreatment include those in Yu-Huan (China), Fukuoka (Japan), Saudi Arabia and Turkey [1]. The major advantage of membrane filtration over the conventional process is its ability to remove a wider spectrum of particles [2] that produces improved water quality and thus reduces fouling and cleaning frequency in the subsequent RO process. Besides having smaller plant footprint size which reduces capital investment [3], MF/UF pretreatment also has lower chemical demand compared to coagulation and flocculation ahead of dual media filtration [4].

Despite these benefits and proven technical and economic feasibility in field studies [3,5,6], conventional granular media filtration is still the main pretreatment technology for current medium and large size desalination plants. One major drawback of implementing membrane filtration pretreatment is the shortened lifespan of these pretreatment membranes compared to wastewater and surface water applications. The life expectancy of the pretreatment membranes is 3–5 years [7] which is much shorter than typical UF/MF membranes treating groundwater and surface water which can last up to 7–10 years [8]. This shorter lifespan is likely to be associated with the harsher environment provided by the water source. Compared to mostly bio/organic particulates present in freshwater, harder and more abrasive particles including sand and silica based debris are found in seawater [9]. In a recent autopsy study of 99 seawater RO membranes from 13 different countries, 11% of the membranes failed due to abrasion apart from biofouling being the major reason (28%) [10]. Also, the quality of the seawater entering the desalination plants varies depending on the sources of intakes. Often, costly deep offshore intakes (10 m below sea level) contain much fewer and smaller particulates compared to on-shore shallow intakes that may be affected by algae blooms and sudden increases in solids brought by surface runoff [11,12]. The ability to withstand abrasive particles would enable MF/UF filtration membranes to pre-treat seawater from all intakes rather than just those accessing higher quality waters. Despite the lack publically available evidence for

* Corresponding author. Tel.: +61 3 99197682; fax: +61 3 99197696.
E-mail address: mikel.duke@vu.edu.au (M. Duke).

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rapid abrasion of membranes for seawater pretreatment applications due to the lack of long-term, full-scale operating history and a reluctance by operators and technology providers to publicise operational issues, abrasive wear is known to be an important issue for membrane suppliers.

In order to protect the pretreatment membranes from abrasive particulates such as shell particles and debris present in seawater, microscreening with mesh size of 120 µm or less is currently employed upstream of the membranes [11]. While this method is generally reliable, the installation and operation of microscreening system adds further cost and it cannot protect the membranes from abrasive objects smaller than its mesh size. For instance, the size of clay/silt aggregates is in the range of 1–40 µm and that of phytoplankton ranges from 4 to 120 µm [13]. It is also reported that some diatoms and algae are smaller than 5 µm and they can abrade the membrane surface with their exoskeletons composed of silicon or calcite [10]. Screening and intake systems are typically installed at a cost to adhere to the membrane company's warranty. Therefore if the filtration membranes are strong enough to withstand the abrasive substances, the microscreening step can be minimised leading to a reduction in the installation and operation costs.

To address this, physical endurance of the membranes needs to be enhanced while maintaining their excellent hydraulic and separation performance. One possible solution is to introduce inorganic materials into the polymer matrix which improves the physical and chemical properties of the membrane material.

While work in the literature has focussed on nanocomposites for anti-fouling improvement [14–16], their ability for enhanced abrasion resistance has not been explored. A common polymer material used for membranes is polyvinylidene fluoride (PVDF), which has gained popularity in water treatment for its chemical robustness, while its porous structures are readily and reliably controlled, which is essential for MF and UF applications. Improvement in mechanical properties of PVDF/nanoclay flat sheet membranes was observed previously [17,18]. The wear property of polymeric and nanocomposite materials, including clay nanocomposites [19–21] has been widely studied, but this has not been extended to the membrane field. This study therefore investigates the improvement to abrasion resistance by incorporating nanoclay into PVDF hollow fibre membranes.

2. Abrasive wear theory

This paper aims to explore the capability to improve wear resistance by the inclusion of nanoparticles, and relate this to material properties and wear theory. Ratner et al. [22] has proposed a theory for abrasive wearing of polymer as

$$W = \frac{k\mu}{H\sigma\varepsilon} \tag{1}$$

where W is the specific wear rate, μ is the coefficient of friction, H is the indentation hardness, σ is the tensile strength, ε is the elongation at max load and k is a proportionality constant. In particular, the product $\sigma\varepsilon$ denotes the work needed to separate a particle from the wearing surface by tensile failure and it is indirectly proportional to the abrasion wear rate. This correlation between wear rate and $\sigma\varepsilon$ has shown very good linear agreement for a number of polymers at room temperature including polyethylene, polysulfone, PTFE and PVC [23]. The convenience of this method is that it relies on mechanical properties that can be readily measured. How this theory applies to wear on porous membranes is yet to be confirmed against actual abrasion resistance.

3. Experimental

3.1. Materials

Powdered PVDF, Solef® 1015 (specific gravity = 1.78, MW = 570 kDa), was obtained from Solvay Solexis. Two types of commercially available nanoclay were used in this study. Cloisite® 30B (specific gravity = 1.98), a natural montmorillonite modified with 30 wt% methyl dihydroxyethyl tallow ammonium shown in Fig. 1a, was supplied by Southern Clay Products. Nanomer® I.44P (specific gravity = 1.90), a montmorillonite clay surface modified with 35–45 wt % dimethyl dialkyl(C14-C18) amine shown in Fig. 1b, was obtained from Nanocor. The inorganic part of the nanoclay has a general formula as $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. The solvent used was industrial grade 1-methyl-2-pyrrolidinone (NMP) from ISP.

3.2. Membrane preparation

Membranes with various nanoclay loadings and a control membrane which contained 0 wt% nanoclay were prepared. Table 1 summarises the various nanoclay loadings used in this work, with nanoclays loadings up to 5.08 wt% used.

The nanoclay was first dispersed in NMP with ultrasonication and a high shear hydrodynamic dispersion process. The dispersion was then mixed with the PVDF based polymer at 90 °C for 48 h under a nitrogen atmosphere. The hollow fibre membranes were extruded with a dry–wet spinning process and they were formed through a non-solvent induced phase separation mechanism using a 60 °C coagulation bath. A portion of the membranes were soaked overnight in a 10 wt% glycerol/water solution in order to preserve

Table 1
Membrane composition.

Name	Nanoclay type	Nanoclay loading % in dope (by weight of PVDF)
0% Nanoclay	–	0
30B 0.88	Cloisite® 30B	0.88
30B 2.61	Cloisite® 30B	2.61
30B 5.08	Cloisite® 30B	5.08
I44P 0.88	Nanomer® I.44P	0.88
I44P 2.61	Nanomer® I.44P	2.61
I44P 5.08	Nanomer® I.44P	5.08

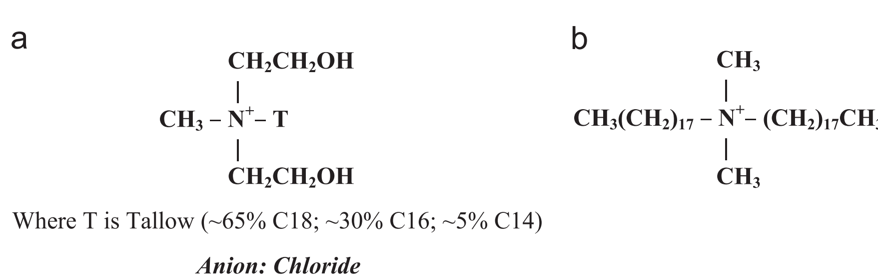

Fig. 1. Organic modifier used in Cloisite® 30B (a) and Nanomer® I.44P (b).