Materials Chemistry and Physics 167 (2015) 209–218

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Inorganic particle enhanced polymer hollow fiber membranes with high mechanical properties

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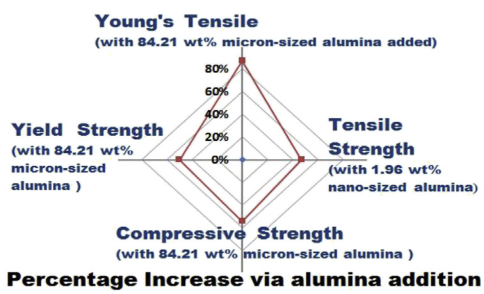
HIGHLIGHTS

- Inorganic-polymer hollow fiber membranes were synthesized.
- Such composite membranes show higher tensile and compressive properties.
- Such composite membranes show improved permeability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 August 2015
Received in revised form
17 September 2015
Accepted 13 October 2015
Available online 3 November 2015

Keywords:
Composite materials
Mechanical properties
Polymers
Microporous materials

ABSTRACT

Inorganic particle/polymer hollow fiber membranes with different inorganic particle sizes and particle loadings were synthesized and characterized in terms of morphology and mechanical properties. The incorporation of inorganic particles induces the formation of large surface pores in the skin layer yet decreases the pore size of large voids in the support layer. The particle size and particle loading are determining factors in such morphology changes. Moreover, due to the different out-diffusion ability of inorganic particles with different sizes, smaller particles migrated and diffused out from polymer much more easily; therefore nano-sized inorganic particles were usually observed on the top surface of polymer whereas micron-sized inorganic particles were usually partially embedded inside the polymer. As a result of such morphology changes and the intrinsic mechanical properties of inorganic particles, both tensile and compressive properties were improved in such inorganic-polymer composite membranes compared to the pristine membranes. Specifically, the tensile strength can be increased by 47.2% with 1.96 wt% nano-sized alumina whereas the yield compressive strength was enhanced by 55.4% with 76.9 wt% micron-sized alumina in comparison with the pristine polymeric membranes. Besides the improvement of strength, the tensile and compressive Young's modulus was increased and the micron-sized particles are more effective to enhance the Young's modulus than the nano-sized particles. Besides the improvement in mechanical properties, the permeability of polymeric membranes was also enhanced via the inorganic particle incorporation. Therefore, such inorganic-polymer hollow fiber membranes are more promising to be used for practical industrial filtration applications regarding their higher mechanical properties to resist breakage and deformation and their higher permeability in comparison with the polymeric hollow fiber membranes.

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http://dx.doi.org/10.1016/j.matchemphys.2015.10.034

1. Introduction

Membrane separation using hollow fiber membranes has become one of the emerging technologies undergoing a rapid growth in scientific research in recent years [1–3]. Compared to other configurations such as flat sheet membranes, hollow fiber membranes offer a compact, cost-effective solution for filtering large volumes of liquids or gases utilizing minimal space and energy [4–6]. Moreover, the hollow shape makes the membranes more easily maintained and cleaned. In terms of the nature of materials, there are two main types of membranes: polymeric membranes and inorganic membranes. Since their first market arrival in 1960s, polymeric membranes have achieved enormous technological innovation and are the preferred option for many separation processes such as water and wastewater treatment, gas separation, bio-separation, etc. [7–13] Their low cost and ease of fabrication make polymeric membranes superior to inorganic membranes.

In practical industrial applications, hollow fiber membranes are usually bonded together and filled in the module. The flow pattern can be either “inside-to-outside” or “outside to inside” and in most cases, high pressure is needed as the driving force for filtration or cleaning [14,15]. Therefore, as self-supporting hollow fiber membranes, high mechanical properties are required to keep the microstructure and the configuration. However, polymeric hollow fibers are liable to be deformed or broken under high pressure. Each breakage of hollow fibers would significantly reduce the efficiency of separation, and result in extra labour to repair/replace the broken fibers; thus increasing the operating and total costs [16,17].

Low tensile strength is the major reason that polymeric membranes can be easily broken whereas low Young's modulus (both tensile and compressive) is responsible for the deformation of the hollow fiber configuration. Therefore, in order to resist the breakage and deformation under high pressure, the hollow fiber membranes should have high tensile strength and high Young's modulus.

Among all the reported methods of enhancing the mechanical properties of polymeric membranes, the incorporation of inorganic particles into polymers offers an easy, effective and economical solution [18–25]. For example, Arthanareeswaran et al. incorporated 2 wt% silica (SiO_2) particles into the cellulose acetate (CA) polymer membranes and improved the yield stress by approximately 25% and doubled the break elongation ratio [19]. Similarly results were achieved whereas nano-sized alumina was added into polyethylene polymer membranes with 54% improvement in Young's modulus and 78% improvement in yield strength [26]. Nevertheless, in most of these studies, only a small amount of inorganic particles have been added, with the intricate relationship between inorganic particle size and loading and the mechanical properties neglected [27–30]. Moreover, the incorporation of hydrophilic inorganic particles into hydrophobic membranes usually causes changes in solvent–nonsolvent demixing rate during the phase inversion process; as a result, the morphology changes would be expected. However, the relationship between inorganic particle size or loading and the morphology change and its subsequent mechanical properties are seldom discussed in previous studies [31,32]. Therefore, in our study, inorganic/polymer hollow fibers with different particle sizes and particle loadings were synthesized and characterized in terms of morphology and mechanical properties (tensile and compressive properties) to study the effects of particle loading and size on morphology tailoring and mechanical properties, providing valuable design criteria for the development of hollow fiber membranes with high mechanical properties for practical industrial applications.

2. Experimental

2.1. Chemicals

The chemicals were used as received. They include Poly (ether sulfone) (PES, Ultrason E6020P, 51 kDa, BASF, Germany), 1-Methyl-2-pyrrolidone (NMP) (anhydrous, purity $\geq$ 99%, Sigma-Aldrich, Australia), micron-sized alumina powder (d_{50} = 1.2 μm, average particle size is 1.0 μm, PP5010, Shell-lap Supplies Pty Ltd, Australia), nano-sized alumina powder (nanopowder < 50 nm (TEM), Z-average particle size and d_{50} particle size is 115 nm, Sigma-Aldrich, Australia).

2.2. Sample preparation

The pristine and the inorganic/polymer hollow fibers were prepared via the nonsolvent induced phase inversion method at room temperature [33–35]. Specifically, 6 g of PES was dissolved in 34 g of NMP to yield 15 wt% PES solution. And then, a given amount of alumina powder was added into the casting solution and the alumina/PES/NMP solution was then ball-milled for at least 2 days to form a homogenous suspension. The amounts of alumina added in solution are listed in Table 1. After ball-milling, the resulting suspensions were degassed at room temperature to remove air bubble and then extruded through a tube-in-orifice spinneret (outer diameter: 2.6 mm, inner diameter: 1.6 mm) using pressurized nitrogen gas. Double de-ionized (DDI) water was used as inner and outer coagulants and the air gap was set as 4 cm. The obtained hollow fiber precursors were maintained in the outer coagulant for 24 h for a complete solution exchange. Then the prepared hollow fibers were removed and dried at room temperature before use.

2.3. Characterization

2.3.1. Morphology study

The cross-sections of membranes were prepared by fracturing membranes in liquid nitrogen and were examined using scanning

Table 1
The amount of alumina added into the casting solution.

Sample	Alumina (wt%, by the weight of total weight)	Alumina (wt%, by the weight of PES)	Alumina (vol%, by volume of casting solution)
M-1*	6.3	6.7	1.0
M-2	40.0	66.7	9.1
M-3	66.7	200.0	23.9
M-4	76.9	333.3	34.4
M-5	84.2	533.3	45.6
N-1*	2.0	2.00	1.0
N-2	16.7	20.00	9.1
N-3	37.4	58.8	23.9
N-4	50.0	99.8	34.4
N-5	66.6	199.7	45.6

Note: M stands for micron-sized alumina whereas N refers to the nano-sized alumina.