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Enhanced performance of inorganic-polyamide nanocomposite membranes prepared by metal-alkoxide-assisted interfacial polymerization

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ABSTRACT

A promising strategy is reported for the synthesis of inorganic-polyamide nanocomposite membranes on an ultrafiltration polysulfone support via metal-alkoxide-assisted interfacial polymerization. Three types of nanocomposite membranes were prepared using three different metal alkoxides. The metal alkoxides used here were titanium tetraisopropoxide, bis(triethoxysilyl)ethane and phenyltriethoxysilane. The as-prepared nanocomposite membranes exhibited performance superior to that of the pure polyamide membrane. Water flux and salt rejection were observed for each of the nanocomposite membranes. Addition of greater amounts of metal alkoxide to the hexane solution increased both pore size and water flux, which were determined by analysis of the membrane permeation data using aqueous solutions of sodium chloride and organic solutes at a pressure of 1.5 MPa and a temperature of 25 °C. The best nanocomposite membrane that was prepared with phenyltriethoxysilane showed water flux that was increased approximately 2-fold compared with the pure polyamide membrane with negligible rejection loss.

1. Introduction

Globally, inadequate water availability and lack of access to fresh water are two of the most significant problems. Membrane-based water purification processes are low-cost, energy efficient and environmentally friendly. Reverse osmosis (RO) is an important commercially available membrane technology that is widely used for water purification processes such as desalination and industrial water reuse [1]. However, the currently available polymeric membranes are often limited by the trade-off between permeance/permeability and selectivity [2–5]. RO membranes with higher water permeability, improved rejection and better fouling resistance are needed to reduce both the capital and energy costs of producing a highly purified product.

Subsequent to the development of polymeric RO membranes, the design of multilayered thin film composites (TFCs) was an important advancement in membrane science. TFCs are composed of an outer ultra-thin skin polyamide layer (0.1–1 μm) fabricated via interfacial polymerization (IP) of m-phenylene diamine in an aqueous phase and trimesoyl chloride in an organic phase, a porous middle polysulfone support, and a non-woven polyester fabric base [6–11]. These membranes have been widely used in water desalination [12,13]. Continual efforts have been devoted to the innovation of porous supports, polymer reactants and membrane structures [14–17] that improve either the membrane permeance/permeability or selectivity for specific applications or that increase the fouling resistant and chemical/thermal/mechanical stability of membranes [18–22]. For example, polyamide membranes with enhanced water flux and reasonable salt rejection have been prepared by addition of alcohols, sulfur-containing compounds or monohydric aromatic compounds in an aqueous solution and not in an organic phase [23–25]. The efficacy of this strategy has been ascribed to reductions in both the solubility difference and the interfacial tension and to facilitate mass transfer of diamine molecules to the organic phase, which increased the membrane surface roughness [26]. In addition, the additives might have increased the fractional free volume of the prepared membrane, thereby increasing water permeability. On the other hand, a limited number of studies have attempted to control membrane performance by using different types of solvents in the organic phase [27]. Although these methods have their advantages, they are far from satisfactory because membrane performance needs additional improvement.

Organic–inorganic polymer membranes that can improve separation, reaction and sorption capacity, as well as enhance chemical and thermal stability, have attracted considerable interest.

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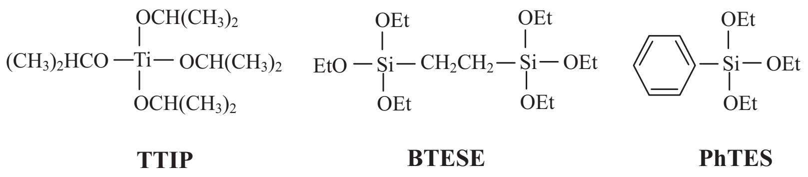

Fig. 1. Chemical structures of titanium tetraisopropoxide (TTIP), bis (triethoxysilyl) ethane (BTESE) and phenyltriethoxysilane (PhTES); (OEt) ethoxy group.

Recently, zeolite NaA, silica and TiO_2 nanoparticles were rationally incorporated into the polyamide layer, which enhanced membrane permeability compared with that of a pure polyamide membrane [28–31]. The incorporated nanoparticles might have provided a direct path for water transport or modified the membrane network structure, thereby increasing water permeability. Although this innovative concept has drawn a great deal of attention, there remain difficulties associated with implementation of this strategy: dispersion of nanoparticles in a nonpolar organic solvent and control of nanoparticles within a thin polymer layer. Nanoparticles readily aggregate when mixed with a nonpolar solvent. On the other hand, metal alkoxides readily dissolve in an organic solvent (hexane). Therefore, fabrication of inorganic-polyamide nanocomposite membranes by the addition of a metal alkoxide to the hexane phase prior to interfacial IP is possible. The performance of the resultant membranes might be superior to that of membranes fabricated from nanoparticles because the metal alkoxide, which is more thoroughly dispersed in the hexane phase, can be hydrolyzed and produce smaller inorganic nanoparticles and an organic alcohol either during or after IP. Previous reports indicate that this process is useful for high-performance-membrane formation.

Herein, we report a promising strategy for the fabrication of inorganic-polyamide nanocomposite membranes using three types of metal alkoxides (Fig. 1). Small particles or silica networks can be produced after hydrolysis reaction, dehydrolysis reaction or condensation reaction, which may control the network pore-size of the resultant membranes. The primary objective of this work was to prepare nanocomposite membranes with enhanced performance in terms of either membrane permeance or selectivity. The inorganic-polyamide composite membranes were examined using thermo-gravimetric analysis (TGA). The surface morphology of the as-prepared membranes was observed using scanning electron microscopy (SEM). The structure of a membrane cross-section was examined using transmission electron microscopy (TEM). These characteristics were then compared with the membrane permeability properties that were measured using permeation equipment and aqueous solutions containing either an inorganic salt or organic solutes at a temperature of 25 °C and a pressure of 1.5 MPa.

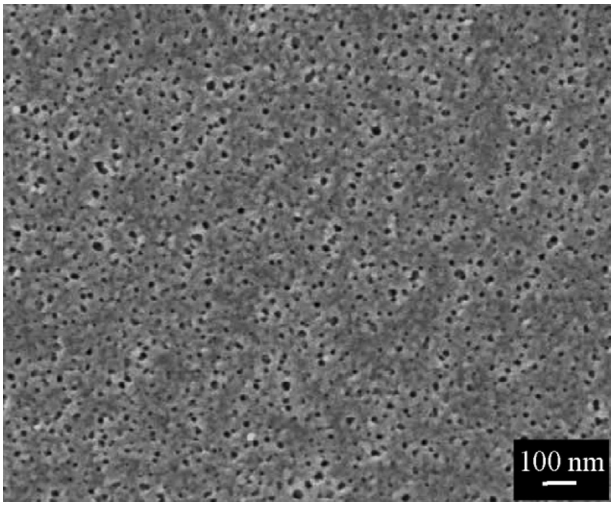

Fig. 2. SEM image of the ultrafiltration polysulfone membrane used as the nanocomposite membrane support.

2. Experimental

2.1. Materials

The chemicals, 1,3,5-benzenetricarbonyl trichloride (TMC, Aldrich), titanium tetra isopropoxide (TTIP, Aldrich), 1,3-phenylenediamine (MPD, Aldrich), bis (triethoxy silyl) ethane (BTESE, Aldrich), phenyl triethoxy silane (PhTES, Aldrich), were used without further purification. All other chemicals were analytical grade. Ultrafiltration polysulfone (PSF) membranes were used as the support. The SEM image (Fig. 2) shows that the pore size distribution of the PSF support was less than 30 nm.

2.2. Synthesis of the nanocomposite membrane

Each of the pure polyamide membranes and the inorganic-polyamide nanocomposite membranes was hand-cast on a PSF support by polymerization of the aromatic MPD with the acid chloride TMC. The inorganic-polyamide nanocomposite membranes were prepared using a novel metal-alkoxide-assisted interfacial polymerization method. The detailed process was as follows. First, an aqueous solution of 2 wt% MPD and 0.15 wt% sodium lauryl sulfate was allowed to cover the top of the PSF support for 2 min. The excess solution was then drained from the support surface, which was blotted with pieces of filter paper at room temperature. Solutions of TMC (0.1 wt%) in hexane containing a metal alkoxide at concentrations ranging from 0 to 5 wt% were poured onto the PSF support. After a predetermined polymerization period, the organic solution was drained off. The as-prepared membrane was dried in air at room temperature for 3–5 min to remove excess organic

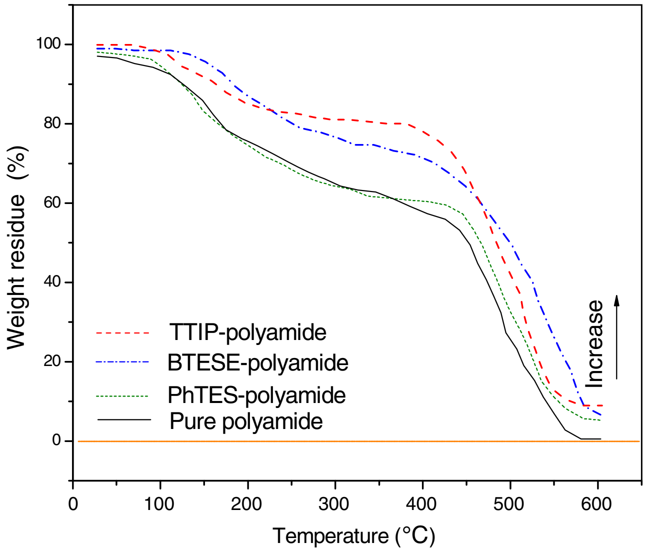

Fig. 3. TGA curves of the pure polyamide membrane and the nanocomposite membranes prepared using the metal-alkoxide-assisted IP method. The content of metal-alkoxide was 1 wt% for all nanocomposite membranes.