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Properties–performance of thin film composites membrane: study on trimesoyl chloride content and polymerization time

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Abstract

The characteristics of polyamide membranes with respect to interfacial polymerization of diamine mixtures with trimesoyl chloride (TMC) are investigated. This study provides the information about the effect of TMC content and reaction time on membrane properties like pore size, effective thickness/porosity and charge density. The membrane properties were determined based on the charged and uncharged solute permeation test and the hypothetical mechanistic structure (pore size, effective thickness/porosity, fixed charged density) was determined using Donnan steric pore flow model (DSPM). It was found that the membrane pore size was reduced at higher TMC content whereas the effective thickness/porosity shows a minimum value at 0.10% TMC content. Besides, the membrane effective charge density achieved its highest absolute value at 0.10% TMC content. The TMC content and reaction time could be optimized for $CuSO_4$ removal. It was concluded from the experimental results that the optimum rejection of $CuSO_4$ could be achieved at low reaction time (5 s) with TMC content around 0.10%. At this optimum condition, the rejection of $CuSO_4$ was more than 95% without compensating for the flux loss.

Keywords: Trimesoyl chloride; Reaction time; Thin film composite; Polyamide; Nanofiltration

1. Introduction

The composition and morphology of composite membranes prepared by interfacial polymerization (IP) method depends on several variables, such as concentration of reactants, partition coefficients of the reactants, reactivity ratios where blends of reactants are employed, solubility of nascent polymer in the solvent phase, the overall kinetics and diffusion rates of the reactants, presence of by products, hydrolysis, cross-linking and post-treatment [1].

Research works had been carried out to find out the optimum conditions to produce optimized and high performance membrane. Basically, the works could be categorized into three areas, which included preparation condition, material selection and kinetic control. Numerous studies have been carried out to find out the effect of preparation condition on membrane performance. These parameters did play an important role in determining the structure of the interfacially polymerized film and subsequently the membrane performance. Rao et al. [2] found a method using attenuated total reflectance infrared (ATR-IR) spectroscopy to study the structural–performance correlation of polyamide thin film composite membranes. They found out that the critical parameters for thin film coating were reaction time, relative humidity and coating temperature. The membrane flux could be improved by optimizing the time of contact between the discriminating layer, the temperature of contact and the pH of the amine solution [3].

In terms of material selection, it was believed that several factors could influence the polyamide film thickness, such as monomer size, solubility, shape and reactivity [4]. Mickols, for example patented the works on flux enhancement by varying the type of amine employed [3]. Moreover, Chen et al. [5] found that wetting agent, monomer concentration as well as swelling agent played a great impact on membrane properties.

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In the case of reaction kinetic control, Lu et al. [6] pointed out that, the key of the IP method was to select the right partition coefficient of the reactants in the two-phase solution and to set the appropriate diffusion speed of the reactants to achieve the ideal degree of densification of the membrane surface. Moreover, the concentration of the diamine is an important factor, which can affect the performance of the resulting composite, since it may control the uniformity and thickness of the ultimate polyamide support on the substrate. If the coating is non-uniform, it can lead to develop small holes, which may adversely affect salt rejection property of the membrane [7]. Since the IP process is diffusion controlled in the organic layer [8], the effect of organic phase reactant is likely to have a great impact on membrane performance.

In the discovery by Cadotte and Rozelle of the NS-100 membrane at Northstar Research Institute, several monomeric amines had been tried as well as piperazine [9]. High rejection composite membranes could be made by interfacial reaction of piperazine with isophthaloyl chloride. Conditions necessary for obtaining good composite membranes of poly(piperazineamide) included concentrations of 1–2% piperazine, use of an acid acceptor and use of a surfactant in the amine recipe [10]. From 1978 to 1988, an intensive research has been carried out to modify the membrane flux and salt rejection with variety of acid acceptor and replacement of a portion of the isophthaloyl chloride with trimesoyl chloride. It was found that the maximum water flux was obtained at roughly 50:50 (w/w) diacyl:triacyl chloride content. The membrane produced could reject 99.9% $MgSO_4$ and 64% NaCl at the flux of 96 gfd (salt flux) under 1500 psig operating pressure and 3.5% synthetic wastewater [11]. NF-40, NTR-7250, UTC-20 and UTC-60 are some of the membranes developed based on the poly(piperazineamide) technology.

In this paper, the effect of TMC on the membrane properties was studied based on the piperazine/3,5-diaminobenzoic acid (PIP/BA) system. It was expected that by incorporating the BA into the membrane poly(piperazineamide) backbone, the membrane will be more hydrophilic due to the carboxylic group of benzoic acid. Subsequently, the hydrophilic nature of the membrane would enhance the membrane performance in terms of water flux. The membrane prepared under different PIP/BA ratio has been studied in our previous paper [12], it was found that the diamine content with 0.05% BA was proved to improve the membrane in terms of flux. However, the excessive incorporation of BA into the membrane skin layer will reduce its flux as well as rejection. In the case of nanofiltration membrane or membrane with higher porosity compared to reverse osmosis, it was speculated that the TMC content has an high impact on the rate and degree of reaction which eventually affect the final performance of the membrane. The relationship between PIP/BA and TMC system were studied throughout this paper and its performance in terms of flux and rejection were evaluated.

2. Experimental

2.1. *Preparation of microporous polysulfone support membrane*

The polysulfone support was prepared by dissolving 15% Udel P-1700 polysulfone (supplied by Solvay Advanced Polymers, L.L.C.) in *N*-methylpyrrolidone (NMP, Fluka) with 18% polyvinylpyrrolidone (PVP-10, Sigma) as the pore-former. The solution was cast onto a tightly woven polyester fabric with a nominal thickness of 100 μm using a lab-developed auto-casting machine. The entire casting machine was kept in an air-conditioned room and the temperature was maintained between 24 and 26 °C with a relative humidity of 59–61% during the casting process. After coating, the membrane was immersed into water bath for at least 24 h until most of the solvent and water-soluble polymer was removed [13].

2.2. *Fabrication of thin film composite membranes*

The support layer, which was taped onto a glass plate, was immediately dipped into an aqueous diamine solution containing 1.95% (w/w) piperazine (PIP, Merck) and 0.05% (w/w) 3,5-diaminobenzoic acid (BA, Merck) for 5 min at ambient temperature. The excess solution from the impregnated membrane surface was removed using a rubber roller. The membrane was then dipped into *n*-hexane solution containing 0.05–0.20% (w/v) trimesoyl chloride (TMC, Fluka) for predetermined time of 5, 10 and 30 s, which resulted in in situ formation of active skin layer over the surface of the polysulfone support.

2.3. *Morphology checking*

Membrane morphology was examined under Variable Pressure Field Emissions Scanning Electron Microscope, VP FESEM (Leo Supra 50VP, German). The membranes were prepared under different TMC content of 0.05, 0.10, 0.15 and 0.20% (w/v) with reaction times of 5 s. The membranes were fractured cryogenically in liquid nitrogen, gold coated and the cross-sectional view was observed under 10,000× magnification.

2.4. *Analytical technique for bonding confirmation*

Bonding confirmation of the membrane active layer was carried out using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy instrument (Perkin-Elmer Series II) with a ATR accessory fixed at the angle of 45°, which caused a 5 μm depth penetration of the IR beam into the surface of the membrane.

2.5. *Membrane performance test*

The membrane permeation test was carried out using the Amicon 8200 stirred cell (Amicon, Inc.) at five different pres-