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ACCEPTED MANUSCRIPT

The performance of integrally skinned polyetherimide asymmetric nanofiltration membranes with organic solvents

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Abstract

Nanofiltration (NF) has become an emerging technology in organic solvent systems and the preparation of organic solvent resistant nanofiltration (SRNF) membranes is the most important aspect of the technology. In this study, integrally skinned polyetherimide (PEI) asymmetric nanofiltration (NF) membranes were prepared by phase inversion in which dimethylacetamide (DMAc) and polyvinyl pyrrolidone (PVP-K30) were employed as solvents and additives in casting solutions. The prepared PEI membranes were characterized by scanning electronic microscopy (SEM) and evaluated in terms of solvent compatibility, solute rejection and solvent flux. The solvents employed were ethanol, isopropyl alcohol, n-hexane and carbon tetrachloride and the solute molecules were rose bengal (molecular weight 1017 Da) and methylene blue (molecular weight 374 Da). The prepared PEI NF membrane was compared with four commercial SRNF composite membranes (MPF-34, MPF-44, STARMEM 122 and Solsep 010706). The results demonstrated that the PEI membranes were stable in all of the four solvents studied and showed better performance than the four commercial SRNF membranes with regard to solvent compatibility and rejection from ethanol solutions. The PEI membrane had ethanol fluxes of 4-8 L m⁻² hr⁻¹ at 100 psi and 95% rejection for methylene blue in ethanol.

Keywords: Solvent resistant nanofiltration; polyetherimide; polyvinyl pyrrolidone; solvent stability; phase inversion

1. Introduction

Nanofiltration (NF) has been intensively applied as a competitive technology against conventional separation and purification processes, such as distillation and evaporation in organic solvent systems [1]. The availability of solvent resistant nanofiltration (SRNF) membranes is limited and many polymeric materials have been used for preparation of SRNF membranes, including polyimide [1-7], polysulfone [8], polyether sulfone [8, 9] and polyvinylidene fluoride [10]. Most of SRNF membranes are a thin-film composite (TFC), which consists of a supporting layer and an active toplayer and is generally prepared via dip-coating or by interfacial polymerization on the porous support-layer. In general, the TFC NF membranes tend to lose their integrity due to different swelling and degradation rates of the polymeric materials when they are exposed in organic solvents in a long-term application[1, 10-15]. Similarly, integrally asymmetric membranes consist of a dense thin active separation layer and porous supporting layer. Both layers are made of the same polymeric material using a single casting step via phase inversion [8, 10, 17] and a wide variety of polymers has been investigated for different applications. Integrally skinned asymmetric membranes are advantageous in solvent compatibility as compared to the TFC membranes [10, 16]. Of the polymers investigated, polyetherimide (PEI) is a high performance polymer material in which the aromatic imide units offer good mechanic strength, thermal stability and chemical resistance and the ether linkages provide enhanced flexibility. PEI asymmetric membranes prepared by phase inversion have been investigated for gas separation [18, 19] and aqueous nanofiltration applications [20, 21].

Kim and Lee [22] prepared asymmetric PEI nanofiltration membranes using Ultem® 1000 (a trademark of commercial PEI polymer), N-methyl-2-pyrrolidone (NMP) as solvent and poly(ethylene glycol) (PEG) 200 as additive by phase inversion for water-ethanol permeation and found that ethanol swell the PEI matrix material thus decreasing membrane pore size. Hying and Staude [23] reported PEI membranes prepared by phase inversion using dimethylacetamide (DMAc) as solvent and polyvinyl pyrrolidone (PVP) as additive for pervaporation separation of toluene/methane mixtures. They found that their PEI asymmetric membranes had good compatibility with toluene and that the separation of toluene and methane was enhanced by the addition of PVP. Pervaporation (PV) studies have also demonstrated good membrane compatibility of PEI asymmetric membranes with ethanol [2, 3, 22, 24-26] and ethyl acetate [27]. SRNF and PV have similarities in transport mechanisms (solution-diffusion) and the membranes are sometimes interchangeable between the two processes [28-30]. Soroko et al. [7] prepared integrally skinned asymmetric SRNF membranes by phase inversion using PEI (Ultem 1000) and polyimide (PI) polymers (P84, HT P84 and Matrimid 5218) and DMF solvent and 1,4-dioxane additive for organic solvent nanofiltration. They found that the PEI-based asymmetric membrane was not attractive in the filtration of styrene oligomers (molecular weight < 800 Da) from N,N-dimethylformamide (DMF) solutions (poor rejection and very low solvent flux). Nevertheless, it is still of great interest to develop integrally skinned

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