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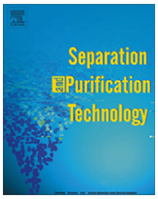

# Development of a novel thin film composite membrane by interfacial polymerization on polyetherimide/modified $SiO_2$ support for organic solvent nanofiltration

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ABSTRACT

In this study, nano thin-film composite (n-TFC) membrane was prepared via the interfacial polymerization for organic solvent nanofiltration (OSN) process. Polyetherimide (PEI)/amino-functionalized silica nanocomposite membrane was used as support layer to fabricate n-TFC membrane. In order to obtain the stable support, nanocomposite membranes with different amount of modified silica (0–20 wt.%) were prepared. The resultant membranes were characterized by scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), swelling test and tensile strength techniques. Results showed that mechanical and chemical stability attained their maximum when silica content was 5%. The solvent resistant n-TFC membranes were prepared using interfacial polymerization with m-phenylenediamine (MPD) and trimesoyl chloride (TMC) on the nanocomposite support. The prepared polyamide/modified PEI nanocomposite membrane was used in a selected OSN. A mixture containing dewaxed oil ($Mw \approx 560$ g/mol) and dewaxing solvent (toluene and methyl ethyl ketone) was selected to investigate the separation performance of n-TFC membranes. The oil rejection of 94.72% and permeation flux of 10.4 $L/m^2$ h (at 15 bar) were achieved which suggest that newly prepared n-TFC membrane has potential in application of the dewaxing solvent separation from the dewaxed lube oil. Pressure dependency of the oil rejection, permeate flux and MEK to toluene mass ratio in permeate of the n-TFC membranes were studied in the pressure range of 10–20 bar. The results revealed that the bulk modification has great effect on chemical stability of prepared membrane even at high pressure.

## 1. Introduction

Nanofiltration (NF) processes has recently attracted great attention due to its advantages. This process is used in both aqueous and organic media to replace the traditional separation methods such as distillation or extraction. NF of the aqueous solution was developed more rapidly and widely used in industry, whereas, by contrast, OSN is still under development due to the lack of proper solvent resistant NF membranes [1,2]. From the early twentieth century, OSN has attracted a lot of growing interest due to its promising energy saving, lower solvent waste, scale up simplicity, etc. OSN has potential applications in various areas, such as the food, petrochemical and pharmaceutical processes [2–5]. In this process, the most important challenge for researchers is the preparation of solvent resistant membrane with appropriate performance. The selection of membrane material is critical step to achieve aforementioned objective. inorganic membranes have superior properties in terms of physical and chemical stability. Although several studies were reported about application of ceramic membranes for OSN processes [6–9] but they are much less widespread than polymeric one due to high cost, brittleness and difficulty to handle [10]. In contrast, polymeric membranes have less stability in harsh chemical environments as compared to inorganic membranes. However, the polymeric membrane advantages such as selectivity, low cost and flexibility in applications make polymeric membranes relevant.

The OSN polymeric membranes generally have been developed are integrally skinned asymmetric membranes up to now [11–19]. The asymmetric OSN membranes usually are facing some troubles such as low permeate flux of some non-polar and polar aprotic solvents [20]. To overcome this limitation, recently, thin film composite (TFC) membranes have been recommended. In a TFC membrane, each layer can be chosen independently from a vast variety of polymers with different chemical structures. Therefore, individual properties of thin selective layer such as the hydrophilicity and chemical resistance can be adjusted apart from support layer. Although, composite membranes including rubbery polymer

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(i.e. PDMS) on UF support were prepared [21–23], the use of polymers like polyamide as the selective layer of organic solvent resistant TFC membranes are less studied in the literature [20,24–26].

The support membranes which are used to prepare polymeric solvent resistant TFC membranes should be stable in organic solvents. As presented in literature, suitable support membrane may be obtained from polymer material including: poly ether ether ketone [26], polypropylene (PP) [25], crosslinked polyacrilonitrile [22–24,27], crosslinked polyimide [20,21,26,28], and crosslinked polyetherimide [28]. Among these polymers, PEI has good film forming properties, high mechanical and thermal stability, commercial availability, and fairly low cost which make it probable candidate in the fabrication of UF, NF, and gas separation membranes [29,30]. Although economical superiority of PEI is violated by PP, the relatively hard preparation process (melting, or solving at high temperature to prepare casting solution) make PP as improper choice when compared with PEI.

Anyhow, the use of pure polyetherimide (PEI) membrane for OSN applications has been limited due to its poor stability in some organic solvents [28]. Generally, chemical crosslinking, thermal annealing and UV crosslinking can increase chemical stability of OSN membranes. However, by crosslinking it is also possible to overcome plasticization of gas separation membranes or increase hydrophilicity of membranes used for aqueous system [31]. In the case of PEI, chemical crosslinking has been proposed to increase the chemical stability of PEI in harsh solvents, [23]. Diamine crosslinkers like hexandiamine, ethylenediamine and para-xylylenediamne are common crosslinkers which are used to react with the aromatic imide groups of PEI. Moreover, other methods like bulk modification can be applied to modify this polymeric membrane. Based on this method, polymer is blended with the modified material to result strong bounds between polymer chains [32,33].

To the best of our knowledge, the preparation of TFC membrane including modified PEI support membrane and its application for OSN is not investigated previously. Also the effect of modified silica on the chemical stability of PEI support membrane was not studied to date.

In the present work, fumed silica nanoparticles were functionalized via aminopropyldiethoxymethylsilane (APDEMS) and the amino-functionalized silica nanoparticles were blended with PEI to prepare solvent resistant support membrane. To obtain the optimal loading of nanoparticles, nanocomposite supports with different amount of modified silica were prepared and then were characterized by applying morphological, mechanical, thermal and chemical tests. A polyamide thin film as selective layer was coated on the optimal nanocomposite support through interfacial polymerization. The resultant membrane was termed nano thin-film composite (n-TFC) to distinguish it from TFC membrane prepared on pure PEI support [34]. The performance of prepared solvent resistant nanofiltration n-TFC membrane was investigated through the separation of dewaxing solvents from lube oil filtrates. Among the conducted studies on the dewaxing solvent recovery through organic solvent nanofiltration, study presented by White and Nitsch [13] demonstrated the best separation performance result. This work led to preparation of commercial spiral wound PI membrane which is used to recover dewaxing solvent at the ExxonMobil refinery in Beaumont (Texas). However, Kong et al. [17] claimed that their prepared OSN membrane, based on the PI 2,2-bis(2,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) is competitive with the commercial PI membrane. Since the lube oil viscosity, lube oil concentration, operating pressure and temperature affect the permeate flux and oil rejection, here, we tried to compare our result with the Kong et al. study because of similar operating condition. Additionally, the effect of pressure on the separation properties of n-TFC membrane was studied.

## 2. Materials and methods

### 2.1. Chemicals

A commercially available PEI, trimesoyl chloride (TMC) 98%, and m-phenylenediamine (MPD) 99% were purchased from Sigma–Aldrich. Hydrophilic fumed silica nanoparticles (Aerosil 380) with 14 nm average particle size were provided by Degussa. N-Methyl-2-Pyrrolidone (NMP) and n-Hexane with analytical grade were supplied by Merck. APDEMS also from Sigma–Aldrich was used as silane coupling agent.

### 2.2. Silica functionalization

APDEMS was used to functionalize silica nanoparticles according to Fig. 1. In this procedure, silica nanoparticles (1 g) were added to the mixture of APDEMS (8 mL) + toluene (200 mL) and stirred for 24 h at room temperature. The functionalized silica nanoparticles were subsequently removed from the mixture by filtration and rinsed with 250 mL toluene to remove the unreacted aminosilane coupling agent. Finally, the modified silica was dried for 1 h at 110 °C.

### 2.3. Preparation of the nanocomposite support layer

Asymmetric PEI/modified $SiO_2$ nanocomposite membrane were fabricated via phase inversion induced by immersion precipitation [35].

Firstly, amino-functionalized nanoparticles at loading of 0, 5, 10, 15, and 20 wt.% (based on the ratio of $SiO_2$ weight to weight of PEI) were added to NMP and stirred for 2 h. Then solutions were placed in ultrasonic bath and sonicated for 60 min to ensure an adequate dispersion of the nanoparticles. PEI was gradually added to the above mixtures to attain desired polymer concentration (20 wt.%) and stirred for 24 h. This technique can create the crosslinking between polymer chains and also minimizes agglomeration of nanoparticles and defective inorganic–organic interface [36].

The homogeneous solutions were cast on (i) a glass plate for characterization and (ii) non-woven polyester for permeation test, using adjustable casting bar (Neurtek2281205) with a thickness of 250 μm and then allowed to be in atmosphere for 15 s for solvent evaporation. The formed films were immersed into a water coagulation bath for 1 day to ensure an adequate solvent–nonsolvent ex-

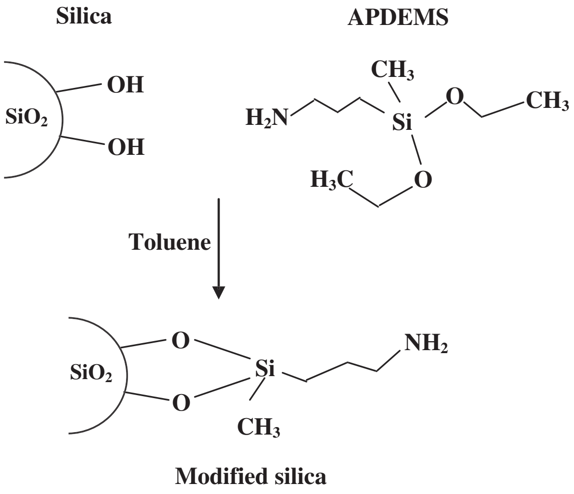

**Fig. 1.** Schematic of amino-functionalization of nanosilica using a silane coupling agent (APDEMS).