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## Mixed matrix membranes for organic solvent nanofiltration



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## ABSTRACT

Polyimide (PI) (P84) based organic solvent nanofiltration (OSN) membranes are well documented in the literature. One drawback of P84 based OSN membranes is the decline in the flux performance over time and with pressure. This is attributed to the compaction of the membrane top layer. The present work introduces novel P84 based OSN membranes which overcome the problem of compaction by incorporating an organic–inorganic hybrid network within the membrane matrix. The inorganic network also acts as a crosslinking agent for the polyimide. 3-Aminopropyl trimethoxysilane (APTMS) was used as a crosslinking agent as well as an organosilicone precursor to generate an inorganic network. An inorganic organosiloxane network (Si–O–Si) was generated in the membrane by hydrolysis and condensation of methoxysilane in APTMS. The impact of APTMS on the resulting PI membranes was investigated using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), water contact angle and energy diffracted X-ray (EDX). FTIR analysis confirmed the presence of the Si–O–Si network in the membrane and EDX analysis confirmed the homogeneous distribution of this network throughout the membrane including in the thin separation layer. Nanofiltration performance of these membranes was evaluated in solvents such as acetone, dimethylformamide (DMF) and dichloromethane (DCM). Flux profiles showed a great improvement in terms of resistance to compaction after treating with this organic–inorganic based crosslinker, although the inorganic network reduced the flux. After treatment with APTMS, membranes increased in rigidity and strength, and there was no swelling even in high swelling solvents such as DCM. Addition of maleic acid to the dope solution provided an improvement in the flux of the crosslinked membrane. The flux could be also manipulated by varying the crosslinking conditions. Nanofiltration (NF) performance of the mixed matrix membrane (MMM) was compared with the commercially available membrane Duramem™300 in different solvents, and was found to be more resistant to compaction but with lower flux as compared to Duramem™. The performance of MMM was also compared with Duramem™200 for a case study of active pharmaceutical ingredient (API) purification.

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## 1. Introduction

In spite of the fast development in OSN technology in the last decade there is still a very limited number of industrial applications in this field [1–7]. Several polymeric and ceramic membranes are already commercialised in the field of OSN [2,3], however they struggle to comply with the main requirements for membrane based processes such as stability, high flux and good separation properties [5]. Other important parameters are durability in certain environments, handleability and ease in scaling up [5].

Polymeric membranes have the advantages of being inexpensive materials for fabrication and easy scale up [8–11]. They have gained popularity due to their potential in a wide range of

applications, but the disadvantages include flux decline over time (often attributed to membrane compaction) and the need for preserving agents, especially in integrally skinned asymmetric membranes. Furthermore, polymeric membranes show relatively low thermal and chemical stability [1–3,5,7]. Ceramic membranes typically show more stable flux performance (not susceptible to compaction), good mechanical strength, high tolerance at extreme conditions and are more resistant to organic solvents but suffer the disadvantages of brittleness and difficulty in scaling up [12]. Consequently, the use of combined organic/inorganic (mixed matrix) membranes is an attractive and logical further strategy [13]. It can combine the advantages of polymeric and ceramic membranes, and may offer a solution to some of the problems faced by OSN technology. A simple way of making these MMMs is the incorporation of inorganic materials in polymeric membranes.

The polymer and inorganic phases could be connected via covalent bonds, van der Waals forces or hydrogen bonds thus producing membranes with different chemistries. MMMs can

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further be prepared in three different ways by dispersing the inorganic filler in the polymer solution, through in-situ polymerisation or through the sol-gel method [15–21]. A reactive group attached to the inorganic material is required to get the inorganic phase covalently bound to the polymer.

Kim et al. [22] reviewed the use of nanoparticles in polymeric membranes. Commonly used fillers for polymeric membranes are titanium dioxide (TiO<sub>2</sub>), nanoalumina, silica, silver, zeolites and carbon nanotubes [17–22]. Polymeric and inorganic phases in membranes provide a mutually positive influence on the membrane performance [17–21]. To obtain polymeric membranes with TiO<sub>2</sub>, different approaches were adopted by different authors. The simplest approach adopted by researchers was the addition of TiO<sub>2</sub> in dope solution [17–20].

Nano-sized alumina was also used in the preparation of MMMs and it was concluded by the authors that membrane rejection performance remained unchanged after the addition of 10 nm sized alumina while the mechanical strength increased dramatically [23–25].

Addition of silica nanoparticles has also been studied by various authors, but not to a large extent [26–28]. It was observed that after the addition of 3 nm sized silica particles in TFC membranes, the number of pores in the top layer increased and pore size was also changed [28].

In addition to nanoparticles, well-defined nanostructures found in zeolites and nanotubes have also been used as fillers to enhance membrane properties. Based on these studies it was concluded that MMMs with zeolite additions were smooth and have a more hydrophilic, negatively charged surface as compared to original membrane [29–31].

Vandezande et al. [32] prepared asymmetric nano-sized zeolite-filled PI membranes through solidification of emulsified polymer solution via phase inversion. Their observation was that by adding more organic nano-zeolite suspension to the casting solution, a morphological change from a finger-like to a sponge-like structure was obtained within the membrane. Micro-sized, spherical pores made the membrane more resistant to compaction. However, these technologies have only been tested on a lab scale and more work is required to scale up the membranes for use in industrial applications.

The most widely used OSN polymeric membranes are prepared from polyimide (PI) which is an excellent membrane material due to its high chemical and thermal stability [12,14,33]. Further stabilisation of the PI membranes can also be achieved by chemical crosslinking of the polymer matrix [33–39]. Chemical crosslinking using diamines is then the most commonly used procedure reported in literature [34,39,40]. Toh et al. [41] studied the effect of crosslinking on the stability of PI membranes in polar aprotic solvents by using aliphatic diamines as the crosslinking agent. The crosslinked membranes were stable in polar aprotic solvents, but the flux was lower in comparison with non-crosslinked membranes of the same composition. A comparison was also made between diamines of different chain lengths, and it was concluded that the membranes crosslinked with a shorter diamine showed less of a decrease in flux [40,41].

Studies also indicate that the use of polyfunctional crosslinkers can result in organic and inorganic fragments. Rzaev et al. [42] studied the crosslinking of anhydride containing copolymer with  $\gamma$ -aminopropyltrimethoxysilane (APTMS). The results demonstrated that anhydride containing binary and ternary copolymers easily undergo crosslinking with polyfunctional APTMS through anhydride unit-amine groups-ethoxysilyl groups intermolecular reactions with the formation of hyperbranched network structure containing amide and siloxane crosslinked fragments.

Nunes et al. [43] prepared a composite membrane with highly dispersed silica in a polyetherimide (PEI) matrix by in-situ

hydrolysis and condensation of tetraethoxysilane (TEOS). A small amount of APTMS was used to generate a well distributed inorganic network at nano-scale level due to the interaction of amine in APTMS with the imide of the PEI matrix. After the incorporation of inorganic material in the polymer dope solution Nunes et al. reported a change in the structure of the membrane from finger-like to sponge-like as well as a better flux performance under pressure. However, incorporation of inorganic materials in polymeric membranes usually results in a decrease in flux. Another problem with this technique is the limitation of the amount and nature of inorganic material used in making the polymer dope solution. Normally solubility issues and non-homogeneity is observed with a higher percentage of inorganic materials in the dope solutions. Additionally, gelation can occur in polymer solutions with the addition of reactive inorganic material to achieve homogeneity [43].

Another way of manipulating the properties of polymeric membranes is by adding low molecular weight additives into the dope solution [1]. The effect of additive maleic acid has been studied for polymeric membranes. An increase in flux and decrease in rejection were reported with an increasing concentration of maleic acid. Bokhorst et al. [44] studied the effect of maleic acid and coagulation bath temperature on the morphology and performance of cellulose acetate membranes. They concluded that with an increasing concentration of maleic acid, the number of pores in the sub-layer increased, while the pore size decreased. With an increase in the concentration of maleic acid, gelation occurred at lower polymer concentration in the top layer of the membrane, making the skin layer less compact. Vasarhelyi et al. [45] also studied the effect of additives on cellulose acetate and cellulose triacetate blends, and concluded that flux is highly dependent on maleic acid concentration though the changes in rejection remain small. The influence of maleic acid on demixing behaviour and membrane structure was also discussed in this study. Maleic acid delays 1-1 demixing and enhances aggregate formation during the phase inversion process. Ronner et al. [46] reported a tendency of maleic acid additions to cause nodule formation resulting in an intermediate layer with increased porosity. There is no extensive study on the effect of maleic acid on the PI NF membranes [47]. Beerlage used a number of dicarboxylic acids (including maleic acid) as additives in PI/dimethylformamide solutions for the preparation of ultrafiltration membranes. It was found that some of the dicarboxylic acids reduce the number of pores in the top layer and suppress the formation of macrovoids. When maleic acid was used as an additive most studies showed a decrease in macrovoids formation which was attributed to reduced polymer chain mobility due to the formation of hydrogen bonds with the acid [47]. Soroko et al. [48] worked on chemically crosslinked PI mixed matrix nanofiltration membranes by dispersing TiO<sub>2</sub> nanoparticles in the polymer dope solution. Authors observed a change in morphology for membranes containing TiO<sub>2</sub> as compared to the membrane without addition of nanoparticles. Macrovoid formation was suppressed by the addition of TiO<sub>2</sub> particles and completely disappeared at higher loadings of particles. Compaction resistance of the membrane was observed to improve without affecting flux and rejection.

A three step process is normally adopted in the preparation of solvent stable PI membranes - membrane preparation via phase inversion, crosslinking with amine and post-treatment with a conditioning agent [49]. The conditioning agent is required to avoid membrane pore collapse upon drying, brittleness, and to ensure ease in handleability during membrane modules manufacturing. Previous studies [43] suggest that generation of an inorganic network in a membrane provides stability to the membrane pores while pore collapse upon drying can be avoided.

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