

## Reactive phase inversion for manufacture of asymmetric poly (ether imide sulfone) membranes



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### ABSTRACT

Poly (ether imide sulfone) membranes were manufactured by combining phase inversion and functionalization reaction between epoxy groups and amine modified polyether oligomers (Jeffamine) or TiO<sub>2</sub> nanoparticles. Polysilsesquioxanes containing epoxy functionalities were *in-situ* grown in the casting solution and made available for further reaction with amines in the coagulation/annealing baths. The membranes were characterized by field emission scanning electron microscopy, porosimetry and water flux measurements. Water permeances up to 1500 l m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> were obtained with sharp pore size distribution and a pore diameter peak at 66 nm, confirmed by porosimetry, which allowed 99.2% rejection of  $\gamma$ -globulin. Water flux recovery of 77.5% was achieved after filtration with proteins. The membranes were stable in 50:50 dimethylformamide/water, 50:50 N-methyl pyrrolidone/water and 100% tetrahydrofuran. The possibility of using similar concept for homogeneous and stable attachment of nanoparticles on the membrane surface was demonstrated.

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## 1. Introduction

Reactive processing is a powerful strategy to compatibilize polymer blends [1] during extrusion and produce thermosetting materials with fine geometry molding [2]. Reactive injection molding is a widespread process in the plastic industry. Reactive processes can be used in quite different way to induce nanostructure in polymer blends and copolymers. Yamanaka et al. [3] described the development of a co-continuous phase separated morphology obtained by reaction-induced spinodal decomposition in mixtures of liquid nitrile rubber and epoxy, which were submitted to cure, leading to incremented damping capacity. Bucknall and Partridge investigated the phase separation during crosslinking of blends of epoxy resins with polyethersulphone [4]. Grubbs et al. [5] reported the incorporation of epoxy functionalized block copolymers to control morphology, inducing order in thermosetting epoxy networks. Landfester [6] reported the preparation of nanocapsules by phase separation induced during polymerization. More recently, Seo and Hillmeyer [7] combined polymerization-induced phase separation, *in situ* block copolymer formation and etching to prepare nanoporous structures.

“Phase inversion”, or phase separation induced by immersion of polymer solutions in water, is a well-established manufacture process for asymmetric porous membrane fabrication. Membranes prepared in this way are present in artificial kidneys, reverse osmosis desalination plants and ultrafiltration systems for food industry. Post-functionalization of membranes is frequently performed to improve resistance to fouling, increase stability in organic solvents [8], by crosslinking, to add specific functionalities like catalytic activity. We combine here the advantage and simplicity of the phase inversion process with *in-situ* functionalization reaction during the membrane formation, leading to membranes with high hydrophilicity, partial crosslinking and incorporation of nanoparticles.

Poly (ether imide sulfone) (Extrem<sup>®</sup> XH1005) (Scheme 1) was chosen in this paper for the membrane manufacture. The chemical structure of Extrem<sup>®</sup> XH1005 combines elements of polysulfone and the polyetherimide Ultem and has demonstrated to have superior thermal properties with suitable processability [9]. Ultem has been frequently used for membrane fabrication, being successful in different applications as a single polymer [10–14] or as a blend with polysulfone [15–17]. Ultem membranes have been tested for gas separation, pervaporation, ultrafiltration and biomedical applications. Extrem<sup>®</sup> XH1005 has been pioneered for membranes by Chung's group [9,18] and has been reported so far only for application in gas separation. Here we developed Extrem<sup>®</sup> XH1005

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membranes with characteristics, which would allow application in ultrafiltration, also in conditions requiring higher temperature and better solvent resistance than addressed by other polyetherimide or polysulfone membranes.

For achieving high water flux, besides porosity, hydrophilicity is a relevant factor. Hydrophilicity is governed by the chemical structure of segments exposed to the pore walls and membrane surface. Good wetting characteristics, demonstrated by low water contact angles, facilitate the water penetration even through small capillary channels, maximizing the pore density available for the transport. Hydrophilicity is also known to increase the fouling resistance of membranes, since most of organic fouling agents are rather hydrophobic and tend to primarily adhere to hydrophobic surfaces. Hydrophilicity can be improved by surface modification, as explored by different groups in the past and summarized in excellent reviews published by Ulbricht [19], Rana and Matsuura [20], Whitesides's [21] and Belfort's [22] groups. Coatings and polymer chemical modifications promoted by UV and plasma treatment are some of the most applied approaches. Grafting of hydrophilic segments on surface is expected to provide a stable modification and is a good strategy as long as reactive groups are available. Effective modifications include growing hydrophilic segments like ethylene oxide and imparting charge, negative or positive, or zwitterionic groups. The strategy we propose here is the preparation of a blend or a semi-interpenetrating polymer network for which one of the polymers is an epoxy-modified polysilsesquioxane. Polysilsesquioxanes are here polymeric or oligomeric chains with the empirical formula of  $\text{RSiO}_{1.5}$ , for which R is an epoxy-terminated segment [23,24].

The modification of polymeric membranes, by incorporating ethylene oxide segments has been explored before by our group and others for application in gas separation to increment  $\text{CO}_2$  permeation [25,26], as well as with the objective of increasing hydrophilicity and fouling resistance [27–30] of membranes used for water-based separations. In the latter case modifications have been promoted by activating reactive carboxylic sites by plasma treatment [30], by adding an intermediary polydopamine layer to facilitate further reaction [27], or by promoting reaction at high temperature directly with imide functionalities in the polymer backbone. Our proposal is the incorporation of ethylene oxide into the membranes by reaction of polyether diamines with the epoxy groups of polymerized silsesquioxanes.

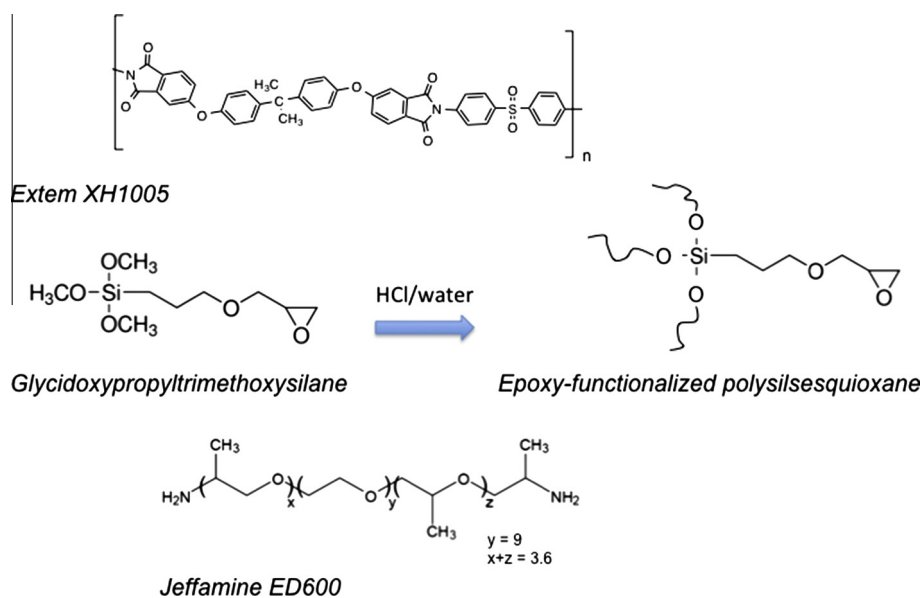
Beside the hydrophilization purpose in the second part of the paper we extended the use of epoxy functionalized silsesquioxanes embedded in the Extem<sup>®</sup> matrix to incorporate nanoparticles to membranes during the phase inversion process. The nanoparticles used here are  $\text{TiO}_2$ . Hybrid polymeric membranes with inorganic  $\text{TiO}_2$  nanoparticles have been explored for membrane application by different groups for reasons, which include catalytic activity, change of mechanical properties, balance permeation and proton conductivity in methanol fuel cells, control gas permeation, improve hydrophilicity and biofouling resistance [31–42].  $\text{TiO}_2$  has also attracted interest due to its photocatalytic activity [43]. Fritsch et al. [31] were one of the first to include  $\text{TiO}_2$  nanoparticles as filler for porous membranes with the dispersion and linking based simply on hydrogen bonding with the polymer matrix. More recently functionalization with polyacrylic acid [32], fumaric acid [33], amino groups [34,38], amino acids [37], chloride compounds [38], alkylsulfonic groups [36], peptoids [33] have been added to  $\text{TiO}_2$  particles dispersed in membranes. We functionalized particles with amine-containing segments and covalently reacted them to epoxy groups available in the dope solution, during the pores formation.

## 2. Experimental

### 2.1. Materials

Poly (ether imide sulfone), Extem<sup>®</sup> XH1005 (Scheme 1), was kindly provided by SABIC. N-methyl pyrrolidone (NMP), dimethylformamide (DMF), tetrahydrofuran (THF), Hydrochloric acid (HCl) and N,N-Dimethylformamide (DMF) were supplied by Sigma Aldrich. Rejections tests were performed with 1 wt% of  $\gamma$ -globulins from bovine blood from Sigma life science in 0.1 M NaCl, from Alfa Aesar; 3-Glycidyloxypropyl trimethoxy silane and O,O'-bis (2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol 500 (Jeffamine) was supplied by Aldrich and Acros Organics, used as received.

$\text{TiO}_2$  nanoparticles (mixture of rutile and anatase, particle size <150 nm (DLS), 33–37 wt% dispersion in  $\text{H}_2\text{O}$ ) and  $N^1$ -(3-trimethoxysilylpropyl) diethylene triamine were obtained from Sigma–Aldrich. The particles were purified by dialysis using Snake-Skin dialysis tubing (7 K MWCO 35 ft. (10.5 m)) supplied by Thermo-Scientific.



**Scheme 1.** Chemical structure of poly (etherimide sulfone) (Extem<sup>®</sup>) and functionalization reactions.

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