



Organic solvent resistant poly(ether-ether-ketone) nanofiltration membranes

João da Silva Burgal, Ludmila G. Peeva, Santosh Kumbharkar, Andrew Livingston*

Department of Chemical Engineering and Chemical Technology, Imperial College, Exhibition Road, London SW7 2AZ, UK

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ABSTRACT

In this work a poly(ether ether ketone) (PEEK) membrane is presented for its suitability for organic solvent nanofiltration (OSN) applications using polar aprotic solvents, such as DMF and THF, high temperatures, and basic/acidic conditions. Four grades of PEEK polymer were tested and it was verified that different grades produced membranes with different performances; the post-phase inversion drying process of membrane fabrication was shown to be crucial in obtaining separation performance in the nanofiltration range. The degree of sulphonation (DS) was also important and was controlled to be in the range of 3.7–6.7 wt%. The tightest membrane, produced from VESTAKEEP[®] 4000P and obtained after drying at 20 °C from water, presented a permeance of 0.22 L h⁻¹ m⁻² bar⁻¹ and molecular weight cut-off (MWCO) of 400 g mol⁻¹ in THF, and a permeance of 0.07 L h⁻¹ m⁻² bar⁻¹ and a MWCO of around 470 g mol⁻¹ in DMF.

To the best of our knowledge this is the first report on a non-sulphonated and non-modified PEEK membrane capable of separations in the nanofiltration range and resistant to DMF and THF and to basic and acidic aqueous solutions.

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1. Introduction

Despite the fact that first research publications on organic solvent nanofiltration membranes can be dated back to the 80s, there is still a limited number of commercial membranes available on the market and most of them are based on polyimide (PI) or polyacrylonitrile (PAN) polymers. However, polyimides are

unstable in some amines and have generally poor stability and performance in polar aprotic solvents (tetrahydrofuran (THF), dimethyl formamide (DMF) and n-methyl pyrrolidone (NMP)) and chlorinated solvents such as methylene chloride (DCM), in which most polyimides are soluble. Cross-linking of PI OSN membranes increases their solvent resistance and the Duramem[™] (crosslinked PI, Evonik MET, UK) series offer long term stability in most polar aprotic solvents (acetone, tetrahydrofuran, dimethylformamide), but are still not recommended in the presence of chlorinated solvents, strong amines and strong acids and bases [1]. In addition the recommended maximum operating temperature is only 50 °C. This poses a limitation for implementing OSN in, for example, catalytic processes. Typically, catalytic reactions are performed at high temperatures (100 °C and above), in aggressive solvents (e.g. DMF), and at high concentrations of base/acid – quite challenging conditions for polymeric membranes. Ceramic membranes possess higher tolerance towards organic solvents and elevated temperatures but in general are brittle, expensive and difficult to produce with separation properties within the nanofiltration range. The Inopor series of ceramic nanofiltration membranes are the only ones available in the market so far [1,2]. Thus the search for efficient and cost-effective solvent resistant and thermally resistant materials continues.

One approach to making a polymeric membrane more resistant to organic solvents is to cross-link the polymer. This approach has been shown for PI [3] (most commercial OSN membranes) and

Abbreviations: AFM, Atomic force microscopy; ATR-FTIR, Attenuated total reflectance Fourier Transform Infrared Spectroscopy; DCM, Dichloromethane or methylene chloride; DI Water, Deionised water; DMAc, N, N-dimethylacetamide; DMF, N, N-Dimethylformamide; DMFC, Direct methanol fuel cell; DMSO, Dimethyl sulphoxide; DS, Degree of sulphonation; EtOH, Ethanol; HPLC, High pressure liquid chromatography; IPA, Isopropanol; MEA, Monoethanolamine; MeOH, Methanol; MF, Microfiltration; MIR, Middle infrared; MSA, Methane sulphonic acid; MW, Molecular weight; MWCO, Molecular weight cut-off; NF, Nanofiltration; NMP, N-methyl pyrrolidone; OSN, Organic solvent nanofiltration; PA, Polyamide; PAEK, Poly(aryl ether ketone); PAN, Polyacrylonitrile; PBI, Polybenzimidazole; PEEK, Poly(ether ether ketone); PEEK-WC, poly(oxa-p-phenylene-3,3'-phthalido-p-phenylene-oxa-p-phenylene-oxa-p-phenylene) with Cardo group; PEK, Poly(ether ketone); PEMFC, Polymer electrolyte membrane fuel cells; PI, Polyimide; PS, Polystyrene; RO, Reverse osmosis; SA, Sulphuric acid; SEM, Scanning electron microscopy; S-PEEK, Sulphonated poly(ether ether ketone); SPEEK-WC, Sulphonated poly(oxa-p-phenylene-3,3'-phthalido-p-phenylene-oxa-p-phenylene-oxa-p-phenylene) with Cardo group; TBPEEK, Modified PEEK with tertiarybutylhydroquinone (TBHQ) (instead of hydroquinone); TGS, Triglycine sulphate; THF, Tetrahydrofuran; UF, Ultrafiltration; UV/vis, Ultraviolet/visible detector; VAPEEK, Modified PEEK with diphenolic acid

* Corresponding author. Tel.: +44 20 75945582; fax: +44 20 75945639.

E-mail address: a.livingston@imperial.ac.uk (A. Livingston).

polybenzimidazole (PBI) [4]. Another approach is to use an intrinsically resistant material such as polyether ether ketone (PEEK) or poly(ether ketone) (PEK).

PEEK is a semi-crystalline high performance thermoplastic with a rigid aromatic backbone structure constituted of a hydroquinone and a benzophenone segment. It possesses good thermal – glass and melt transition temperatures of 143 °C and 340 °C respectively – and mechanical properties, broad chemical resistance, oxidative stability and passive biocompatibility [5–8]. At room temperature PEEK is only soluble in sulphuric acid (SA) and methanesulphonic acid (MSA), while at temperatures close to the melting point, PEEK dissolves in high boiling point esters, benzophenone or diphenyl sulphone [9]. On one hand the high chemical resistance of PEEK makes it an excellent material for OSN membranes, but on the other hand this resistance reduces its processability. When dissolved in SA, PEEK undergoes a sulphonation reaction (Fig. 1) which modifies its chemical structure, reducing crystallinity and consequently increasing solubility.

Thus it is necessary to strictly control the degree of sulphonation (DS) because it will strongly influence the stability of the membrane in solvents such as DMF, DMSO or DMAc. PEEK membranes are only resistant to strong polar organic solvents such as DMF, DMAc, DMSO and pyridine when DS is low (DS around 4 mole%) [10]. In fact, above 30 mole% DS PEEK is soluble in hot DMF, DMSO and DMAc; above 40 mole%, in the same solvents at room temperature; above 70 mole% in MeOH and at 100 mole% in hot water [11].

PEEK membranes have been reported in the literature for different applications such as continuous catalysis, gas separation, fuel cells, MF, UF, NF and RO [12].

PEEK membranes can be in non-sulphonated form, PEEK, or in sulphonated form, S-PEEK; both sulphonated and non-sulphonated forms can be modified. Due to the difficult processability of native PEEK most reports are on sulphonated PEEK membranes. S-PEEK is mainly reported in the literature as being used in gas separations [13,14], polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), posing an alternative to Nafion membranes [15]. S-PEEK can be obtained via post-sulphonation of PEEK [16] or directly via sulphonated monomers [13]. In the first case, concentrated sulphuric acid is used at room temperature for long reaction times; the sulphonation reaction is initially a heterogeneous process and, as a consequence, it produces different fractions of polymer with a variable degree of sulphonation (DS) [15,16].

Modifying PEEK is also a common technique to solubilise it in order to prepare membranes via the phase inversion technique. PEEK-WC [poly(oxa-*p*-phenylene-3,3'-phtalido-*p*-phenylenoxa-*p*-phenylenoxo-*p*-phenylene) with Cardo group] is a modified PEEK that is amorphous and soluble in many organic solvents with medium polarity (e.g. chloroform, dichloromethane,

dimethylsulphoxide, dimethylacetamide (DMAc), dimethylformamide, 1-methyl-2-pyrrolidinone, etc.), whereas it is not soluble in water and alcohols. PEEK-WC can also be in its sulphonated form as SPEEK-WC [17]. Another recent approach for modifying PEEK was reported by Hendrix et al. [18,19]. This research group proposes two ways of modifying PEEK, either by adding a different monomer [18] or by crosslinking PEEK [19] (see Table 1).

In terms of non-sulphonated or “native” PEEK membranes, little has been reported in the literature besides a few patents. Two U.S. patents [20,21] disclose preparation of PEEK membranes from non-sulphonating acid solvents that include methane sulphonic acid and trifluoromethane sulphonic acid. Another patent [22] discloses preparation of improved polymeric membranes based on PEEK mixtures with polyethylene terephthalate. The membranes are formed by the solution casting process from a methane sulphonic acid/sulphuric acid solvent mixture. Yuan [23] presents a process for the preparation of porous poly(aryl ether ketone) (PAEK) articles from PAEK/polyimide blends by a melt extrusion process followed by the removal of the polyimide phase. Two membrane manufacturers PoroGen and Novamem are claiming to be able to produce “native” PEEK membranes for separations in the nanofiltration and ultrafiltration range, respectively [24,25]. To the best of our knowledge up to date there is no detailed investigation presented on production of native PEEK membranes capable of separations in the nanofiltration range.

In our previous work we already proved the excellent stability and performance of native PEEK nanofiltration membranes prepared in our laboratory [26,27]. We used a PEEK nanofiltration membrane (MWCO ~395 g mol⁻¹) in a continuous catalytic reaction/separation (Heck reaction) for 300 h. The membrane was resistant to high temperature (80 °C) and high concentration of base (> 0.9 mol L⁻¹ triethylamine) in DMF. In addition, the retention of catalyst was around 75% throughout the experiment [27]. Since the aim of the work was to demonstrate successful application no details on the membrane production and characterisation were presented. This research work communicates a detailed investigation on the production of non-sulphonated PEEK nanofiltration (MWCO around 350–500 g mol⁻¹) membrane resistant to polar aprotic solvents (such as DMF), high temperature, acids and bases. Different factors affecting membrane separation performance are studied including degree of sulphonation and membrane post-treatment procedures. It is shown that the post-manufacturing membrane drying step is of vital importance for the nanofiltration performance.

2. Experimental design

The methodology used in this study was based on the comparison of PEEK membranes produced from four different polymer grades (coded PM-A, PM-B, PM-C and PM-D) in terms of performance (permeance and rejection). For each of the different membranes (PM-A to PM-D) four replications were performed in order to have a statistically robust sample. All the results were analysed using *F*-test. For the permeance data the *F*-test was used for permeance values obtained after 24 h. For rejection data the *F*-test was applied to each individual polystyrene (PS), i.e. for each solute size (different MW) the four different membranes were compared with each other. Statistical significance was considered at *p* < 0.05. Data are presented as mean ± standard deviation of the mean (SDM).

3. Methods

3.1. Materials

2,4-Diphenyl-4-methyl-1-pentene (α -methylstyrene dimer), methanesulphonic acid (MSA), sulphuric acid (SA) 95 vol%, sodium

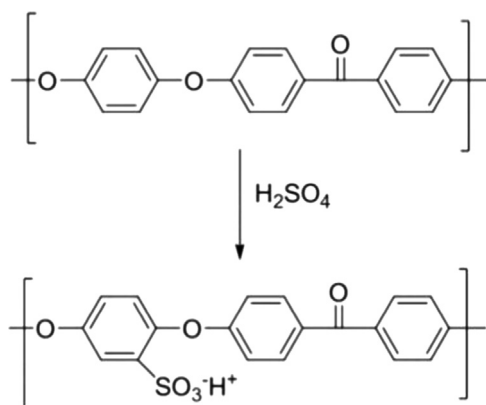


Fig. 1. Schematic principle for the sulphonation of poly(ether ether ketones).

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