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New membranes for organic solvent nanofiltration

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Introduction

Solvent resistant nanofiltration (SRNF) is an energy-efficient separation process suitable for many branches of industry, ranging from petro-chemistry [1] to pharmaceutics [2-6], and it is capable of effective separation of molecules in the range of 200-1000 g mol^{-1} in various organic solvents. Most of the SRNF membranes are either asymmetric integrally skinned [7] or composites comprising of a thin separating layer on a suitable support [8-15]. In order to improve chemical resistance to organic solvents, often crosslinking is applied [16]. In the majority of industrial processes, commercial polymeric membranes in a spiral wound form (e.g. SolSep NF 030306; MET Starmem™) are used almost exclusively.

The state-of-the art PI membranes are crosslinked by diamines in an imide-ring opening reaction [17] either during phase separation [16] or in post casting process [18]. The covalent bond created there is not thermally stable and at temperatures above 100^{o}C re-imidization might occur leading to loss of membrane stability [18, 19]. It is beneficial to crosslink the PEI membranes in such a way that the resulting membranes can be applied for separation processes at elevated temperature.

It is well known that a membrane in hollow fibre (HF) or capillary form has some advantages over membranes in a flat sheet configuration. A HF membrane provides a high surface to volume ratio, does not require spacers and thus enables the design of more compact and much simpler modules. Despite this, HF membranes for SRNF are not commercially available and literature reports very little on this [20].

In this work, we describe preparation and characterization of new membranes for organic solvent filtration. The membranes are prepared by either crosslinking of commercial polyamide-imide membranes using di-isocyanates or spinning integrally skinned polyimide HF. All membranes are systematically investigated including permeation experiments (permeance/molecular weight cut off (MWCO) with polystyrene (PS) oligomer solutions [21]) and study of morphology using scanning electron microscopy (SEM).

Results and discussion

Chemistry in a spinneret to fabricate HF

Here, we explore a new HF spinning method called “chemistry in a spinneret” [22] towards fabrication of membranes for organic solvent filtration. Table 1 presents characterization of various HF prepared using P84 polyimide as a base polymer and poly(ethylene imine) (PEI) as crosslinking agent. The interplay between crosslinking and phase inversion during spinning is studied by varying systematically the composition of bore liquid i.e. PEI, N-methyl-2-pyrrolidinone (NMP) and water concentrations. In general, the HF membranes have MWCO

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(measured with PS/toluene mixture) in the range 2500-3500 g mol^{-1} whereas toluene permeance is relatively low: 0.2 - 1.1 l m^{-2} h^{-1} bar^{-1} (Table 1).

The membranes are partially stable in NMP. The most stable one (B6, see Table 1) maintains 80% of its mass after 11 days immersion in NMP. The PEI crosslinking results in hydrophilization of the HF and therefore makes them suitable for separations in alcohol systems. In fact, these HF have high ethanol permeance (14.6 - 17.2 l m^{-2} h^{-1} bar^{-1}) and low rejection of polyethylene glycol (PEG) (14-23% of 4000 g mol^{-1}) [23].

Table 1. Characterization of HF

HF code	$NMP:H_2O$ in bore liquid	PEI in bore liquid, % (w/w)	Layer(s) (SEM)	Mass loss, %	Permeance of toluene, l m^{-2} h^{-1} bar^{-1}	Toluene / PS	
						Permeance l m^{-2} h^{-1} bar^{-1}	MWCO g mol^{-1}
B1	6:1	20	2	99±0	0*	n.m	n.m
B2	5:1	20	2	98 ± 2	0*	n.m	n.m
B3	4:1	20	2	98 ± 1	0*	n.m	n.m
B4	3:1	20	1	83 ± 1	0*	n.m	n.m
B5	2.5:1	20	1	74±3	n.m	0.5±0.3	3300
B6	2:1	20	1	20 ± 3	1.5 ± 0.1	0.9±0.2	3300
B7	1:1	20	1	64 ± 8	24.5 ± 1	n.m	n.m
B8	2:1	23	1	43±6	n.m	0.2±0.1	2500
B9	3:1	15	1	61±4	n.m	1.1±0.3	3300

**No toluene permeation observed at 30 bar over 8 hours.*

n.m.- not measured

New crosslinking method of polyamide-imide membranes

Here, we report for the first time successful crosslinking of polyamide-imide (Torlon®) based membranes using diisocyanates (see example in Figure 1). The crosslinked membranes are resistant to NMP which is solvent of the non crosslinked membranes and have good mechanical properties. In contrast to the state-of-the-art polyimide crosslinked membranes, the created covalent bond is thermally stable and for this reason the membranes may be potentially employed for high temperature applications. The transport characteristics of the new membranes (permeance, MWCO) can in principle be tailored via the crosslinking.

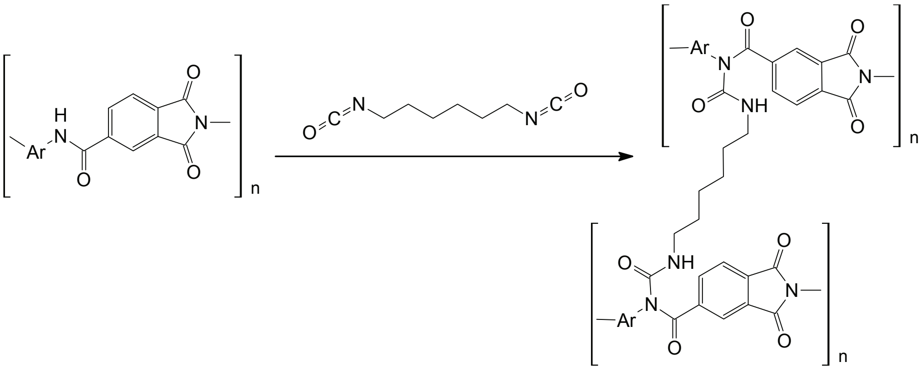

Figure 1. Crosslinking of polyamide-imide by hexamethylene diisocyanate (HMDI).

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