Membrane characterisation by SEM, TEM and ESEM: The implications of dry and wetted microstructure on mass transfer through integrally skinned polyimide nanofiltration membranes

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ABSTRACT

Due to their excellent resistance to a range of solvents, integrally skinned polyimide membranes have been used to achieve selective separations in a range of solvent-based industrial and lab-scale chemical operations. These include: homogeneous catalyst recycle, petrochemical dewaxing, solvent exchange and chiral resolutions. However, despite the widening scope of use of these membranes, there is still little understanding of how the microstructure defines their separation performance. As a first step towards determining this, integrally skinned nanofiltration membranes were fabricated by phase inversion using Lenzing P84 polyimide. The microstructures of these membranes, dry and wetted in solvent, were investigated by SEM, TEM and ESEM (where appropriate).

SEM and TEM imaging of dry membranes revealed that this type of polyimide membrane has three microstructurally distinct polyimide layers, not the two indicated in prior literature. Furthermore, TEM images reveal nano-sized pore-like features in the polyimide structure, which indicate that the transport mechanism is probably neither only solution-diffusion nor only pore flow. ESEM imaging showed that when saturated in ethanol at the working pressure of the ESEM (5.50 Torr), the microstructure of the membranes changes; it is wispy and thus quite different to the more solid polymer nodules and interconnected polymer network observed in the dry membranes. Thus, transport and separation mechanisms based on the structure of the dry membranes may not be accurate. Overall, these results indicate that the current theory used to describe polyimide membrane mass transfer and separation performance (where it is based on dry membrane microstructures), most likely needs to be rethought.

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1. Introduction

Lenzing P84 (BTDA-TDI/MDI, co-polyimide of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and 80% methylphenylene-diamine + 20% methylene diamine; Fig. 1) is a co-polymer which has recently been identified as a robust material for the preparation of membranes for ultrafiltration, nanofiltration, gas separation and pervaporation [1] due to its excellent solvent resistance. A number of recent studies have looked at the formation of these P84 co-polyimide membranes [1–11].

This study concerns only Lenzing P84 nanofiltration membranes. Such nanofiltration membranes have been found to be effective for many applications, in particular for non-aqueous filtrations (organic solvent nanofiltrations) such as separating of

solvents from lube oil and the separation of aromatics [2–4], recycling homogeneous catalysts and bases [12–15], separating chiral diastereomers [16] and green organic synthesis [17]. Despite the widening scope of use of these membranes, there is still little understanding of how the microstructure defines their separation performance in solvent-based operations. In particular, the following questions are yet to be answered: (1) What is the transport mechanism through these membranes in organic solvent nanofiltrations (i.e. how do we reliably predict the separation that these membranes give)? (2) What is their microstructure? (3) How do different solvents affect their microstructure and how does this impact on the separation performance?

Despite not having understood the microstructure of the membranes, the transport mechanism through these membranes has been attempted to be modelled, typically using models that are related to the dry membrane microstructure. The two most commonly used are:

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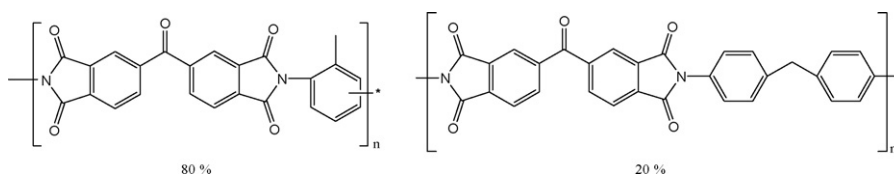E-mail address: darrell.patterson@auckland.ac.nz (D.A. Patterson).

Fig. 1. Chemical structure of P84 co-polyimide.

1. The solution-diffusion model [18–20], which is typically used to describe transport through pore-less membranes, like those used in reverse osmosis. The solution-diffusion model assumes that the permeating species dissolves in the membrane material and diffuses through the membrane down a concentration gradient. A separation is achieved between different solutes due to differences in the amount that dissolves in the membrane and the rate at which it diffuses through the membrane [18–20].
2. The pore-flow model [18–20], which is used to describe the permeation through porous membranes (ultrafiltration, microfiltration). It describes the separation based on pressure-driven convective flow through tiny pores. Selectivity results from exclusion, based on incompatibility of molecule parameters such size, shape and charge, with the pores in the membrane.

Nanofiltration membranes, including these Lenzing P84 membranes, are used for molecular separations. Such separations occur in the transition between ultrafiltration and reverse osmosis membrane operations [19,20], separating molecules with molecular weights of 200–1000 g mol^{-1}. Therefore without resolving the microstructure of these membranes, it is uncertain which of the above mechanisms (or indeed a combination of both) governs mass transport through nanofiltration membranes.

Consequently, attempts have been made to resolve the microstructure of Lenzing P84 nanofiltration membranes. It has been reported [4] that these integrally skinned co-polyimide membranes have a three layer structure (Fig. 2), with polyimide split into a dense separation layer and a porous support layer that gives little resistance to mass transfer compared to the skin layer. A polyester non-woven support layer typically adds strength to this matrix. However, this type of microstructure does not correlate with some filtration results obtained with Lenzing P84 membranes. It has been assumed in the past that this sort of dense skin layer implies that separation is best described by solution-diffusion [20]. However, Patterson et al. [15], for example, concluded that for the organic solvent nanofiltration of trialkylamine bases, the main transport mechanism was pore flow with solution diffusion becoming significant if the concentration at the membrane caused by concentration polarisation and/or fouling becomes sufficient. Pore-flow cannot be excluded as a mechanism, since in the prior literature there has been no evidence establishing the presence or absence of pores or pore-like features (which in this context could

be fixed nano-scale voids between polymer chains and/or clusters of polymer, aligned into channels, or a fluctuating free volume that could act like pores). Consequently, a more detailed analysis of these membranes could reveal very different microstructure to what has been previously established. Moreover, Vankelecom et al. [21] have demonstrated that the transport mechanism through MPF-50 and PDMS membranes depends on the physico-chemical nature of these membranes. Consequently, the transport mechanism can change depending on the filtration conditions, as seen in the results by Patterson et al. [15]. Very thin porous top layers, very viscous solvents, strongly swelling solvents, low top layer porosities and high pressures, all make the porous support dominate the transport mechanism, giving convective flow [21]. This all indicates that a more detailed investigation of this nature is required for Lenzing P84 membranes, investigating the physio-chemical properties of the membrane in order to clarify the relationship between microstructure and transport mechanism.

In order to do this, the microstructure of the membranes must be imaged and characterised. This is typically done using dry membranes. However, during an organic solvent nanofiltration, the structure of the membrane changes when in contact with the solvent to be used, especially due to swelling [8]. Therefore, although imaging a membrane outside of a solvent (i.e. dry) may give an indication of the initial microstructure prior to filtration, in order to understand how the microstructure affects the transport mechanism and thus membrane separation performance when it is being used, the membrane must be imaged when in solvent (i.e. wetted).

Consequently, as a first step towards addressing these issues, integrally skinned nanofiltration membranes were fabricated by phase inversion using Lenzing P84 polyimide. The microstructure of these membranes were characterised using a scanning electron microscope (SEM) and a transmission electron microscope (TEM) for dry membranes and an environmental scanning electron microscope (ESEM) for ethanol wetted membranes. The implications of these microstructures to the aforementioned filtration results and the transport mechanism through these membranes were then considered.

2. Materials and methods

2.1. Polyimide membrane fabrication

Membranes were fabricated from P84 co-polyimide (CAS# 58698-66-1, HP polymer GmbH) which was used as received. The main membrane characterised (hereafter referred to as M1) was fabricated with 22 wt% P84 and any additives were dissolved in dimethylformamide (21 wt%) and 1,4-dioxane (57 wt%). This was stirred continuously at 50 °C overnight to obtain a homogeneous dope solution. Following this, the polymer solution was allowed to stand at room temperature for 24 h to remove air bubbles. 200 mm thick polyimide films were then cast on a non-woven polyester backing material (Holytex 3329) using an adjustable doctor blade casting knife on an automatic film applicator (Braive Instruments). The solvent was allowed to evaporate from the surface of the film for approximately 10 s before immersion into a water bath at room temperature overnight. The membranes were subsequently immersed in solvent exchange baths of isopropanol
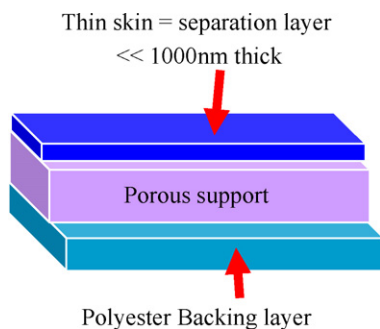

Fig. 2. Microstructure of Lenzing P84 nanofiltration membrane based on White [4].