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Pore structure characterization of asymmetric membranes: Non-destructive characterization of porosity and tortuosity

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ABSTRACT

Internal concentration polarization (ICP) in osmotic processes is largely influenced by the porous structure of the support layer of the membrane. Recent publications on osmotic separations have described a 'structural parameter', S (function of the thickness, tortuosity, and porosity of the support layer), that represents the support layer's contribution to the overall mass transfer resistance during osmosis. To date, S has only been calculated as a fitted parameter in a model that requires experimental flux measurements. Such a method is inaccurate since the models fail to account for all of the different mass transfer phenomena. An alternative is to characterize the thickness, tortuosity, and porosity independently and thus calculate the actual value of the structural parameter. However, for soft materials like porous membranes, no standard methods have been established for measuring porosity and tortuosity. In this study, we propose the use of X-ray microscopy (XRM) for determining the structural parameter of thin film composite (TFC) membrane support layers. The S value could be calculated from the XRM images and was compared to the results obtained from more conventional mercury intrusion porosimetry as well as an existing model used with empirical data. Substantial differences between the values obtained from the different techniques indicated the need to revise the traditional approaches of characterizing membrane structures.

1. Introduction

Engineered osmosis (EO) is an emerging technology platform comprising a number of membrane-based technologies. These include forward osmosis (FO), pressure-retarded osmosis (PRO) and direct osmotic concentration, which can be used for desalination, power production and dewatering, respectively. These technologies rely on osmotic gradients between a concentrated draw solution and a relatively dilute feed solution. In EO, water flux performance is critical and is dependent on the osmotic pressure gradient over the selective layer of the membrane. The membrane support layer however, poses a resistance to draw (in FO) and feed (in PRO) solute mass transport that can dramatically reduce this driving force. This phenomenon is known widely as internal concentration polarization (ICP) and is largely responsible for preventing the use of existing commercial reverse osmosis (RO) membranes in EO processes.

Most EO membrane developers have focused on optimizing the support layer characteristics in order to reduce the severity of ICP. The structural parameter, S, has been widely used as a metric to assess the membrane's contribution to ICP. S is defined as

$$S = \frac{t\tau}{\varepsilon} \tag{1}$$

where t is the thickness, τ is the tortuosity, and ε is the porosity. These individual characteristics can be manipulated in order to minimize the value of S, which is the goal of many membrane development teams in industry and academia. However, when making a new membrane, the exact value of some of these characteristics, and by association the value of S, is unknown. So far, S has only been indirectly calculated using models based on experimental flux measurements and an assumption of film theory dictating mass transfer. One such model is shown below

$$S = \frac{D}{J_w}\left(\ln\frac{B + A\pi_{D,b}}{B + J_w + A\pi_{F,m}}\right) \tag{2}$$

where D is the solute diffusivity, J_w is the water flux, A is the pure water permeability of the membrane, B is the solute permeability of the membrane, $\pi_{D,b}$ is the osmotic pressure of the bulk draw solution and $\pi_{F,m}$ is the osmotic pressure of the feed solution at the membrane interface. It is explicitly clear that the above parameters do not define the membrane structure and that changes in these values should not

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influence the support structure. However, investigators still use this model as a means of calculating S from osmotic flux measurements [1].

Recently, a method was proposed to standardize FO membrane testing. This investigation found that even when the same conditions were used amongst a number of research groups, S values could still vary when using this fitted parameter technique [2]. One must note that the models used to calculate S are constantly evolving in the literature in order to distinguish the different resistances to mass transport in the system and uniquely identify the resistance offered by the membrane structure itself. Many of these studies still rely on assumptions that are likely inaccurate. One such assumption is that *external* concentration polarization on the support layer side of the membrane is negligible. Most models fail to account for this phenomenon, effectively lumping any external CP into the S parameter calculation. For poorly performing membranes, fluxes are low enough that this assumption is a reasonable approximation. However, with the advent of high performance EO membranes at both the laboratory and commercial scale, the resulting high fluxes mean that external CP can no longer be ignored [3]. Existing models that continue to combine external and internal CP will overestimate S values as the fitted parameter of the equation. This results in an unreliable calculation of the structural parameter and an overestimation of the membrane's contribution to mass transfer resistance. If such a parameter could be calculated directly, rather than as a fitted parameter of a model, we would be able to better understand exactly how membrane structure plays a role in osmotic flux performance. However, few techniques are available to accurately characterize the structural characteristics of membranes, such as porosity and tortuosity.

A review of the methods used to calculate porosity and pore diameter distribution in soft nonwovens has been presented in a previous publication by the authors [4]. Models that relate tortuosity to porosity and pore architecture, negating the need to directly measure the tortuosity [5–7], are available. However, these models are empirical and can only be applied to specific isotropic structures. No models are available for asymmetric or composite structures, which include many of today's TFC membrane supports. Average tortuosity can be measured through conductivity and diffusivity measurements of a dissolved solute through the porous material [8–10], but such efforts are complicated, difficult to reproduce, and have limited value in characterizing asymmetric composite structures. At the time of this writing, the only study on pore structure characterization of EO membranes is on microscopic characterization [11]. The techniques used include scanning electron microscopy (SEM), transmission electron microscopy (TEM) and confocal laser scanning microscopy (CLSM). While this study provides some interesting insights on the structure of the particular membrane studied, the accuracy of using 2D imaging techniques (SEM, TEM) to characterize asymmetric pore structures is debatable. Also, the two electron microscopy techniques were used to image the membrane in the dehydrated state and then comparisons were made to CLSM images of the wetted membrane. The membrane studied was made of cellulose acetate, a hydrophilic polymer, which likely exhibits swelling when hydrated. In general, techniques should be chosen carefully so that the sample preparation does not significantly alter or damage the structure being analyzed.

The objective of this study is to evaluate tools for characterizing the 3D structure of commercially available TFC reverse osmosis (RO) membrane support layers. These membranes were chosen since they possess a composite and anisotropic structure typical of many TFC membranes today [12,13]. The membranes tested in this study have also been previously evaluated for their performances in FO [14]. TFC membranes are now finding broader application in EO, with Oasys Water™ and Hydration Technology Innovations™ both releasing their own commercially available versions in 2012 [15,16]. Two characterization techniques have been used as a part of this study – an analytical method, mercury intrusion porosimetry (MIP) and an imaging technique, X-ray microscopy (XRM). MIP is a widely used tool in the analysis of porous materials [4]. XRM is a non-destructive 3D imaging technique that is widely used in biomedical, geological and archeological applications. Recently, with the advent of improved phase contrast optics it has been increasingly used to image soft materials [17]. The results from the two approaches were used to evaluate the membrane structures and calculate the intrinsic structural parameters. These values were then compared to values obtained from the conventional method of using an empirical model. The comparison demonstrates the inaccuracy of empirical approaches and the need for better understanding of mass transport occurring during osmosis across anisotropic and composite membranes.

2. Materials and methods

2.1. Materials

The membranes used in this study were the BW30 and SW30-XLE thin film composite reverse osmosis membranes from Dow Water & Process Solutions™. These membranes were used as-received and characterized in their dry state.

2.2. Methods

2.2.1. Analytical characterization

Mercury intrusion porosimetry (MIP) was used to characterize porosity and tortuosity of these membranes in their dry state. The porosimeter used was a PoreMaster from Quantachrome Corporation. In addition to pore diameter distribution and porosity, tortuosity of the pore structure was calculated using a generalized correlation [18,19].

$$\tau = (2.23 - 1.13 V_{tot}\rho_b)\left(0.92\left(\frac{4}{S}\sum\frac{\Delta V_i}{d_i}\right)^{1+\varepsilon}\right) \quad (4)$$

where τ is the tortuosity factor, V_{tot} is the total pore volume (cm^3/g), ρ_b is the bulk density of sample (g/cm^3), S is the Brunauer–Emmett–Teller (BET) surface area (m^2/g), ΔV_i is the change in pore volume within a pore size interval (cm^3), d_i is the average diameter within a pore size interval (cm), and ε is the pore shape exponent. A value of $\varepsilon = 2.1$ was assigned for both membranes in accordance with a previous study [18].

Triplicate porosimetry experiments were performed for each membrane to obtain average porosities and tortuosities. The experiment was set up as such that the instrument will only measure pore size below 1 μm (which is the maximum resolution of the Xradia MicroXRM) in order to enable a fair comparison. The thicknesses of the two membranes were determined using a micrometer. Ten measurements were taken to obtain an average thickness.

2.2.2. Imaging characterization

Both scanning electron microscopy (SEM) and X-ray microscopy (XRM) were used to image the two membranes used in this study. A JEOL 6335F field emission SEM was used to obtain cross-sectional images of the two membranes. The membranes were fractured along orthogonal axes. One cross section represents the membrane in the direction in which the cast polysulfone (PSu) support was introduced into the precipitation bath. The second