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Impact of liquid-filled voids within the active layer on transport through thin-film composite membranes

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ABSTRACT

Transport through composite membranes is strongly influenced by the morphologies of both the porous support membrane and overlying selective thin-film (i.e., active layer). Recently, the occurrence of water-filled voids within the active layer has been suggested in the literature; however, their effects on transport are uncertain. Here, we theoretically consider, through numerical modeling, the effect that liquid filled-voids have on the transport of water and solutes through supported thin-film morphologies. Specifically, we evaluated the effect of volume void fraction, void size, and relative location of the voids within the active layer with respect to both surface roughness features and the pores of the support. Transmission electron microscopy image analysis was used to obtain evidence supporting the existence of voids in two commercial brackish and seawater reverse osmosis membranes; the volume fraction of the active layer the voids occupied was determined to be about 30% for both membranes. Our calculations show that, for films with a constant polymer volume, a rough film containing voids is more permeable than an equivalent, homogeneous flat film, due to the creation of shorter paths for diffusion, not due to increased surface area, though the latter is shown to correlate positively with permeability when no base-film exists under the void. Results further illustrate the importance of void position within the thin-film, indicating that even with a significant void fraction, the presence of an underlying polymer base-film negatively impacts the permeability. Voids created closer to the bottom of the active layer will increase membrane permeability. Conversely, results show that even at significant void fractions, voids located closer to the top of the active layer negatively impact the permeability. Variations in the proportion of the active layer overlaying the voids will impact the flux distribution along the membrane, and may be used to reduce flux 'hotspots', which may enhance localized concentration polarization and fouling propensity. A strategy for creating high permeability membranes with relatively even flux distributions may include a combination of a rough film with a reduced base thickness, and with thicker regions of the film aligned with the support pore locations. Understanding the role of the voids in determining the transport properties of the membranes provides motivation for controlling their formation.

1. Introduction

State-of-the-art reverse osmosis (RO) and nanofiltration (NF) membranes are comprised of an ultra-thin polyamide film formed over a porous support membrane (typically polysulfone cast over a polyester non-woven fabric). Despite their dominant role in the water purification, reuse and desalination industry, basic questions of how the morphology of the support (e.g., porosity, pore size, structure and distribution) and of the thin-film impact transport through the composite membrane, and the consequent implications on membrane fouling propensity, have not received much attention in the open literature. Classical treatment of membrane transport, e.g. within the framework of the solution-diffusion model [1], is normally employed with the assumption of a homogeneous film of uniform thickness. Recent modeling efforts have extended this framework to consider the effects of the porous support as well as a non-uniform film thickness [2–4], illustrating

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the pronounced effect on transport of purely geometrical considerations, unaffected by polymer chemistry, which is assumed to be constant within the model framework. This assumption facilitates the de-coupling between the polymer chemistry and the film morphology-these appear to be intimately linked, yet are not very well understood. When considering identical monomers from which the polymer backbone is created, it has been demonstrated that the polyamide permeability may be modified through the interfacial polymerization conditions; these include temperature, choice of solvents, monomer concentrations, co-solvent additions and the properties of the support membrane, to name a few [5–9]. These conditions also impact the film morphology; therefore, it is important to remember that the assumption of keeping constant polymer properties (i.e., as embodied in parameters such as partitioning and diffusivities of permeating species) while changing the morphology cannot depict the full, complex picture. A recent study has demonstrated that, even after accounting for some geometrical considerations, variations in transport properties still exist [10]. Separating the effect of geometry from chemistry in an experimental setting is difficult (if not impossible); thus, model simulations afford us the luxury of probing geometrical effects separately, so as to shed insight on their relative impact and motivate further attempts at their manipulation.

Experimental work has previously attempted to correlate the roughness of RO membranes with their permeability, with some suggesting that an increased permeability is to be expected due to roughness-increased surface area; these studies obtained mixed results, showing no clear correlation [9,11–14]. Theoretically, it has been shown that roughness can only increase permeability if it is created via a redistribution of polymer into thin and thick parts [3]. However, the previous theoretical efforts have assumed that the thin film is comprised of a homogeneous polymer. The question may be raised – is this indeed the case and, if not, what would be the impact of a non-homogeneous structure? This question is also motivated by recent advances in higher resolution imaging that have allowed improved characterization of RO and NF membranes revealing, in detail, the thin film morphology. A representative collection of recently published images is compiled in Fig. 1, highlighting the globular features and rough morphology of RO membrane thin films. Scanning Electron Microscopy (SEM) surface images of RO membranes (Fig. 1a) show the “ridge and valley”, “leafy protrusions” or “carpet-like” morphology typical of fully aromatic polyamide films. Transmission Electron Microscopy (TEM) images (see Fig. 1b–d) show that the films are not uniform in composition, with regions of dense polymer film and regions of what appear to be open voids or regions of lower polymer density. A few research groups have observed this structure in RO thin films [15–19], that is, a dense basal region near the support layer, overlain by polymer leafs surrounding globular voids, and it has recently been demonstrated that these voids are fluid-filled when immersed in water [10]. The introduction of hollow, fluid-filled domains within the thin film and possibly between the film and support membrane raises interesting questions with respect to transport mechanisms through composite NF/RO membranes.

We note that a first approximation of transport through a polymer containing voids seems quite straightforward, using results from ‘effective medium theory’ [20]. A polymer film of a given permeability, containing liquid voids that may be considered as having much higher permeability, will be more permeable than the pure polymer phase. However, this theoretical framework is limited to non-interacting inclusions; in other words, the liquid-filled voids must be far apart, and cannot amount to a significant fraction of the total volume ($< 10\%$). Furthermore, the effective medium theory cannot specifically account for the effect of the porous support as well as geometry and spatial distribution, e.g. whether voids are located close to the film-support interface, whether they are close to support pore locations, etc. Clearly, a more elaborate calculation is needed to better understand the effect of the voids on the permeation of water and solutes for the composite structure and morphological features relevant to NF/RO membranes.

Apart from impacting permeability, film morphology has also been linked to fouling propensity. For example, experimental evidence suggests that colloidal fouling is lower for smooth, integrally-skinned cellulose acetate RO membranes, compared with that observed for rough, thin-film composite membranes (see, for example, [21,22]). While this observation has been explained primarily using arguments related to hydrophilicity, recent theoretical studies of transport through composites have also suggested that increased fouling propensity may be induced by flux ‘hot-spots’, that is, regions of greatly increased permeability, where initial deposition is expected to occur [2,3]. These hotspots have been shown to result via three main contributions: (1) thin-film thickness; (2) variations in film thickness (i.e., roughness) and their relative positioning with respect to support pore locations; and (3) the permeability of the solid make-up of the support

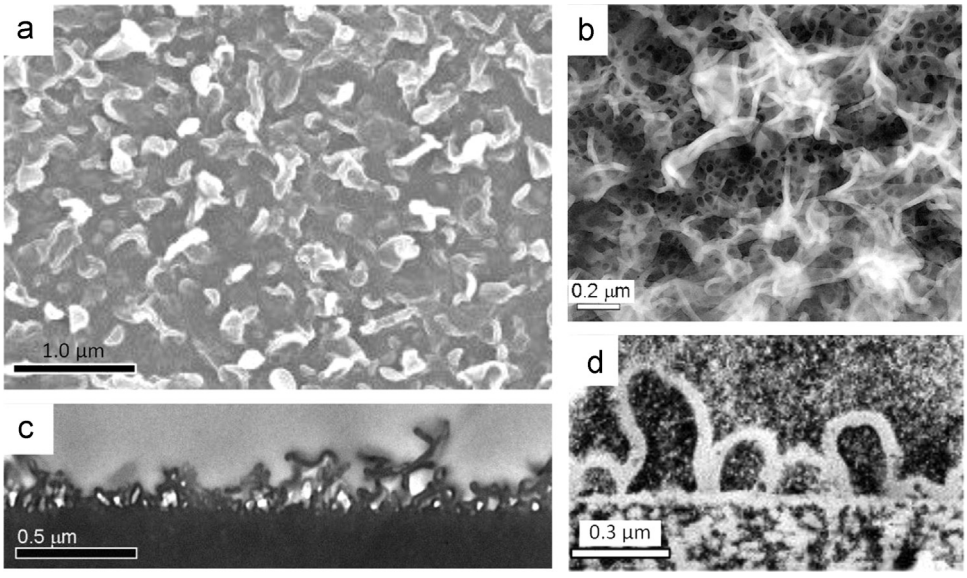

Fig. 1. (a) Surface SEM [8], (b) top view [9] and (c/d) cross-sectional TEM images [9,10] of polyamide RO membrane thin films, collected from the published literature.