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Micro-to nano-scale characterisation of polyamide structures of the SW30HR RO membrane using advanced electron microscopy and stain tracers

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ABSTRACT

The development of new reverse osmosis (RO) membranes with enhanced performance would benefit from a detailed knowledge of the membrane structures which participate in the filtration process. Here, we examined the hierarchical structures of the polyamide (PA) active layer of the SW30HR RO membrane. Scanning electron microscopy combined with focused ion beam milling (FIB-SEM) was used to obtain the 3-D reconstructions of membrane morphology with 5 nm cross-sectional resolution (comparable with the resolution of low magnification TEM imaging in 2D) and 30 nm slice thickness. The complex folding of the PA layer was examined in 3 dimensions, enabling the quantification of key structural properties of the PA layer, including the local thickness, volume, surface area and their derivatives. The PA layer was found to exhibit a much higher and convoluted surface area than that estimated *via* atomic force microscopy (AFM). Cross-sectional scanning transmission electron microscopy (STEM) was used to observe the distribution of a tracer stain under various conditions. The behaviour of stain in dry and wet PA indicated that the permeation pathways have a dynamic nature and are activated by water. High resolution STEM imaging of the stained PA nano-films revealed the presence of < 1 nm pore-like structures with a size compatible with free volume estimations by positron annihilation lifetime spectroscopy (PALS). This study presents a comprehensive map of the active PA layer across different length scales (from micro- to sub-nanometre) and mechanistic insight into their role in the permeation process.

1. Introduction

Reverse osmosis (RO) membrane filtration is frequently utilised in water purification and recycling for domestic, industrial and agricultural purposes [1,2]. Membranes designed for molecular separations in water usually comprise a “tight” separating layer of polyamide (PA) on a more open support layer of polysulfone (PSf). The PA and PSf layers are mounted on a woven fabric backing of polyethylene (PE) or polypropylene (PP) [3,4]. The topmost PA layer is thought to play the active role in the filtration process as a molecular sieve and an ion barrier [5]. Improved knowledge of the structure and chemistry of the PA layer is required to design membranes, which achieve higher performance in water desalination and purification [6]. Characterisation of the PA layer is particularly challenging due to its complex and interconnected ridge-valley structure, thinness of the active film, the sub-nanometre size of structures within the film, and beam sensitivity intrinsic to polymer materials in electron and ion beam microscopes.

The organisation of the PA layer at the meso-scale is often assessed by cross-sectional transmission electron microscopy (TEM) [7,8], isometric or top-down scanning electron microscopy (SEM) imaging [3,9–11] supported by topological information acquired *via* atomic force microscopy (AFM) [5,9,11,12]. The overall thickness of the PA layer ranges from 20 to 400 nm [12]. PA morphology is typically estimated by the maximum ridge-to-valley distance, average roughness and apparent surface area [5,13]. It is commonly accepted that water permeability increases with the apparent surface area of the PA layer [1].

The inner structures of the PA layer are usually characterised using electron microscopy (EM) imaging of membrane cross-sections [5]. The PA layer might be divided in two regions: a relatively

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flat and semi-porous base at the PA-PSf interface and a more open structure of protuberances spreading from the base, giving rise to the well-known ridge-valley structure [14]. Recently, it has been suggested that the PA layer is formed of a continuous sub-10 nm, highly crumpled PA nano-film [15]. The crumpling of the thin nano-film results in the formation of multiple voids within the PA layer, especially in the basal region. Some studies suggest that these voids contribute to an increase in surface area (as the voids are open to the surface at one end [6,16]), which might be connected with increased flux [17–19]; other studies suggested that the voids are discrete [19,20].

The molecular-scale mechanisms of particle/ion filtration are not fully understood and are typically rationalised in terms of classic pore-flow or solution-diffusion models [21,22]. Separation studies postulated that permeation is modulated by both continuous pores and the density of cross-linked polyamide [23,24]. Molecular dynamics (MD) simulations suggested that the filtration occurs through a network of sub-nanometre pores, which may play an active or passive role in the process [25,26].

"Porosity" at such small length scales likely corresponds to a modulation of density and free volume inherent to polymeric networks, rather than to actual pores in the macroscopic sense. In addition, segmental and cooperative polymer dynamics, under solvation and pressure conditions, might be expected to modulate solute transport [27]. Evidence of sub-nanometre pores within the PA layer has been obtained by positron annihilation lifetime spectroscopy (PALS) [5,22,28] and solution permeation rate calculations [29]. Until now, the only spatially resolved imaging methods used to study pores smaller than 10 nm were based on the tracking of nanoparticles [30].

Few attempts have been made to validate the permeation models (pore flow *vs.* solution diffusion) described above. Nanoparticles have been used as contrast agents in attempts to map classic pores and/or permeation pathways within the PA and PSf layers. To enhance the visibility of these structures in transmission electron microscopy (TEM), membranes were infiltrated with nanoparticles such as Au or OsO_2 [14,30]. These studies used particles of known size to visualise the crumpled topography of the PA layer [14] and to measure the sizes of pores in the PA layer [30]. As the nanoparticles are often inhomogenously distributed within the membranes, it is difficult to observe the direct transport pathways or draw conclusions about the behaviour of membranes during the filtration process. Furthermore, nanoparticles of set size may not accurately reflect the size of voids within the membrane, due to complex transport mechanisms, the variation in the sizes of the pores or the dynamic nature of these pores.

In addition to nanoparticles, heavy metal stains such as osmium tetroxide, ruthenium tetroxide, uranyl acetate or lead citrate may be used to reveal the structural features of the PA layer. By contrast to nanoparticles, metal stains diffuse more homogeneously through the material due to their small size (initially ionic); selectively lodge in charged regions; additionally fix the material and could be delivered in both liquid and vapour phases. To date, staining has mainly been used to enhance contrast of membranes in TEM and map the distribution of functional groups in the PA layer [7,12,14]. As most of the TEM studies were conducted at relatively low magnifications, it is difficult to characterise any structural features smaller than 30 nm.

The question of how the micro- to nano-metre scale features and their morphology modulate the permeation process remain unanswered [6]. Spatially resolved imaging techniques, such as SEM, TEM or AFM, do not provide a complete picture of the 3-dimensional (3-D) architecture of the PA layer and the impact of the structures within the PA on the filtration process at the micro- to nano-scale. At the sub-nanometre scale, little is known about the 3-D distribution of the pores, their chemistry and role in solute (water/ion) transport. PALS studies provide only statistical information about the bulk of the membrane and computational models generally lack validation with spatially resolved experiments.

High resolution electron microscopy (EM) studies of RO membranes are so far limited. EM has mainly been used for relatively low magnification, bright-field TEM imaging showing cross-sections of commercial membranes [5,14] or SEM imaging of the PA surface [10,11]. However, EM methods are exceptionally well-suited to provide spatially resolved maps of the hierarchical structures of the polyamide layer. Advanced nanoanalytical techniques, available on modern scanning TEMs (STEMs), have a spatial resolution sufficient to observe structural features smaller than 1 nm.

The combination of tomographic EM methods allows 3-D visualisation of hierarchical membrane features from the micro- to nano-metre length scales. Yan et al. [16] highlighted the significance of large voids (10–50 nm in diameter) within the PA layer and the possible pathway in the BW30 membrane. Pacheco et al. [19] have recently examined void spaces (15–30 nm in diameter) within the PA layer of ESPA3 and SWC3 in 3-D and proposed a link between an increased volume of these voids with increased permeance of the membrane. A 2-D study by Lin et al. [20] estimated that these voids may constitute up to 30% of the PA layer volume. The focus of our work is therefore to comprehensively examine and precisely quantify the structures within the PA layer envelope at the micro-scale, and examine structures within the PA nano-film at the nano- to sub-nano-scale with unprecedented spatial resolution.

We combine a range of EM techniques with heavy metal staining methods to visualise the hierarchical structure of the PA layer of the commercially available SW30HR (Dow Filmtec) membrane, selected for its common industrial use in high rejection water desalination [31].

Focused ion beam scanning electron microscopy (FIB-SEM) was used to reconstruct the features of polyamide in 3-D with high spatial resolution. Staining was used not only for contrast enhancement, but also for elucidation of the PA structure, specifically for mapping the nano-pores within the PA nano-film using high annular dark field scanning transmission electron microscopy (HAADF-STEM; atomic number, Z^2 contrast imaging). Moreover, by varying the staining methods, potential permeation mechanisms in the polyamide film could be proposed.

2. Materials and methods

2.1. Sample preparation for electron microscopy

SW30HR (Dow Chemical Company, USA) flat sheet membranes were stained with RuO_4. In general, staining improves the overall contrast for electron microscopy (EM) imaging, stabilises the polymer under the electron beam (by crosslinking oxidised moieties, such as amide and carbonyl groups) and highlights the distribution of functional groups. The varying behaviour of stain tracers in different staining conditions may also reveal the permeation pathways.

1×1 cm^2 membrane coupons cut from a larger sheet were stained using standard (as received) stabilized 0.5 wt% aqueous solutions of RuO_4 (Acros Organics, Geel, Belgium). Four different staining methods were used:

I. A membrane coupon was fully immersed in liquid stain for 5 min and immersed in 10 ml of water for 30 min.
II. The top surface of membrane coupon was exposed to the stain vapours for 1 min.