Journal of Membrane Science 527 (2017) 180–190

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Multiscale molecular simulations of the formation and structure of polyamide membranes created by interfacial polymerization

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ABSTRACT

Large scale molecular simulations to model the formation of polyamide membranes have been carried out using a procedure that mimics experimental interfacial polymerization of trimesoyl chloride (TMC) and metaphenylene diamine (MPD) monomers. A coarse-grained representation of the monomers has been developed to facilitate these simulations, which captures essential features of the stereochemistry of the monomers and of amide bonding between them. Atomic models of the membranes are recreated from the final coarse-grained representations.

Consistent with earlier treatments, membranes are formed through the growth and aggregation of oligomer clusters. The membranes are inhomogeneous, displaying opposing gradients of trapped carboxyl and amine side groups, local density variations, and regions where the density of amide bonding is reduced as a result of the aggregation process. We observe the interfacial polymerization reaction is self-limiting and the simulated membranes display a thickness of 5–10 nm. They also display a surface roughness of 1–4 nm. Comparisons are made with recently published experimental results on the structure and chemistry of these membranes and some interesting similarities and differences are found.

1. Introduction

The use of polymer membranes is one of the most promising routes to separating mixtures of global significance [1]. Desalination and the economical purification of large volumes of water are among the greatest challenges the world faces [1]. This is commonly done by reverse osmosis, where a pressure gradient is applied across a membrane allowing water to flow preferentially, leaving behind the impurities, such as ions in the case of desalination. The crux of the process is the membrane itself. Among the many materials choices, a common morphology is an asymmetric composite membrane, where a highly crosslinked polyamide (PA) thin layer is formed by interfacial polymerization on a porous support [2]. In this system, the separation of the water from ions occurs in a thin layer which may be only a few nanometers thick.

Membrane thickness, chemical composition, cross-linking structure and surface roughness are all important properties that are highly dependent on the conditions at which the interfacial polymerization is carried out and are difficult to predict [3]. Furthermore, in spite of the decades of progress in the development and optimisation of PA membranes, little is known about the detailed molecular mechanisms involved in the transport of water through them, largely because the experimental characterisation of polymer films at nanometer scales is very difficult.

Molecular modelling has the potential to shed light on the process of the formation of the membrane through interfacial polymerization, the properties of the membrane itself and on the transport processes of water and ions through it. The decisive point however is to produce a reliable molecular model for the system both in terms of the morphology of the cross-linked polymer and in terms of the reliability of the atomistic force fields employed [4]. While the latter is rather well accepted by the use of "standard" intermolecular potentials, for the former (i.e. setting up a model structure of the networked polymer) there is much more scope for debate.

If one believes that the polymerization process itself has no influence on the morphology of the resulting structure, then the

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http://dx.doi.org/10.1016/j.memsci.2016.11.024
Received 2 September 2016; Received in revised form 30 October 2016; Accepted 13 November 2016

process of building a model of the membrane reduces to postulating an arrangement which is both chemically sound and a stable equilibrated atomistic configuration. For the case of the PA membranes the idealized chemical structure corresponds to a highly cross-linked polymer matrix with a known stoichiometry.

Roux et al. [5] have built virtual membranes by progressively bonding the constituent solvent-free monomeric species on the basis of a heuristic distance criterion during MD simulations until the system interconnectivity reaches completion and a target (experimental) density is achieved. Realizations of membrane models of this type [6–9], with different heuristic protocols and annealing procedures have been used these to study the transport of water and ions. Colina et al. [10] have progressed these ideas by championing the use of a systematic algorithm [11] that combines chemical moieties in a virtual environment in an ad-hoc randomized way. This produces cross-linked polymers model structures with predetermined properties that can later be employed in studying transport and/or structural properties. This process has also been used to produce PA model membranes [12].

Instead of starting off with monomer units, one could consider only a packing of linear oligomers. However, this produces membranes with significantly different characteristics from those that are cross-linked and at odds with experimental information [13,14]. Nevertheless, suitably packed collections of linear chains have been employed as building blocks for PA membrane models [15–17]. Hughes and Gale [18] cross-link pre-formed linear polymer chains, each consisting of 23 repeat units, by solvating them in water and randomly bonding carboxylic acid groups that were 5–9 Å apart to generate a cross-linked polymer layer. An interesting aspect of this work is that the authors considered explicitly the effect of the support layer and compared in their simulations a free-standing thin film with films supported on a flat porous or non-porous substrates. An important outcome of the work of Hughes and Gale is that they observe no influence of the presence of the substrates on their simulations. Ding et al. [19–21] further employ the conceptual idea of artificially cross-linking linear polymer segments as a methodology to create appropriate membrane models.

In spite of the apparent success implied by the agreement between the above mentioned models and the limited atomistic level characterization available for PA membranes, there is still the lingering question as to the faithfulness of these ad-hoc models to provide a reliable picture of the molecular details of relevance to the transport of fluids across PA membranes. One would expect that a “mimetic” or evolutionary approach, based on a model that mimics the formation of the real material, would provide the most accurate representation of the membrane molecular structure. This approach has been championed in other areas of materials science and has proven to be successful in producing models of activated carbons [22] and porous materials for adsorption [23]. The issue with the mimetic production of an interfacial polymerization membrane by simulation is that the time frames for the experimental process are many orders of magnitude larger than those accessible by molecular modelling. To our knowledge, the first attempt to adopt a mimetic approach was the work of Nadler and Srebnik [24], who employed a cluster-cluster aggregation scheme to simulate dynamically the formation of a PA membrane from the constituent monomers. The membrane model produced, albeit a coarse-grained (CG) representation, gave insights into the kinetics of formation and the structure of the membrane, but lacked the atom-level detail needed for the description of water and ion transport. CG models, where some degrees of freedom have been removed, provide a means to access longer time scales than do conventional MD simulations and have been explored as a means to generate plausible configurations by interfacial polymerization. In particular dissipative particle dynamics (DPD) has the appropriate level of integration that allows the merging of groups of molecules into “blobs” of matter while removing the explicit effect of the solvent. DPD, however does not account for the kinetics of the reaction, which must be added artificially. Berezkin and Kudryavtsev [25–27] have recently reported a hybrid adaptation of DPD with larger scale continuum finite difference methods. The results obtained provide a quantitative picture of the effects of cross-linking of the polymer, adding to the picture that the degree of cross-linking has a profound effect on the morphology of the membrane, as it disallows the movement of the monomeric species in the core of the polymer matrix producing a strongly heterogeneous environment. On the other hand, fully analytical models (e.g. Ref. [28]) fail to describe the molecular level detail that is crucial to understanding the transport processes of water and ions through these inhomogeneous membranes.

In spite of the above progress, it is clear that current computational resources are insufficient to simulate in atomic detail either the polymerization process or transport processes in realistic system sizes and experimental timescales. Despite advances in parallel processing and algorithms, the use of graphical processing units and the reduction in costs of hardware, these computational limits are bound to remain essentially unchanged (see the comments made during a Faraday Discussion on the topic [29]) in the near future. In this paper we describe a way around this limitation by means of a multi-scale modelling technique where we model the interfacial polymerization process using a coarse-grained representation which retains the shape and connectivity of the underlying monomers, while emulating diffusion of monomers through their solvents without treating the solvents explicitly. We are then able to map these CG models onto fully atomic configurations through a further relaxation procedure. In this way the underlying physical processes involved in the interfacial polymerization are captured faithfully, including the conformationally correct bonding during polymerization and the aggregation of polymer clusters while ultimately reporting atomically detailed models of membranes.

The paper is organised as follows. In Section 2 the experimental procedure for creating membranes by interfacial polymerization is reviewed to identify the processes that should be included in a realistic simulation. The coarse-grained representations of the MPD and TMC monomers, their reaction products and the simulation protocol are described. The results in Section 3 begin with the mechanism and kinetics of the formation of the membranes through the growth and aggregation of clusters. The atomic structures of membranes formed from three different ratios of concentrations of the two reactant monomer species are presented alongside maps of amide bonds and amine and carboxyl side groups within them. Similar atomic structures and maps are also presented for a variety of oligomer cluster sizes prior to their incorporation in the membranes. The discussion in Section 4 contains comparisons with earlier simulations and experiments of dry and hydrated membranes and in particular with the recent experiments of Karan et al. [30].

2. Method

2.1. Overview of experimental procedure

Thin-film composite PA membranes are experimentally manufactured by interfacial polymerization, as first documented in 1959 by Morgan et al. [31,32]. In this process two reactive species undergo a polymerization reaction at the interface between two immiscible solvents [33]. Typically these reactants consist of an amine and an acid chloride dissolved in an aqueous and organic solvent respectively. A microporous backing, typically polysulfone, is immersed in the aqueous solution containing the amine reactant. This backing film is brought into contact with the organic solution of acid chloride. The amine component diffuses into the organic solvent, but the acid chloride is almost insoluble in water and remains in the organic solvent. As a result, the polymerization reaction takes place in the organic solvent at and near the interface between the two solvents. The reaction is self-limiting because the precipitating PA becomes a barrier to the intermixing of the reactants. A common choice of reactants for reverse