



Asymmetric porous membranes from binary polymer solution by physical gelation induced phase separation



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ABSTRACT

Phase separation induced by physical gelation has been identified, based on systematic experimental data, as the mechanism responsible for the generation of porous structures in elastomeric polydimethylsiloxane (PDMS) assisted drying of binary polymer solution. Comparative experiments of natural drying have enabled one to clarify the similarities and differences in those different drying processes. Based on experimental observations, qualitative explanatory drying models have been suggested for those drying processes. Slow, equilibrated solvent removal in natural drying has led to the formation of gel-phase skin, and this gel-phase skin undergoes wrinkling instability due to large volume shrinkage. The gelation-induced phase separation has occurred at the very last stage of natural drying, leading to nanoscale pores in very thin bottom-most layer. On the other hand, rapid, instantaneous absorption of solvent into PDMS in PDMS-assisted drying has yielded glassy skin at the initial stage of drying. Then the underlying, trapped solution has been separated, induced by physical gelation, into solvent-rich sub-phases embedded into polymer-rich matrix, leading finally to microporous support layer in asymmetric polymeric membrane structure. Physical gelation-induced phase separation, ahead of vitrification of amorphous polymer, has been found to be the responsible mechanism for the generation of porous structure in elastomeric PDMS-assisted drying process. The elucidated phase separation mechanism involved in PDMS-assisted drying, when combined with quantitative kinetic models for drying processes, can pave the way for the fabrication of asymmetric polymeric membranes using other amorphous polymers.

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1. Introduction

Polymeric membranes have long been used in variety of fields such as filtration, separation, and purification, to name a few [1,2]. Among them, asymmetric membranes, thin and dense top layer supported by a thick and porous layer, have long been used for separation. The thin and dense top layer is responsible for the separation, while the thick and porous layer plays the role of mechanical support. This asymmetry in membrane configuration is especially useful in reverse osmosis, where the thin layer enables high rejection rate and the porous support guarantees very high flux. Considering the fact that the membrane science and industry have long history, there are many fabrication methods for the preparation of membranes [1]. Except some very special cases, most of the polymeric membranes are fabricated based on the

phase separation phenomenon of polymer solution. Thermodynamic variables, such as temperature and concentration, can be controlled to induce phase separation of otherwise homogeneous polymeric solution into solvent-rich and polymer-rich sub-phases. After removing solvent(s) molecules, the dried polymeric materials would have voids or pores that were previously occupied by solvent-rich phases, i.e., porous polymeric membranes.

Traditional methods for the preparation of asymmetric membranes have been the phase separation combined with the formation of integral skin. For example, the polymeric solution is dried for specific time duration, which forms the dense skin layer. Then the whole sample can be underwent phase separation process, controlling either temperature or concentration, for the formation of porous support layer. These traditional methods involve multitude of materials and processing steps, which makes them expensive and complex. Previous work [3] has demonstrated a novel way to prepare asymmetric membranes. High permeability and solvent absorption capability of elastomeric polydimethylsiloxane (PDMS)

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have been exploited to generate the asymmetric geometry. Upon contact of PDMS slab onto binary polymer solution, rapid and instantaneous sorption of solvent into the elastomer forms a thin and dense skin layer, and the polymer solution under this dense skin undergoes liquid–liquid demixing into polymer-rich matrix embedding solvent-rich sub-phases. Final drying of the sample has led to a polymeric film having thin dense skin supported by thick porous layer, i.e., asymmetric membrane. No other (non)solvents or polymers are involved in this approach, and the process can be done at room temperature (RT) without any manipulation of system temperature. Thus the method was found to be low-cost, simple way to prepare asymmetric membranes. The detailed discussion, however, on the mechanism responsible for the liquid–liquid demixing in the polymeric solution under the skin has not been elucidated yet.

In this article, we investigate the phase separation mechanism of binary polymer solution in the PDMS-based asymmetric membrane fabrication process (termed as ‘PDMS-assisted drying’ hereafter). To elucidate the underlying mechanism for the liquid–liquid demixing, natural drying of polymer solution without PDMS have been performed for comparative studies. Ruling out the conventional phase separation mechanisms such as methods based on an intentional control of temperature or concentration, the possible phase separation mechanisms have been narrowed down to vitrification or gelation. Based on our experimental measurements on gelation concentration, physical gelation of amorphous polymer network, polymethylmethacrylate (PMMA) in the present work, has been found to be the mechanism responsible for the phase separation in our system. Further, systematic investigations have enabled us to set up qualitative models for natural drying and PDMS-assisted drying, respectively. This in-depth understanding of detailed mechanism occurring in PDMS-assisted drying method may be a valuable help in fabricating asymmetric porous membranes with other polymers.

2. Experimental section

Amorphous polymer, polymethylmethacrylate (PMMA, $M_w = 120,000$; Sigma–Aldrich) was dissolved in toluene as a solvent, in concentrations ranging from 4wt% up to 20wt%. The asymmetric porous PMMA membrane was prepared using similar approach as in Ref. [3]. In short, a known concentration of PMMA/toluene solution was dispensed onto cleaned Si or glass substrates. A flat slab of cured PDMS (Sylgard 184, Dow; 10:1 ratio in weight, cured at 70 °C for >4 h), backed with slide glass to minimize swelling-induced deformation, was simply made conformal contact with the solution. It took >30 min. to completely dry the sample in this PDMS-assisted drying approach. On the other hand, the solution on a substrate was simply dried in room ambient in the case of natural drying method, typically for >3 h, as a comparison. In certain control experiments, the cured PDMS slab was further extracted in toluene for 3 days to remove uncured siloxane oligomers, which resulted in the weight loss of ~6%. Also, a drop of siloxane oligomer (part A in Sylgard 184 kit) was intentionally added into PMMA/toluene solution, leading to a ternary solution of siloxane/PMMA/toluene.

The morphology of the prepared samples was investigated by various imaging techniques, scanning electron microscopy (SEM; S-5000, Hitachi), atomic force microscopy (AFM; MFP-3D, Asylum), and optical profiler (Contour GT-X, Bruker). To measure the drying rate, the change in sample weight was monitored by precision balance (KE-ABT220, Kern) as a function of time. The change in solution height was measured by optical microscope attached in contact angle measurement system (Attension Theta, Biolin Scientific).

3. Results and discussion

3.1. Natural drying vs. PDMS-assisted drying

Previous work [3] has shown that asymmetric porous membrane could be fabricated by simple PDMS contact onto binary polymer solution, but there was no detailed discussion on the relevant phase separation mechanism(s). The generation of porous structure in fully dried polymer film suggests that there should be specific liquid–liquid de-mixing mechanism(s). Here systematic investigations have been carried out to elucidate the mechanism responsible for the observed porous structure.

Among various techniques for porous polymeric membrane, non-solvent induced phase separation (NIPS) [2] has been widely used due to its simplicity and versatility. In this approach, added non-solvent(s) or polymer(s) induce the phase separation or precipitation of polymer-rich phase, leading to the formation of porous structure. In our experimental system (PMMA/toluene), the unintentional addition of uncured siloxane oligomers may trigger the liquid–liquid de-mixing via NIPS mechanism. It is very well-known that the out-diffusion of oligomers is responsible for the “hydrophobic recovery” in electrical insulation [4,5], unwanted contaminants in micro-contact printing [6], and novel patterning technique called “inkless micro-contact printing” [7], where a cured slab of PDMS is an essential element for these processes. To check this possibility, PDMS slab was extracted in pure toluene for 3 days. The weight of PDMS was decreased by ~6%, which is due to the removal of uncured siloxane oligomers. This extracted PDMS has led to similar result (Fig. 1b) to that from pristine PDMS (Fig. 1a), so that we can rule out the possibility of phase separation by unwanted addition of siloxane oligomers in our system. In another experiment, a drop of siloxane oligomers (Part A in Sylgard 184 kit) was directly mixed into the PMMA/toluene solution. This ternary solution has also resulted in similar porous membrane by PDMS-assisted drying, as shown in Fig. 1c. Therefore, we can conclude that the NIPS is not responsible for liquid–liquid de-mixing and thus pore generation in the present system.

Another very well-known technique for the preparation of porous polymeric membrane is to control the temperature of polymer solution. For example, polymer solutions that show upper critical solution temperature (UCST) behavior can be phase-separated simply by decreasing the solution temperature below the critical temperature (T_c), so called thermally induced phase separation (TIPS) [8]. The temperature was maintained at room temperature in our experiments, while the T_c of PMMA/toluene system is 225 K. This means that TIPS cannot be the mechanism for the observed phase separation. Further, PDMS-assisted drying experiment has been performed at an elevated temperature (80 °C) and the result is shown in Fig. 1d. The PMMA/toluene binary solution was found to be phase-separated even at such high temperature, thus we can rule out the possibility of TIPS for the phase separation observed in our system.

To further elucidate the mechanism of phase separation responsible for our system, we have performed control experiments of natural drying and the results are shown in Fig. 2. The natural drying has led to almost dense layer of dried polymer without having any noticeable microscopic pores at a glance, as shown in Fig. 2a. There exist very thick and dense layer on air side (Fig. 2b), on top of thin (~3 μm) bottom layer. There exists a discontinuity in film morphology transitioning from bottom to top layer, as can clearly be seen in Fig. 2c. Upon magnification, the bottom portion of dense, top layer has very small, nano-scale pores, as shown in the inset of Fig. 2c. The bottom layer looks like columnar at/around the interface between substrate and polymer layer (Fig. 2d), due probably to directional flux of solvent at the final

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