Composite Membrane Formation by Combination of Reaction-Induced and Nonsolvent-Induced Phase Separation

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Introduction

A novel method of preparing skinned asymmetric membranes with two distinctive layers called reaction induced phase separation RIPS (Aburabie *et al*, 2017) is described: a top layer composed of chemically cross-linked polymer chains (dense layer) and a bottom layer of non-cross-linked polymer chains (porous substructure). With this approach it is possible to finely control the structure and functionalities of the final membrane. The thickness of the dense layer can be easily controlled over several orders of magnitude and targeted functional groups can be readily incorporated in it. In addition to the previous advantages, RIPS allow the possibility of forming free-standing thin membranes by immersing the resulting membranes in good solvent to dissolve the uncrosslinked sublayer.

Material and Methods

The membranes were prepared using a polymeric solution of 15 wt.% Polythiosemicarbazide PTSC (Campbell, 1962) in DMSO. The preparation process consisted of casting a 250-μm-thick polymer solution film with a membrane knife, followed by immersing it in a solution of Dibromo-p-xylene (DBX) or bromo Triptycene (Tr-X) (Bonaccorsi *et al*, 2013) in DMSO to form the dense layer. Different concentrations of DBX or Tr-X and different immersion times were used. Finally membranes were transferred to a water bath to form the porous sublayer.

Results and Discussion

The resulting membrane following RIPS method poses a composite-like asymmetric structure that has a dense top layer consisting of chemically cross-linked polymer chains and a well-defined interface with a porous non-crosslinked support Figure 1a-c. The residence time in the crosslinking solution had a strong influence on the thickness of the top layer; longer contact time resulted in thicker dense layers. Not only the reaction time but also the crosslinking concentration and type affect the thickness of the top layer, Figure 1d.

Good rejection of aqueous PEG mixtures results were obtained with membranes prepared using the DBX crosslinker; however, the permeances were low. The membranes prepared using 2% DBX/ DMSO (20 s) and 5% DBX/DMSO (20 s) presented a water permeance of 0.65 and 0.06 L m^{-2} h^{-1} bar^{-1}, respectively (Table 1). Solvent permeances also were tested using these membranes.

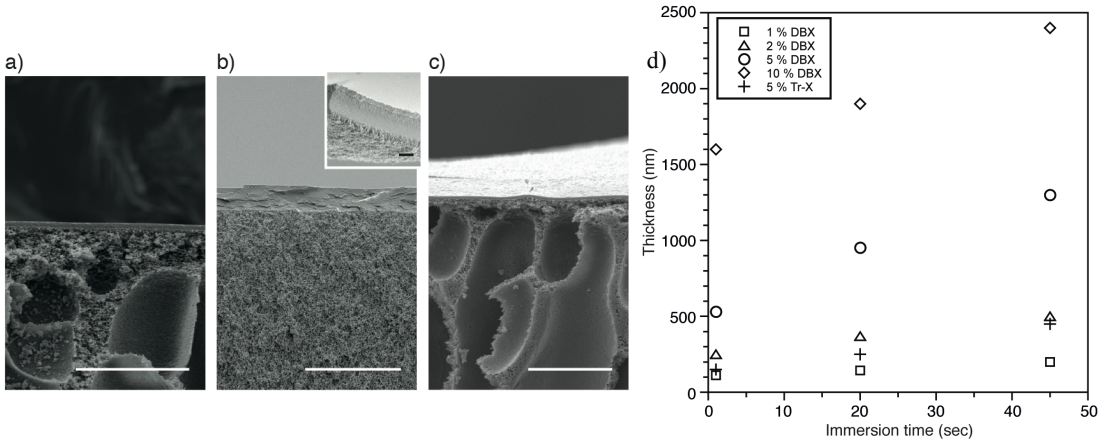


Figure 1. Cross section of a polythiosemicarbazide (PTSC) membrane prepared by RIPS. a) Dense layer prepared with 2% DBX crosslinker for 20 s (top-layer thickness: 370 nm). b) Dense layer prepared with 10% DBX crosslinker for 20 s (top-layer thickness: 2000 nm). c) Dense layer prepared with 5% Tr-X crosslinker for 20 s (top-layer thickness: 250 nm). Scale bars represent 10 μm in the main images and 1 μm in the inset. d) Effect of the crosslinker concentration and immersion time in the dense layer thickness for two different crosslinkers: DBX and Tr-X.

Table 1. Water permeances for membranes prepared using different parameters.

Membrane	Permeance (L m^2 h^{-1} bar^{-1})	Structure
NIPS (immersed directly in water bath)	650	Porous surface
RIPS, 1% DBX, 20 s	191	Dense top layer with many defects
RIPS, 2% DBX, 1 s	10.5	Dense top layer with few defects
RIPS, 2% DBX, 20 s	0.65	Defect-free top layer
RIPS, 5% DBX, 20 s	0.06	Defect-free top layer
RIPS, 5% Tr-X, 20 s	7.7	Defect-free top layer

Conclusions

A new method was successfully added to the family of phase inversion techniques to prepare composite-like asymmetric membranes. The method was developed using the PTSC, a polymer which can be cross-linked with a sufficiently high reaction rate to favor the crosslinking reaction and not the dissolution reaction. The study showed the tunability of the membrane structure and the possibility to incorporate specific functionalities (like Triptycene) in the top dense selective layer only.

References

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