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Polymeric microsieves produced by phase separation micromolding

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Abstract

The fabrication of polymeric microsieves with tunable properties (pore size, shape or porosity) is described in this work. Perfectly structured freestanding membranes and accurate replicas of polyethersulfone (PES), copolymers of polyethersulfone and polyethylene oxide (PES–PEO), and blends of PES and hydrophilic additives were produced by phase separation micromolding (PSμM) using a microstructured mold. Phase separation occurred in two stages: vapor-induced phase separation (VIPS), where shrinkage and subsequent perforation of the polymer film took place, and liquid-induced phase separation (LIPS), where lateral shrinkage that facilitated the release of the polymer replica from the mold occurred. The dimensions of the perforations were tuned either by using molds with different pillar diameter or by thermal treatment of the polymer above its glass transition temperature. By the latter method, microsieves with initial pore sizes of about 5 or 2.5 μm were reduced to 1.5 and 0.5 μm, respectively, whereas perforations down to 1.2 μm were achieved by tuning the dimensions of the mold features.

Keywords: Polymeric microsieves; Polyethersulfone; Polyvinylpirrolidone; Phase separation micromolding

1. Introduction

Conventional microfiltration membranes are often compromized by the poor correlation between permeability and selectivity. In order to improve the properties of such membranes, microsieves were introduced about a decade ago [1,2]. Microsieves differ from conventional membranes by their well-structured morphology and controlled porosity, which results in good separation behavior and high flow rates [3]. The fact that large volumes can be filtered with such membranes seems very advantageous. However, large product throughput can often result in extreme fouling [4]. Protein fouling with inorganic microsieves, for instance, can be reduced most effectively either using air sparging and/or applying surface modification procedures using PEG polymers [4,5]. Unfortunately, some of these strategies cannot be used in certain applications in the medical, pharmaceutical or food industry. Air can cause foaming and denaturation of some compounds, and only biocompatible and/or food-grade approved polymers can be applied as coatings. Until today, microsieves were fabricated out of silicon-based materials. This limited material range stems from their fabrication process, which relies on expensive cleanroom technology [1,6]. An alternative for producing low cost microsieves can be found in the use of polymers. The properties of polymeric microsieves can be tuned very easily depending on the material used, costs can be greatly reduced and the manufacturing process can be greatly simplified.

Phase separation micromolding (PSμM) is a novel technique for polymeric microsieve fabrication. It allows the production of uniform, defect free microstructures and is suitable to process a wide range of materials [7–9]. PSμM is based on the principle of polymer phase separation in order to obtain microstructured polymer replicas, by means of casting a thin polymer film on a microstructured mold [10]. In the case of microsieve fabrication the mold contains pillars that perforate the polymer film. Its design is critical for the final microsieve morphology: pillar shape, diameter, support dimensions, etc.

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Few commercial polymeric membranes with such specific and well-defined structural properties like the ones of microsieve membranes are available on the market. Track-etched membranes also possess straight-through pores. However, their porosity and pore size distribution is sometimes compromized. Nowadays, research groups are also working on the fabrication of structures with well-defined pores. Goedel and co-workers have successfully prepared ultra-thin freestanding porous membranes with very narrow pore size distribution and small pore diameters (50–100 nm) by particle-assisted wetting [11–13]. Other methods used to obtain well-patterned microporous structures include self-assembly of rod-coil block-copolymers and templating with particles, emulsions, water droplets, etc. [14–18].

In this research the fabrication of polymeric microsieves and the parameters that affect their properties are explored. As a reference polymer polyethersulfone (PES) is used, which is a well-known membrane material due to its good chemical resistance, thermal stability and mechanical properties [19–21]. The influence of fabrication parameters (co-solvent, temperature, non-solvent immersion time, etc.) on the microsieve morphology is investigated. Pore size tuning will also be considered via two approaches: either by using pillars of various diameters (modified mold features) or by applying a thermal treatment to induce structural shrinkage. Furthermore, the fabrication method will be tested by using other polymers or by adding hydrophilic additives like polyvinylpyrrolidone (PVP) in the casting solution. Many authors have reported the ability of PVP

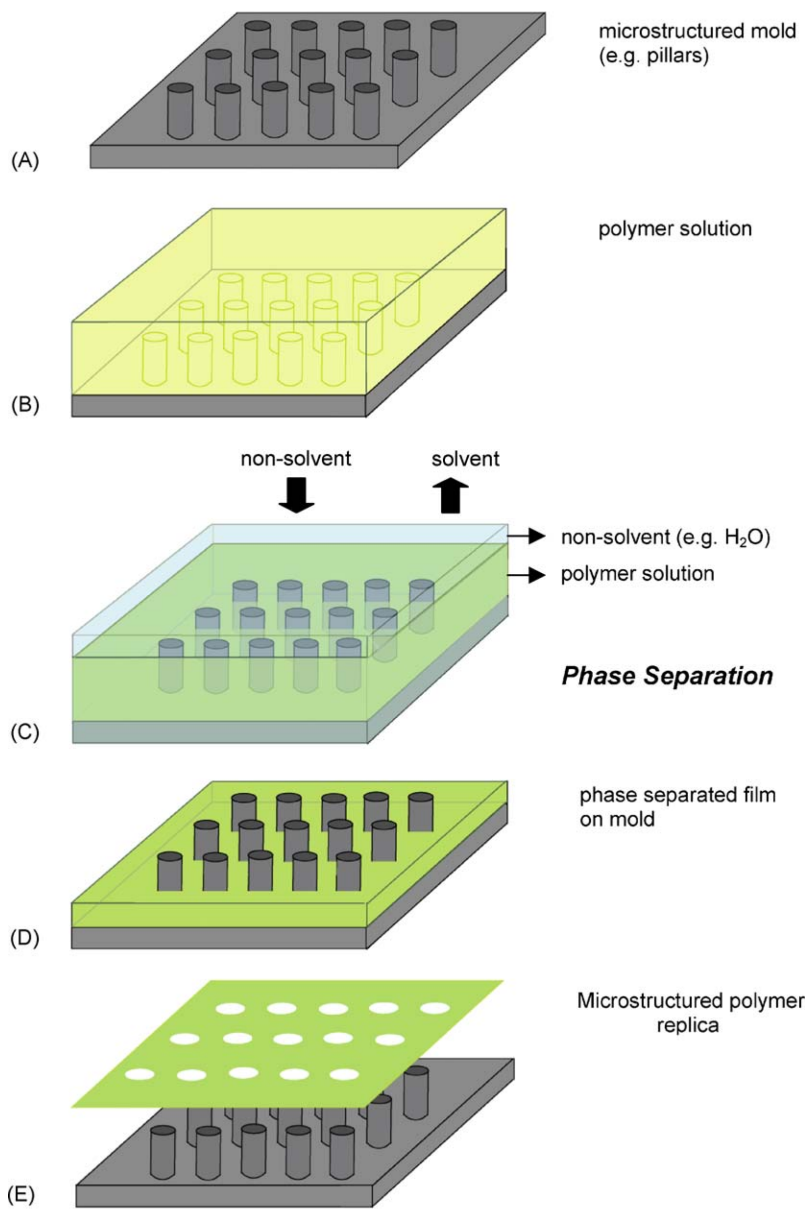

Fig. 1. Schematic representation of liquid-induced phase separation micromolding. The process starts by casting a polymer film (B) on a structured mold (A). The system is immersed into a non-solvent for the polymer and phase inversion or polymer coagulation takes place (C). In this step the polymer assimilates the mold structure (D) and a polymer replica is obtained (E). This scheme represents the fabrication of polymeric microsieves.