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Polysulfone filtration membranes with isoporous structures prepared by a combination of dip-coating and breath figure approach

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ABSTRACT

While many honeycombed films have been recently produced using the vapour induced phase inversion or breath figures approach, few have achieved the open channels that allow fluid flow through the films. In this work, isoporous polysulfone membranes were prepared by a process consists of dip coating and breath figure technology to provide facile formation of honeycombed open channels suitable for filtration. A thin robust, porous polymer film was formed due to the film drainage and formation of assemblies of water micro-droplets on the surface of a dip-coated nylon mesh. Dip coating conditions including withdraw speed and holding time in the membrane solution were varied, and their effect on membrane morphology was examined. To modify the membrane isoporosity, non-ionic surfactants and anionic–cationic surfactant mixtures were added to polysulfone at different concentrations to mediate the formation of the pores. Membranes prepared from Pluronic P123 generated the pore size, pore interconnectivity and pore density suitable for microfiltration. Increasing the concentration of P123 from 0.5 to 0.75 wt%, led to less permeable membranes with higher rejection when yeast was used as a model foulant.

1. Introduction

Porous polymer films used as filtration membranes are conventionally prepared by a phase inversion process, resulting in a wide distribution of pore sizes. In such porous films, the large pores tend to carry a disproportionate amount of the flux. For example, more than 50% of the flux may pass through less than 20% of the pores. This disproportionate amount of flow can in turn, make conventional porous films prone to fouling by particulate plugging as more material passes through the large pores. In addition, the size exclusion mechanisms that govern the retention capability of the membranes can be compromised. Isoporous polymeric membranes have advantages for many microfiltration applications such as: sterilization and clarification of all kinds of beverages and pharmaceuticals, particle removal during the processing of ultrapure water in the semiconductor industry, cell harvesting and as a part of membrane bioreactor (involving a range of biological conversion and separation), metal recovery of colloidal oxides or hydroxides and waste-water treatment.

A number of techniques have been used to prepare “isoporous” polymer films, which have a distribution of pores having a low variance in pore size diameter. Isoporous films and membranes may be prepared using complex molecular templating techniques or through track etching via neutron bombardment and chemical etching [1]. However, such fabrication methods are often limited by factors including high cost, the inability to form films of various sizes or geometry, and relatively low density of open pores (up to 15%). Examples include commercial track-etched polymer membranes prepared from polycarbonate (PC; e.g. Nuclepore) or polyethylene terephthalate (PET; e.g. RoTrac) films with a thickness between 6 and 35 μm [2]. Anodically oxidized alumina asymmetric membranes have a much higher porosity (up to 50%) than track-etched materials, with pore sizes ranging between about 10 nm and a few 100 nm. Scale up to large membrane areas of such membranes is complicated due to the brittleness of the substrate, and inorganic membranes are relatively costly compared to polymeric membranes. Nevertheless, these membranes have been used as support materials for novel polymeric separation layers or systems [3,4]. Isoporous microsieves present a very well-controlled structure and pore size. Their high porosity leads to very high fluxes, and thus can be operated at extremely low pressures. Silicon nitride microsieves are produced by techniques well known in the semiconductor industry, including standard mask lithography or laser interference lithography [5,6].

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The outstanding features of microsieves lies in the thin resistant selective layer, the high surface porosity and precisely engineered patterned pore and substrate structure. Since the fabrication techniques provide full control on the membrane design, microsieves contain pores with the same size and shape all over their surface. However this approach is very expensive and only applicable to silicon or silicon-based materials, which limits the potential application.

A complementary method, phase inversion micro-moulding, is based on micro-sieve technology and was developed to overcome some of the issues with silicon based substrates [7]. In this method a thin layer of polymer solution is applied on a mould, which has a micrometer to nanometer sized surface profile. Membrane forms and takes the shape of the mould by a change in the solution temperature or by immersion in a non-solvent. By incorporating a subsequent process step, carbon, ceramic, and metallic microstructures can also be fabricated from a polymeric or hybrid precursor. Under suitable post fabrication treatments, perforation of the polymer film can be obtained, resulting in completely open pores which span the bulk microstructure. However the replication process is still complicated and the process has yet to be scale up commercially. In Table 1 commercially available isoporous microfiltration membranes are given, along with some of their limitations.

Block copolymers have been widely used in preparation of isoporous membranes via their self-assembly properties leading to formation of isoporous nanoporous membranes with pore sizes down to tens of nanometer [8–10].

An alternative approach is to use a non-solvent templating approach from the vapor phase to generate isoporous microstructures. Vapor induced phase inversion (VIPS) or breath figures (BF) technologies have been used extensively to create highly ordered surface pores in polymeric and inorganic films [11–13]. The mechanism involves condensation of a non-solvent (usually water) from humid air to form highly ordered water droplets on the surface of a polymer–solvent solution. Precipitation of polymer around the water droplet stabilizes the water droplets while capillary forces, thermal currents, and surface tension gradients affect the degree of ordering them (Fig. 1). Under suitable conditions subsequent evaporation of the solvent and the non-solvent result in honeycomb structures of various morphologies. Some films have highly ordered surface pores, well separated from each other, while others resemble hexagonally shaped cells. Factors affecting pore size and porosity include: humidity, concentration of polymer solution, air flow and polymer molecular weight [14]. While ordered surface pores have been readily formed over a wide range of conditions and materials [15], ordered interconnected open pores required for membrane filtration and other applications remain difficult to achieve. Typically, cellular structures are formed by the water droplets upon condensation on the polymer–solvent interface, with open pores only on one side of the film. Spin-coating, casting on water [16] and dip-coating methods have

Table 1
Commercial isoporous membranes.

Type of membrane	Trade name/company	Application	Drawbacks
Track-etched polycarbonate or polyester isoporous membranes	Nuclepore® Nuclepore Corporation 0.1–12 μm pore size	– General filtration – Removal of red blood cells from plasma – Flow control of reagents through assay – Precise filtration and pre-filtration – Water microbiology	– Low pore density (2–20%) – Relatively weak resistance to alkali – Not robust enough to be incorporated into a compact module
Electrochemically made alumina inorganic membrane	Anopore	– Laboratory filtration – Precise filtration	– Brittle – Difficult to scale up – Expensive
Microsieves made by silicone micromachining	Twente, Netherland Aquamarijn Microsieve	– Filtration and clarification of beer	– Expensive

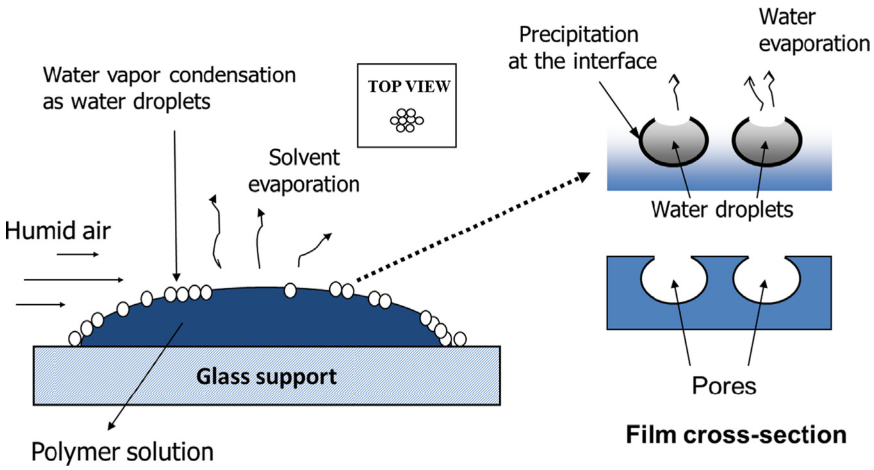

Fig. 1. Mechanism of pore formation by breath figure technology and drop casting [11,14].