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Novel micro-/nano- porous cellular membranes by forced assembly co-extrusion technology

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ABSTRACT

Production of novel membranes for filtration applications is still a burgeoning demand with the rising environmental concern about pollution in different spheres of human biota. This paper presents a novel approach, yet a continuous production method, to fabricate bi-component cellular membranes. Multilayer membranes having thousands of alternating layers, where cells are aligned vertically and separated by thin, solid polymer layers, were produced using unique multilayer co-extrusion and multiplication technology. Post-drawing techniques, both uniaxial and biaxial, were employed to create interconnected through pores in cellular membranes. Two different polymer pairs, polystyrene/polypropylene (PS/PP) and polypropylene/nylon 6 (PP/PA6), have been chosen to develop multilayer cellular membranes. The modulus contrast between film and foam layers played an important role in creating hierarchical porous structures in the membrane. Uniaxially drawn membranes exhibit very narrow pore size distribution whereas biaxially drawn membranes exhibit slightly larger pore size distribution. In addition, the porosity can be varied (20–60%) either by changing the chemical blow agent (CBA) concentration, foam content or the draw ratios of membranes. The membranes also exhibit high water flux and high micro-particle separation efficiency.

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1. Introduction

Separation of pollutants from any liquid or gaseous continuum has always been a prime concern for clean environment. With the growing concerns about environmental sustainability, treatment of wastewater or exhaust air to remove pollutants has become an obvious need in many industries [1–3]. Thus, filtration plays key role in the treatment of pollutants. In the last few decades, scientists and engineers have used numerous materials ranging from wood dust, clays, metal mesh, porous ceramics and recently, polymer based membranes and membranes. Polymeric membranes have become very popular in the recent years due to their cost-effective manufacturing and flexibility in use [3].

There are many different techniques for the production of polymeric membranes and they have various architectures which are obviously related to their cost effective production and filtration efficiency. Most membranes involve the size-exclusion principle in order to separate pollutants of difference size scales [4]. Many research works have reported the importance of developing micro- and nano- porous membranes, utilizing techniques ranging from microfiltration to reverse osmosis, in order to separate most of the pollutants from air or water [4,5]. Among most influential techniques, phase inversion technology, axial drawing (uniaxial and biaxial) of films at their softening points, woven and non-woven fibrous

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membranes by electro spinning or melt-blown fibers [6–12]. In addition, production of membranes by foaming of polymers is also a well-known technique and has been applied as air, water and oil separating medium [5,13–19].

Polymeric foams, especially open-cell-foam-based membranes have been used intensively as separation membranes [5,13,14]. Hang et al. developed melt-extruded open cell foams of polycarbonates using super critical CO_2 [13]. Microcellular foam based membranes have been used in many separation applications, such as blood oxygenation, microfiltration and other separation process [5]. Polyurethane-based open cell membranes have been used as particle collectors from air. They have been very useful to separate particulate matters from air and as high volume sampling device for sampling airborne dust [15,16]. In addition, Jones investigated the use of foam as the facemask pre-membrane filter to collect dust particles in coalmines [17]. Foam-based membranes have also been used as water purification membranes. A recent investigation by Hariharan et al. reveals that foams made by a sol-gel method have nanoscale pores that can eliminate most of the pollutants from industrial effluents [19]. Another study shows that foam membranes incorporating silver nanoparticles can work effectively as antibacterial water filtration membranes [19]. Another important application of foam-based porous membranes is as battery separators [20]. Li et al. developed foamed PVDF-HFP porous membranes as a battery separator for lithium ion batteries [21].

It is important to mention that many research woks have reported the development of micro- to nano-cellular foams [22–27]. Aram et al. reviewed several techniques such as foaming by chemical blowing agents, foaming by physical blowing agents (e.g. gas), phase separation, etching, and leaching to micro- to nano- cellular foams [27,28]. However, creating open cell foam with submicron to nano scale pores, especially using chemical blowing agent, is still a challenge.

Baer et al. developed a miniaturized coextrusion and multiplication technique capable of producing materials incorporating thousands of layers/domains of multiple polymers to achieve unusual mechanical, optical, and energy storage properties [29–33]. Multilayer film/foams is one such material produced by coextrusion and multiplication technology containing alternating horizontal layers of solid and porous polymer layers [34,35]. Producing foamed materials with vertical rather than horizontal layers enables the transportation of substances through the membrane and the filtration of particulates from continuums. This is the first time we report the development of multilayer film/foams having thousands of vertical cellular layers.

This work presents an innovative approach to develop multilayer cellular membranes from multilayer film/foams having thousands of vertical layers. The cellular morphology and the micro-filtration behaviors of the cellular membranes have been discussed in detail.

2. Experimental

2.1. Materials

In this study, four different polymers were used to produce vertical layer film/foams. Low density polyethylene (LDPE, 501I from the DOW Chemical Co.), polypropylene (PP, H700-12 from Dow Chemical Company) with melt flow index (MFI) of 12 g/10 min (230 °C/2.16 kg), polyamide 6 (PA6, BASF Ultramid B 36 01) and polystyrene (PS, Dow 685D) was used as the separating material in the extrusion process. The bulk densities of each polymer, as provided by the suppliers, were 0.912, 0.896, 1.13, and 1.08 g/cm^3, respectively. Actafoam (AZ -130 Galata Chemicals) was used as the chemical blowing agent. The nucleating agent in the foam layer was 1 wt% Talc (Jetfine® 1H, IMERYS Talc). Polystyrene micro-particles with diameter of 10.4, 5.35, and 1.04 μm were purchased from Corpuscular Inc.

2.2. Processing & preparation of vertical layered multilayer film/foams

Two-component coextrusion with a series of layer multipliers was used to produce the vertical layered foamed membranes with desired pairs of polymers.

In order to create vertically oriented open-cell morphology in multilayer film/foam systems, multipliers are aligned vertically so that each foam layer is vertically exposed rather than being confined horizontally. During the coextrusion, the melt flow of two polymers merge into a horizontal layer feedblock, and then the two-layer-flow goes through a series of vertical multipliers to form an architecture that contains 2^n alternating vertical layers, where n is the number of vertical multipliers. The first extruder contains the foam layer polymer, chemical blowing agent (CBA) (Actafoam) and nucleating agent (Talc). The second extruder contains the film layer polymer. Fig. 1 gives a general overview of the two-component coextrusion and multiplication setup. The pump rate in both extruders are varied to change the volumetric composition of film and foam layers in each sample. Table 1 summarizes the vertical layer film/foams that have been produced and discussed in this paper. LDPE/LDPE film/foams with vertically oriented layers were chosen to visualize the layered morphology (Fig. S1). However, pairs of hard/soft polymers were chosen so that strain induced fractures could initiate in brittle phase, which is the foam cell wall materials, and could eventually open the cells for producing the open-cell membranes.

2.3. Post-processing strategies to produce open and interconnected pores

Post-extrusion drawing of film/foam was performed to produce the interconnected pore structures. Two different post-drawing techniques, uniaxial and biaxial drawing, were used to create through-pores in the film/foam composite systems.