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Highly ordered and robust honeycomb films with tunable pore sizes fabricated via UV crosslinking after applying improved phase separation

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ABSTRACT

Highly ordered hexagonal patterns of a commercially available polystyrene (PS) thin film are successfully fabricated via an improved phase separation method. A mixture of chloroform (ChL) and methanol (MeOH), which is used as a solvent/non-solvent pair, exhibits strong potential and high sensitivity for producing highly ordered honeycomb films with mono-dispersed and tunable pore sizes. It is demonstrated that a ChL/MeOH volume ratio of 90/10 is the optimal ratio for fabricating the highest quality of honeycomb films. The patterned film is further modified to enhance the solvent resistance as well as thermal stability through crosslinking the PS via deep UV irradiation. The convergence of cost effective, large-scale production and the robustness of highly ordered honeycomb film enables new applications for commercialization in the fields of microporous films and outdoor applications.

1. Introduction

Microporous polymeric films with highly ordered structures are of significant interest in current research due to their potential applications in the fields of microtemplates [1–3], membranes [4,5], organic optoelectronics [6–8], advanced electronics [9,10], biosensors [11,12], and tissue engineering [13,14]. For practical applications that contend with harsh environments, the use of porous films requires them to have solvent resistance and thermal stability. However, the polymers used in fabricating porous film are mostly soluble in common solvents and weak at high temperatures [15–19]. The crosslinking of the polymer matrix via UV irradiation has become the simplest and most environmentally friendly strategy that targets the fabrication of films robust against solvent and thermal effects. Nonpolar linear polystyrene (PS), which is a commercially available and cheap plastic, can be effectively crosslinked under deep UV irradiation at room temperature [20–23]. As a result, PS has become one of the most promising candidates for producing robust films. PS undergoes crosslinking, chain scission, and oxidation processes upon exposure to UV light; however, the effect of crosslinking dominates when an irradiation dose of 25 J/cm^2 is applied [21]. The crosslinking mechanism of PS is primarily attributed to the formation of macro-radicals as crosslink agents induced by hydrogen abstraction [21,22].

Honeycomb structures have been obtained from PS using the breath figure (BF) method [21,24–26]. However, the creation of highly ordered structures is only possible under highly humid environments after drop-casting the polymer solution onto the substrate surface, and the preparation conditions are strictly controlled due to the inherently hydrophobic properties of PS polymers [24]. These limitations are critical obstacles to commercially producing large-scale films. Recently, we developed a new strategy referred to as the "improved phase separation method" for preparing highly ordered honeycomb film from various starting polymers in ambient air environments, and the surface morphologies of the patterned films were effectively controlled through varying the solvent mixture compositions as well as modulating the experimental processing conditions [27,28]. In this paper, we apply this strategy in order to fabricate ordered honeycomb structures in PS and we thoroughly investigate the effect of the solvent compositions and experimental processing conditions on the surface morphology of the patterned films. Moreover, the crosslinked honeycomb structure, which is formed after applying the UV irradiation, is well

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preserved and powerfully resists organic solvents as well as elevated temperatures.

2. Experimental section

2.1. Materials

Commercially available PS (GPPS 15NFI) in pellet form was purchased from LG Chem Co. (Seoul, Korea); it was dried in a vacuum oven at 60 °C. Copper substrates with a thickness of 0.5 mm were purchased from 4Science (Korea). These substrates were washed with a 0.1 M sulfuric acid solution and distilled water followed by blow-drying in nitrogen gas prior to use. Chloroform (ChL) (anhydrous; with amylenes as stabilizers; 99.8%) and methanol (MeOH) (anhydrous; 99.8%) were purchased from Sigma–Aldrich (USA) and used as received.

2.2. Preparation of porous structures

In the first step, a homogeneous solution containing 10 wt% PS in ChL was prepared. Then, the polymer solution was coated onto the copper substrate via spin coating (1000 rpm for the first 10 s and 3000 rpm for the following 30 s); it was left in ambient air to completely evaporate the solvent, which resulted in the formation of a thin polymer film with a uniform thickness. For large area fabrications, other coating techniques can be applied, including bar or roll coatings. The binary mixtures of the solvent/non-solvent were prepared with different volume ratios of ChL and MeOH, and were stirred continuously for 24 h before use. The patterned porous structure was fabricated using the method available in the literature [27]. Briefly, the polymer film coated on the copper substrate was dipped into a mixture of solvent and non-solvent for 5 s using a dip-coater (E-flex, Korea). Then, the specimen was withdrawn from the solvent mixture and the residual solvent on the surface of the specimen was allowed to evaporate completely under ambient air conditions. The optimum dipping conditions were a dipping speed of 50 mm/min and a withdrawal speed of 60 mm/min. The humidity and temperature controller (TH-TG-1000, Jeio Tech, Korea) was used to precisely control the ambient humidity and temperature.

2.3. Crosslinking of honeycomb film

The crosslinking process was performed in an Oriel Flood Exposure System (Model 92521, Newport Corporation, USA) in air. The film was exposed to 220–260 nm UV light with a power density of 19.0 mW/cm^2 for 6 h. The distance between the UV source and film surface was 5 cm.

2.4. Solvent and thermal treatment

The solvent resistance of the crosslinked PS films was examined through soaking in common good solvents for PS, including chloroform and acetone. The thermal stability of the crosslinked films was characterized via heating to 250 °C on a hot stage (METTLER TOLEDO FP82HT, USA) in air. The temperature was increased at a rate of 10 °C/min and maintained at 250 °C for 2 h.

2.5. Characterization

The morphology of the obtained specimen was characterized using a field emission scanning electron microscope (FESEM; JSM-7000F, JEOL, Japan) and atomic force microscope (AFM; Autoprobe CP, Park Science Instruments, Korea). Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 EP Thermal Analyzer (Germany). The samples were heated from 25 to 600 °C at a rate of 10 °C/min. Fourier transform infrared (ATR-FTIR) spectra were obtained using a Nicolet Avatar 360 instrument (Thermo Fisher Scientific, USA). The static contact angle measurement was performed using a drop-shaped analyzer (Krüss DSA 100, Germany). Distilled water (DW) was used as the probe liquid for this measurement, and a minimum of five readings was averaged.

3. Results and discussion

3.1. Surface morphology of a typical honeycomb patterned film

The surface morphology of a typical patterned film, which was prepared using the improved phase separation method with a solvent/non-solvent volume ratio of 90/10 under an ambient air environment (i.e. RH of 55% and temperature of 25 °C), was characterized using field emission scanning electron microscopy (FESEM, Fig. 1(a) to (c)) and atomic force microscopy (AFM, Fig. 1(d) to (f)). In Fig. 1(a) and (b), a relatively large area and a perfectly ordered array of the hexagonal micropore domains are depicted, respectively. The mono-dispersed pore array was uniformly formed with a diameter of approximately 1.8 μm and an interval of approximately 1.6 μm. The fast Fourier transform (FFT) pattern, which is depicted in the inset of Fig. 1(a), further confirms the long-range hexagonally ordered array. The inset of Fig. 1(b) illustrates the surface morphology of the honeycomb film after peeling part of the top layer, and this demonstrates that each pore has a spherical jar shape with an internal diameter of 2.3 μm. Fig. 1(c) presents a cross-sectional image of the honeycomb film that exhibits a monolayer of pore arrays on the substrate surface. Each pore is closed at one end and they are isolated from each other. The thickness of the film was approximately 1.8 μm and a bottom thin layer inside the pore that is in contact with the surface substrate can be observed. For more insight into the geometry, the 2D and 3D AFM images are also presented in Fig. 1(d) and (e), respectively. As seen in Fig. 1(f), the scan profile at the cross-section of Fig. 1(d) further confirms the diameter, interval, and depth of the pores. In addition, the production of the honeycomb film has potential to be scaled up through exploiting solution coating techniques such as bar coating and continuous roll coating. A uniform honeycomb film with a dimension of approximately 30 cm^2 was prepared easily through following this strategy (SI, Figure S1).

3.2. Control of the surface morphology of the honeycomb patterned film

It has been reported that phase separation can be realized with the introduction of a non-solvent to the polymer solution [29,30]. When a non-solvent is used in conjunction with a solvent, it has dual roles of increasing the number of nucleation sites and reducing the crystallization time of the polymer through increasing the extent of the phase separation [27,28]. Accordingly, the non-solvent content can be expected to determine the aggregate size and pore volume of the resulting porous structure. Thus, the pore size, pore density (number of pores per unit area), and conformational entropy of the patterned film were comprehensively characterized at various compositions in order to investigate the influence of the ChL/MeOH compositions on the surface morphology.

Fig. 2 presents the FESEM images of the PS film surface prepared with different compositions of ChL/MeOH under an evaporation temperature of 20 °C and a relative humidity (RH) level of 60%. An experiment using only ChL without adding a non-solvent resulted in a pockmarked surface with few micropores, as seen in Fig. 2(a). This result implies that water might be condensed from the ambient air through solvents in the evaporation process, which is