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Porous polyurethane films having biomimetic ordered open pores: Indentation properties

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ABSTRACT

The dramatically improved indentation hardness and modulus of ordered porous films prepared by directional crystallization were reported herein, which to the best of our knowledge, have not been reported. The directional crystallization process of porous materials seems to have the unique advantage of strengthening along the pore direction. This processing technique provides freedom in the design of porous materials, as the pore direction can be engineered in an arbitrary direction. Anisotropic structures in such materials can be engineered to any direction by simply changing the temperature gradient of the surrounding polymer solutions.

Cellular materials from nature, such as porcupine quills, bird bones, and toucan beaks, have been adapted for use as high strength, lightweight materials with insulating properties [1–5]. Various foaming agents produce artificial cellular plastics, which have been used as the most common materials for protection and insulation [6]. The modern electrical industry also adapts the same methodology to protect integrated elements from external shock or deformation. Thin porous films are often inserted in between electrical elements that require excellent mechanical performance and thin film thickness. Unfortunately, common foaming agents for cellular plastics are not quite appropriate for this application, as they produce relatively large pores compared to the required film thickness, preferably less than 50 μm [7].

Freeze drying has been used as a common drying method for water soluble compounds and ceramic slurries for many decades [8–10]. Recently, this drying method was combined with the directional freezing (crystallization) technique, and as a result, biomimetic ordered cellular structures have been reported [11–13]. This technique has provided 3D control of pores and walls in graphene, composites, and polymeric materials [14–16]. If organic solvents are used that are crystallizable, this technique can be applied to most polymers [17]. The crystallization of solvents can be engineered to produce well-ordered biomimetic porous structures by carefully controlling the temperature gradients [18]. Through-thickness porous membranes have been developed from various polymers, which could be used as ideal thin films for protection [17,19]. However, the mechanical properties of thin polymer films having these ordered biomimetic pores have rarely been investigated.

This study explores the indentation properties of ordered porous thin films, which are critical for the protection and shock-absorbing performance, for the first time. Tensile or bending tests cannot reliably produce the basic mechanical parameters for protective thin film applications, as their stress conditions are different. Furthermore, compression tests are not quite feasible due to their thin nature. Thus, a micro-indentation test is a reliable solution to probe the basic mechanical properties useful for protection performances [20,21]. Because of the micro-porous nature, the size of the indenter should be sufficiently large compared to the pore size, and therefore nano-indentation is not adequate. Because of the high porosity and the micron size of the pores of these foams, indentation requires a relatively large indenter and accurate measurement of a small indentation force. These quite unusual indentation conditions required us to build our own micro-indentation system. We performed micro-indentation tests on these materials using a relatively large 2-mm spherical indenter and a sensitive load measurement system (readability 9.8 μN). Polyurethane (PU) was selected as a typical material for thin and light foams [22,23].

Ordered pores were first produced by directional crystallization of a solvent and subsequent solvent removal by sublimation. The PU solution was introduced to the top of a liquid nitrogen reservoir

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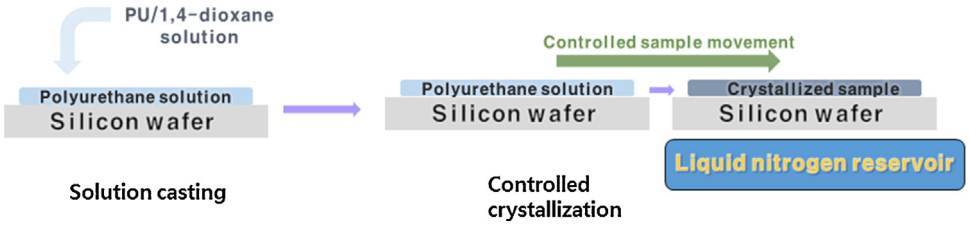

Fig. 1. Preparation of porous PU films by directional crystallization of a solvent.

at a speed of 200 μm/s (Fig. 1) [24]. As a result, crystal nucleation started from the region closest to the liquid nitrogen reservoir and propagated into the rest of the sample. The direction of the crystal growth lay between the direction of the sample movement and the tangential direction to the liquid nitrogen reservoir, resulting in a slanted direction. A temperature gradient in the polymer solution also developed in the same direction. Therefore, crystallization propagated along the slanted direction, from the bottom to the top, and from the one side close to the reservoir to the other side. As we previously reported, this condition greatly reduced the strain mismatch from cryostress and desiccation stress [24]. As a result, defect-free thin porous films could be prepared.

The crystallization of solvent molecules by cooling along a temperature gradient separates a PU solution into crystal phases and cryoconcentrated phases [25,26]. Since the solubility of polymer chains in the crystal phases of the solvent is extremely poor, the majority of polymer chains are expelled into the cryoconcentrate phases [18]. The crystal phases become pores after sublimation. Therefore, the content of the solvent is approximately the porosity of the final materials, which is 0.9 (0.89, if the densities of PU and dioxane are considered to be 0.9 and 1.033 g/cm^3) [19].

The crystal phases of the solvent should be highly connected due to the low possibility of homogeneous nucleation, compared to that of heterogeneous nucleation, common in crystallization [27]. Thus, connected open pores generally form [18]. The cross-sectional images of Fig. 2 show the ordered structures of pores and their connectivity. The major line structures are slanted, which

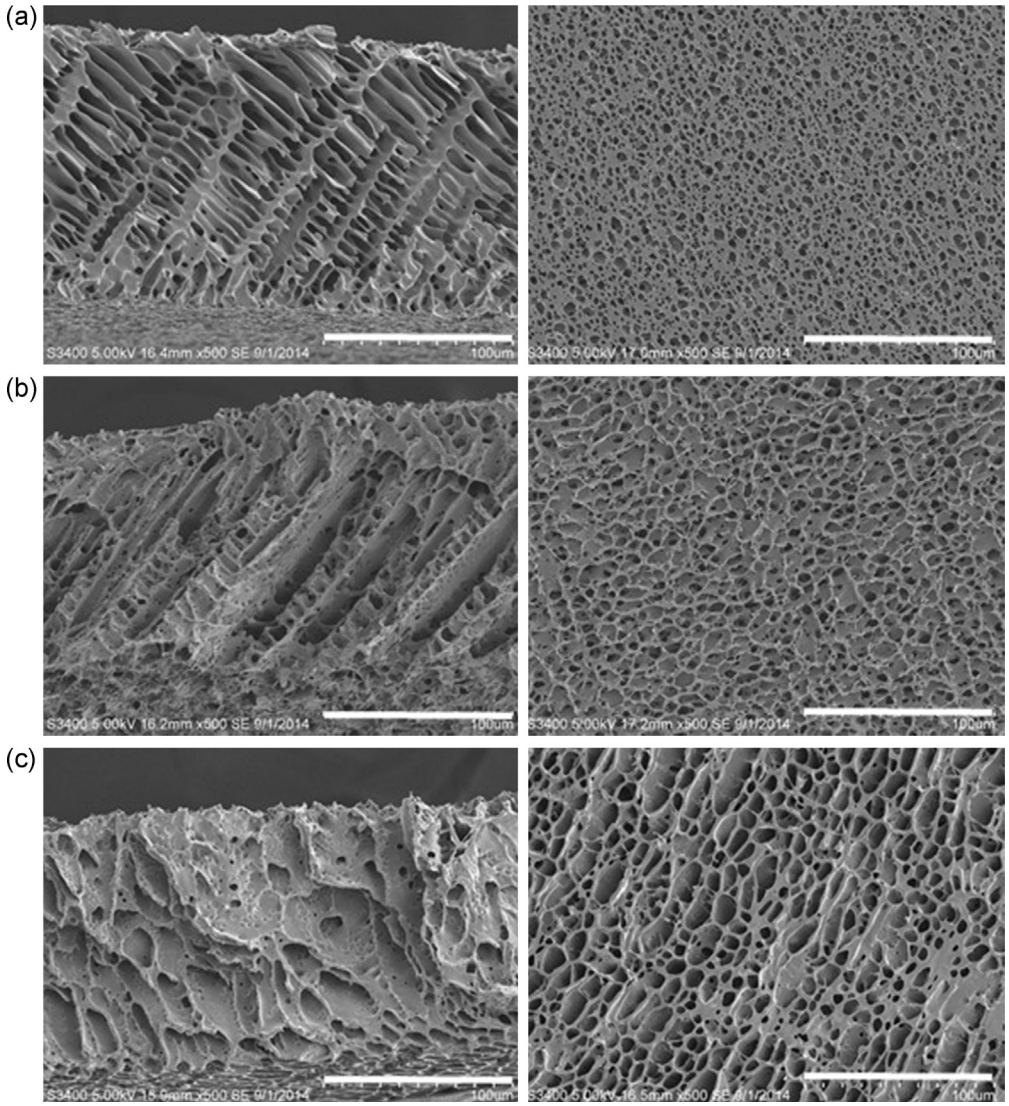

Fig. 2. SEM images of cross-sections (left) and surfaces (right) of porous PU films with different hard segment contents: (a) 50%, (b) 37%, and (c) 25% (scale bar = 100 μm).