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A Biomimetic Approach for Creating Thermally Stable Polyimide-coated Honeycomb Films

Hiroshi Yabu,*[1,2] Yuki Nakamichi,[3] Yuji Hirai,[1] and Masatsugu Shimomura[1,4,5]
[1]*Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University,*
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577
[2]*Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST),*
5 Sanbancho, Chiyoda-ku, Tokyo 102-0075
[3]*Graduate School of Engineering, Tohoku University, 6-6 Aramaki-aza-Aoba, Aoba-ku, Sendai, Miyagi 980-8579*
[4]*WPI-Advanced Institute for Materials Research (AIMR), Tohoku University,*
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577
[5]*Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST),*
4-1-8 Honcho, Kawaguchi, Saitama 332-0012

(Received March 22, 2011; CL-110245; E-mail: yabu@tagen.tohoku.ac.jp)

In this paper, we show a simple biomimetic approach for fabricating thermally stable porous films with multilayered structures by mimicking beetle wings. Honeycomb-patterned porous films (honeycomb films) of poly(1,2-butadiene) (PB) were successfully prepared by casting chloroform solution of PB and amphiphilic polymer under humid conditions. After formation of layer-by-layer (LbL) film of poly(amic acid) (PAA), which is a precursor of polyimide, and poly(allylamine hydrochloride) (PAH) onto the surface of PB honeycomb films, PAA was successfully converted to polyimide by chemical imidization. After imidization, the LbL-coated honeycomb films have high thermal stability.

Recently, biomimetic approaches are emerging as a novel concept for creating functional and high-performance materials from limited resources by a few fabrication steps.[1] In nature, there are many examples of functional materials including superhydrophobic lotus leaves,[2] antireflective moth eyes,[3] high adhesive gecko hands,[4] and so on.[5] By mimicking their surface structures, artificial superhydrophobic surfaces,[6] moth eye coatings,[7] and artificial dry adhesives[8] have been invented. In terms of mechanical, thermal, and chemical stabilities, multilayered structures were often found in nature, too. Nacre shells,[9] which consist of multilayered structures of calcium phosphate crystals and proteins, have high mechanical stability. Ikkala et al. reported that nacre-mimetic inorganic–organic composite films consisting of clays and polymers with high thermal and mechanical stabilities.[10] The multilayered structures of insect's cuticles also show high mechanical toughness.[11] Especially, beetle wings have a unique multilayered structure, which is stacked cuticle layers on microporous matrixes, to achieve desired weight and mechanically toughness.[12]

Breath figure is a useful bottom-up approaches that allow fabricating microporous polymer films (honeycomb films) having uniform-sized and hexagonally arranged pores ranging from submicrometer to micrometer scale.[13] Water microdroplets condensed on the surface of hydrophobic polymer solution owing to evaporation cooling caused by solvent evaporation. After complete evaporation of solvent and template water droplets, microporous polymer films are formed. Some efforts have been made to improve thermal and chemical stabilities of honeycomb films. Crosslinking is a promising way to improve stability of honeycomb films. Bunz et al. reported the photocrosslinking of honeycomb films of PPV derivative.[14] We have also reported that stable polymer films can be fabricated by photocrosslinking of honeycomb films of photocrosslinkable oligomers.[15] Karthaus et al. reported chemical crosslinking of honeycomb films of poly(styrene-*co*-maleic anhydride) or poly(cinnamoyl acrylate) and their high chemical stability.[16] Gover et al.[17] and Ejima et al.[18] show the preparation of robust carbon honeycomb films by calcination of polymer. By using engineering plastics, thermally and chemically stable honeycomb films can be prepared. Since engineering plastics have thermal and chemical stability, they are not dissolved in any organic solvents used in the honeycomb film preparation. We have reported that polyimide honeycomb films can be prepared by casting poly(amic acid) and lipid complex and imidization.[19]

In this paper, we show a simple biomimetic approach for fabricating thermally stable porous films with multilayered structures by mimicking beetle wings. To create multilayered structures onto honeycomb films, we used layer-by-layer (LbL) self-assembly.[20] LbL self-assembly is one of the most well-known coating methods that provide thin films consisting of alternate assembly of polycations and polyanions on solid surfaces. This surface coating allows modifying the surface and chemical properties of honeycomb films. LbL films of poly(amic acid) (PAA), which is a precursor of polyimide, and poly(allylamine hydrochloride) (PAH) were prepared on poly(1,2-butadiene) (PB) honeycomb films. After conversion of PAA to polyimide by chemical treatment, the thermal stabilities of the film were evaluated.

The synthesis of an amphiphilic copolymer has been described elsewhere.[21] PB (RB820) was kindly supplied by JSR, Co., Ltd., Japan. Honeycomb films of PB and the amphiphilic copolymer were prepared according to the literature.[22] Typically, chloroform solution of PB and the amphiphilic copolymer (mixing ratio = 10:1, $10\,\mathrm{mg\,mL^{-1}}$) was cast on a glass substrate ($400\,\mathrm{mm} \times 110\,\mathrm{mm}$) under applying humid air (relative humidity ≈90%). After complete evaporation of solvent chloroform and template water droplet, the film was cut into $10\,\mathrm{mm} \times 20\,\mathrm{mm}$ pieces with glass substrate.

Schematic illustration of LbL process onto PB honeycomb films is shown in Figure 1a. Poly(amic acid) (PAA, poly(pyromellitic dianhydride-*co*-4,4′-oxydianiline)) was purchased from Aldrich, Co., Ltd., USA as a 15 wt % solution in *N*-methyl-2-pyrrolidone (NMP). PAA was reprecipitated in aceto-

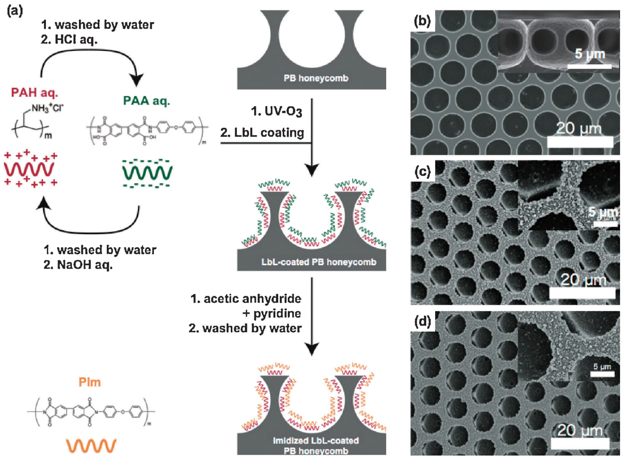

Figure 1. Schematic illustration of LbL and imidization process of PAA on PB honeycomb films (a), SEM images and closeup SEM images of honeycomb films (b), LbL-coated honeycomb films (c), and imidized LbL-coated honeycomb films (d), respectively.

nitrile (EP, Wako Chemical Industry, Co., Ltd., Japan), and white precipitate was removed by centrifugation and dried in vacuo.

The PB honeycomb films were treated with UV-O_3 for 1 min to make their surface hydrophilic during which anionic groups were formed on their surface. Before soaking in PAH aq., the honeycomb film was treated in ethanol, and then the film soaked in water to wet the surface. After wetting the surface, the film was soaked in PAH aq. for 20 min and the film was then washed with water for three times. The film was soaked in PAA aq. for 3 min after treating the film with HCl aq. (pH 4) for 10 s. After washing with water three times, the film was treated with NaOH aq. (pH 10) for 10 s. After 50 cycles of these procedures, the LbL film of PAH/PAA was formed on the PB honeycomb film.

Imidization of LbL-coated honeycomb films was performed by immersing the films in a solution of acetic anhydride and pyridine (1:1) for 12 h.[23] The film was washed with ethanol.

The surface structures of the as prepared, LbL-coated, and imidized LbL-coated PB honeycomb films were observed by using a field emission scanning electron mictroscope (FE-SEM, S-5200, Hitachi, Japan). For FE-SEM observation, the sample was cut into 1 mm × 2 mm specimen, and then Os was sputtered on the surface of the specimen. The imidization of LbL-coated honeycomb film was confirmed by Fourier transform infrared spectroscopy (FT-IR, FT-6000, Jasco, Japan). The film was embedded in a NaBr pellet for FT-IR spectroscopy.

Honeycomb films of PB with uniform-sized pores were successfully prepared as shown Figure 1b. The average pore size of the film was 10 µm. From the cross-sectional SEM image, the PB honeycomb films had double-layered structures supported with pillars (inset SEM image of Figure 1b). The surface of the PB honeycomb film was smooth; however, granular aggregations were observed on the surface of the LbL-coated honeycomb film (Figure 1c). This roughness increase was caused by formation of LbL deposition of the polyions. After imidization treatment, the structure of the film was not deformed (Figure 1d). From the cross-sectional image of the film, the thickness of the film was ca. 100 nm after deposition 50 cycles of polyions (see Supporting Information).[24]

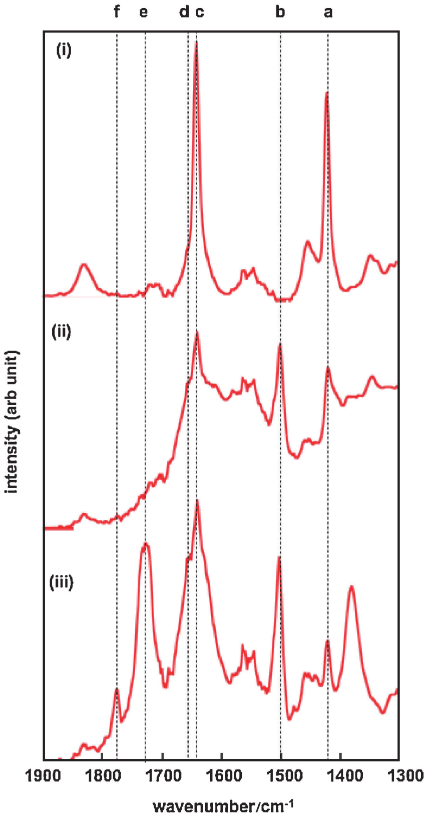

Figure 2. FT-IR spectra of as prepared (i), LbL-coated (ii), and imidized LbL-coated (iii) honeycomb films, respectively.

The imidization of LbL-coated honeycomb film was confirmed by FT-IR spectroscopy. Figure 2 shows spectra of as-prepared (i), LbL-coated (ii), and imidized LbL-coated honeycomb films (iii), respectively. Characteristic absorption bands of PB at 1640 (c, $\nu_{(C=C)}$) and 1410–1460 cm^{-1} (a, $\delta_{(C\text{–}H\ \text{in-plane})}$) were observed on the absorption spectrum of as-prepared honeycomb film. After deposition of LbL film, $\delta_{s(N\text{–}H)}$ of PAH (b, 1500 cm^{-1}) and $\nu_{s(C=O\ \text{amide})}$ of PAA (δ, 1650 cm^{-1}) were clearly observed. From this result, the LbL film of PAH/PAA was successfully formed on the honeycomb film. Characteristic absorption of $\nu_{(C=O\ \text{imide})}$, which is proof of formation of polyimide, was observed at 1725 (e) and 1770 cm^{-1} (f) in the spectrum of the imidized LbL-coated honeycomb film.

The film was heated on a hot stage to evaluate thermal stability of the film. Before heating, the PB honeycomb film has double-layered structure supported by pillars (inset SEM image of Figure 1b). Since the glass-transition temperature (T_g) of PB is 92 °C, the surface structure of the honeycomb film disappeared after heating at 100 °C for 1 h (Figures 3a and 3b). On the other hand, the surface structure of LbL-coated honeycomb film was kept at 250 °C (Figures 3c and 3d). From the cross-sectional SEM image (Figures 3e and 3f), the thickness of the film decreased to less than half of the original size due to the deformation of thin pillar portions. Surprisingly, the three-dimensional structure of imidized LbL-coated honeycomb film was retained after chemical imidization. The LbL film containing rigid and thermally stable polyimide supports the surface

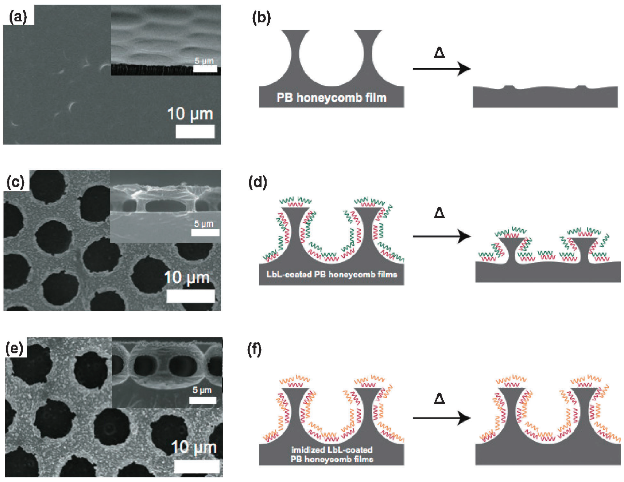

Figure 3. SEM images and schematic illustration of honeycomb films (a), (b); LbL-coated honeycomb films (c), (d); and imidized LbL-coated honeycomb films (e), (f) after heat treatment, respectively.

structure of the honeycomb films, and as a result, the three-dimensional structure was retained.

We show a simple formation of thermally stable polyimide-coated honeycomb films by using the LbL self-assembly technique. After formation of LbL film of PAH and PAA onto the surface of PB honeycomb films, PAA was successfully converted to polyimide by chemical imidization. After imidization, the LbL-coated honeycomb films have high thermal stability. It is noteworthy that the polyimide LbL coating makes the honeycomb film of commodity polymers robust. This simple biomimetic coating process provides a novel way to create high-performance separation membranes, cell-culturing substrate, and so on.

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24 Electronic Supporting Information (ESI) available: cross-sectional SEM image of polyimide-coated honeycomb films. ESI is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.