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# Optimal processing for hydrophobic nanopillar polymer surfaces using nanoporous alumina template

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ABSTRACT

A highly uniform and hydrophobic nanopillar film was fabricated by nanoimprinting using the AAO template as a mold in this study. Nanoporous anodic aluminum oxide (AAO) templates are fabricated using an anodization method. The mean diameters of nanoporous anodic aluminum oxide templates are 100 nm and 200 nm by various processing parameters of the anodization method. The surface properties of the molded plastic thin film are discussed using various nanoimprinting process parameters. The results reveal that the contact angles of the molded plastic thin film with the nanopillar exceed those without the nanopillar. The molded plastic thin films with a nanopillar and a hydrophobic surface are formed, and their contact angles exceed 120°. The results also appear that the hydrophilic property of molded plastic thin film without nanopillar changes to hydrophobic property of molded plastic thin film with nanopillar.



## 1. Introduction

Anodic aluminum oxide (AAO) films are formed by anodization of elemental aluminum (Al) in suitable acidic or basic electrolytic solutions. The AAO film is fabricated with many nanopores. Pore diameter and cell size, measured as the distance between the centers of two neighboring pores, is controlled by applying a pore-widening treatment, in which pores are etched chemically [1,2]. Because of their unique thermal, mechanical, structural, optical, and chemical properties, AAO films have garnered considerable interest for various applications, including separation [3], catalysis [4], biosensing [5], adsorption [6], photonics [7], energy storage [8], and drug delivery [9]. Masuda [10] adopted anodization approaches to fabricate porous metallic membranes for nanoimprinting. Tapered holes were formed by repeated anodization with a pore-widening scheme. A polymer surface was then achieved by filling the tapered holes. The polymer with this unique surface geometry had anti-reflective properties. Notably, AAO films have been used as templates in metal plating processes. Electroplating nickel (Ni) is a well-known metal plating process. This approach can control numerous properties, including the structure, hardness, and electrical and magnetic properties by altering plating conditions and metal content in the plating solution, and by heat treatment [11]. Uniquely shaped functional nanomaterials, such as those with a conical geometry, have recently attracted interest [12]. Nickel particles and films with a localized nanocone structure, a nanoconical film, are useful in nanostructured molds and functional nanomaterials.

Puukiliainen et al. [13] investigated the surface properties of polyethylene (PE) and polypropylene (PP) melts blended with 2.0 wt% perfluoropolyether (PFPE). They fabricated nanoporous mold by anodizing aluminum in polyprotic acid. Both polyethylenes formed blends with PFPE and exhibited improved hydrophobic properties. Puukiliainen et al. [14] prepared superhydrophobic polyolefin surfaces by simultaneous microstructuring and nanostructuring. A static contact angle between PP and water at 165° was obtained. Koponen et al. [15] achieved patterning using a nanoporous AAO membrane as a mask for injection molding or imprinting, using cyclo olefin copolymer (COC) and polyvinyl chloride (PVC) as molded materials. The contact angles of PVC and COC smooth surfaces were roughly 89–90°. The contact angles of COC microbumps and nanopillars were 120–140°. The COC surface on which nanostructures were superimposed on microstructures was hydrophobic. Chan and Guo [16] developed a hard mold to imprint the polymer film (polycarbonate (PC), polymethyl methacrylate

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(PMMA), and polystyrene (PS)) directly to form optical waveguides. This technique is a cost-effective method for fabricating integrated photonic circuits based on microring resonators. Yanagishita et al. [17] developed anti-reflection (AR) structures of a polymer, polyethylene terephthalate (PET), composed of an ordered array of holes with tapered shapes formed by imprinting using a Ni mold prepared from anodic porous alumina. The transmittance of the PET sheet with the AR structure was higher than that of the PET sheet with a smooth surface.

Many microplastic embossing process applied to the micropattern including hybrid extrusion rolling embossing [18], gas-assisted embossing [19], UV molding method [20], micro dispensing combined with hot embossing process [21], and micro electrical discharge machining (μ-EDM) combined with hot embossing process [22]. Nanoimprinting process has been attracting attention from industrial company because it is used to mass-produce nanostructure product at low cost and high throughput. The mold in nanoimprinting process must be in direct contact with the replication material. So the de-molding stage is the very important on nanoimprinting process. Okada et al. [23] developed a mold coated with an antisticking layer (fluorinated self-assembled monolayer (F-SAM)) for preventing material from adhering to it. The results show that the F-SAMs annealed at 500 °C had a sufficiently large releasing effect in nanoimprinting. Song et al. [24] used the 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane ($CF_3$-$(CF_2)_7$-$(CH_2)_2$-$SiCl_3$ or FDTS) material to investigate the anti-adhesion for UV-nanoimprinting process. Their results revealed that the FDTS is an excellent and promising release agent material for UV-nanoimprinting process.

Chen et al. [25] developed that the ferroelectric vinylidene fluoride-trifluoroethylene copolymer [P (VDF-TrTE)] film with ultrahigh nanodot density has been successfully fabricated a facile, high throughout, and cost-effective method of imprinting by using disposable anodic aluminum oxide (AAO) mold for nano-imprinting process. Cauda et al. [26] prepared arrays of one-dimensional polymeric nanowires showing piezoelectric features by template-wetting two distinct polymers (PVDF, PVTF) into anodic porous alumina (APA) membranes. The results revealed that the crystallization of bath polymers into a ferroelectric phase is directed by the nanotemplate confinement. Hong et al. [27] fabricated, poled, and characterized PVDF-TrFE nanograss structures with aspect ratios up to 8.9 by nanoimprinting using a silicon nanograss mold. The results showed that the piezoelectricity of the developed PVDF-TrFE nanograss structures was 5.19 times larger than that of the PVDF-TrFE flat thin films. Öztürk et al. [28] indicated that the ZnO nanowires had been fabricated using an anodized aluminum oxide (AAO) template by a cathodically induced sol–gel method. The result appeared that the high ordered ZnO nanowire arrays are approximately 70 nm in diameter and 10 μm in length with a high aspect ratio of 142. Liu et al. [29] showed that the Pt@$CoAl_2O_4$ inorganic peapod nanostructures, which consist of well-defined Pt nanoparticles (NPs) encapsulated in continuous $CoAl_2O_4$ nanoshells, were realized by electrodeposition of Co/Pt multilayered nanowires (NWs) into nanoporous anodic aluminum oxide (AAO) membranes and subsequent solid-state reaction at high temperature. Liu and Pippel [30] reported that the synthesis of low-platinum-content quaternary PtCuCoNi nanotubes by means of template-assisted, one-step electroposition (using the porous anodic aluminum oxide as the template) and testing of stability of suitability of these hollow multimetallic nanotubes as effective oxygen reduction reaction electrocatalysts. Liu et al. [31] indicated that the nanoporous $Pt_{46}Ni_{54}$ nanowires were prepared by electrodeposition of $Pt_{46}Ni_{54}$ alloy into an anodic aluminum oxide (AAO) membrane, followed by a mild dealloying treatment. Their results showed that a remarkably enhanced electrocatalytic activity toward methanol oxidation and good $H_2O_2$ sensing properties.

The aim of this study is to identify an effective and rapid mass-production method for plastic thin films. The aim of this study is also to emphasize the hydrophilic property of flat plastic thin film to change to the hydrophobic property of plastic thin film with nanopillar. In this study, a concave, nanoporous AAO template is adopted as a mold for nanoimprinting to fabricate a plastic thin film with a convex nanopillar nanostructure. The aim is to elucidate the surface properties on the nanopillar of the plastic thin film for various nanoimprinting parameters.

## 2. Experimental

An AAO template (concave) with localized conical pores was formed by repeated anodization and pore-widening processes, during which the two anodization steps were alternated. Each anodization step was short while manufacturing cones with low aspect ratios (cone height divided by cone base diameter). A conical AAO template with a low aspect ratio can be applied in fabricating several functional nanomaterials. This template can be used in electrochemical deposition, sol–gel dipping, or an evaporation process. The low aspect ratio of pores enables easy material deposition. The materials tend to deposit at the pore top, such that the pore bottom is not filled. This worsens as the pore aspect ratio increases. A 99.99% pure aluminum sheet ($100 \times 20 \times 10\,mm^3$; Wako Pure Chemical Industry, Ltd., Taiwan) was electrochemically polished in a solution of 95% $C_2H_5OH$ and 60% $HClO_4$ at a ratio of 4:1. This specimen was utilized to fabricate a conical AAO template following ultrasonic cleaning in ethanol and pure water. The specimen and a carbon electrode were the anode and cathode, respectively. The aluminum was anodized at 40 V or 60 V in a 0.3 M oxalic acid solution at 20 °C. To fabricate the AAO template, anodization for 1 h was applied to generate a hexagonally ordered pore array. The AAO film was dissolved in a solution of 6 vol% phosphoric acid and 1.5 wt% chromic acid. The substrate was then anodized using the same solution and voltage to produce uniformly sized pores. The pores were then widened by chemical etching, and the substrate was once again anodized under the same operating conditions. At this time, pores were tapered; the interior of each pore was a two-step structure. To obtain the desired inverted conical structure, each step in the anodization and pore-widening process was performed twice. Each anodization step was at 9 °C and 40 V or 60 V in the same solution. Anodization time was 25 s in the first step and 20 s in each subsequent step. During the pore-widening treatment, the specimen was dipped in a 5 vol% phosphoric acid solution at 30 °C for 12 min. The experimental results show that the mean diameter of nanoholes in AAO where 100 nm and 200 nm using anodized voltage of 40 V and 60 V on anodized oxidation.

Specimen morphology was observed by field emission scanning electron microscopy (JSM-6700F; JOEL, Japan). The cross sections of AAO templates were prepared by bending the aluminum until the substrate fractured, revealing the template cross section. The AAO film specimen was coated by platinum sputtering prior to observations. The detailed specimen morphology was observed using atomic force microscopy (Nanosurf Mobile S; Swiss). Prior to replication, the AAO template was self-assembled to form an anti-adhesive monolayer (1H, 1H, 2H, and 2H-perfluorodecyltrichlorosilane, FDTS) by vapor phase deposition, and minimization of AAO template surface energy, which is required for easy de-molding of the plastic thin film from the AAO template.

After the AAO template was formed, a nanoimprinting machine (NIL-3.0 Imprinter; Obduct AB, Sweden) performed imprinting. Fig. 1 shows the process from AAO template fabrication to nanoimprinting. The imprinting process parameters were imprinting temperature, pressure, time, and de-molding temperature. Table 1