

Modification of cycloolefin copolymer and poly(vinyl chloride) surfaces by superimposition of nano- and microstructures

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Abstract

Cycloolefin copolymer (COC) and poly(vinyl chloride) (PVC) surfaces were patterned with nanopillars or with microbumps on which nanopillars were superimposed. The area of patterned surfaces was several square centimeters. Patterning was achieved by applying nanoporous anodized aluminum oxide (AAO) membrane as a mask in injection molding or imprinting. Nanostructures superimposed on microstructures were achieved by patterning the AAO mask with microstructures before anodization. Micro- and nanometer-sized structures could then be transferred simultaneously to polymer surfaces. Structures were characterized by SEM, AFM, and contact profilometry. The effect of different-sized structures on properties of the polymer surface was studied by contact angle measurements. Relative to the smooth surface, the increase in water contact angle on a COC surface with nanostructures superimposed on microstructures was up to 50°.

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1. Introduction

Micrometer- and nanometer-sized surface structures affect optical and wettability properties of the solid surface. Surface structures can suppress surface reflectivity [1], while increased surface roughness of hydrophobic material enhances water repellency, so that with sufficient roughness even a superhydrophobic surface is formed. A superhydrophobic surface can be defined as a water-repellent solid surface whose water contact angle (θ) is over 150° and sliding angle low. Such a high contact angle cannot be achieved through modification of chemical composition of the smooth surface but rough topography is essential in achieving superhydrophobicity [2,3].

Superhydrophobic surfaces have self-cleaning properties as best exemplified in the leaves of the lotus plant [4,5]. The self-cleaning properties derive from the hierarchical micrometer- and nanometer-sized structures. Micrometer-sized papillae are covered with nanometer-sized epicuticular wax crystalloids.

Although the wax crystalloids are not highly hydrophobic in themselves ($\theta = 100^\circ$), the combination of micro- and nanometer-sized structures induces high water contact angle on the surface. The intricate structure causes air to be enclosed between the wax crystalloids and a composite surface is formed. Water drops are unable to penetrate into the composite structure and wet the surface, but instead they roll off the surface, taking contaminating particles with them [6].

The superhydrophobicity and self-cleaning properties of lotus leaves can be mimicked by creating a structure that traps air under drops on a hydrophobic surface, or an already structured surface can be modified by materials with low surface free energy. The versatility of polymer materials has created considerable research interest in superhydrophobic polymer surfaces. Since many polymers are naturally hydrophobic, mere surface roughening is often sufficient to achieve superhydrophobicity. Superhydrophobic properties have been reported for porous polypropylene [7], fluorinated polypropylene [8] and rough poly(tetrafluoroethylene) [9] surfaces and for porous polyelectrolyte films with SiO₂ nanoparticles [10]. Polyether [11] and poly(dimethylsiloxane) [12] replicates of lotus leaves with superhydrophobic and self-cleaning properties similar to

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the lotus have been fabricated. The artificial lotus structures were achieved by evaporating polymer solvent under controlled conditions. Water contact angles of 161° and 173° have been achieved on low-density polyethylene [13] and polycarbonate [14] surfaces containing micro- and nanometer-sized structures of floral shape.

The fabrication of large superhydrophobic polymer surfaces in a one-step process is required to enable the application in large-scale processes. With present polymer processing methods, the feasible approach is to fabricate a mask that can be applied in injection molding or imprinting. In order to mimic the surface structure of lotus leaves the mask should contain the superimposed micro- and nanometer-sized structures.

Anodized aluminum oxide (AAO) has a hexagonally ordered nanoporous structure, which self-organizes during anodization of aluminum [15,16]. Anodization parameters can be adjusted to achieve the desired pore diameters and interpore distances [17,18]. The self-organization of the structure makes possible the fabrication of large surfaces with ordered nanopores. Since nanopores can be formed on curved surfaces, microstructured aluminum can be covered with nanostructures. AAO masks have been used in imprinting nanometer-sized pillars ranging in size from 10 to 250 nm on polymer and metal surfaces [19,20]. Our research group has earlier reported the fabrication of well-arranged, high aspect ratio nanopillars on polyolefin surfaces using AAO as a mold insert during injection molding [21].

The aim of the present study was to modify the surface properties of polymer surfaces by patterning them with micro- and nanometer-sized structures. A fabricated AAO mask with microdepressions was applied in simultaneous micro- and nanometer-sized polymer patterning during injection molding and imprinting. The effect of nanopillars alone was studied as well. The surface properties of the patterned polymer surfaces were investigated by measurements of water contact angles. Polymers chosen for patterning were cycloolefin copolymer (COC) and poly(vinyl chloride) (PVC).

2. Materials and methods

2.1. Fabrication of AAO mask

Aluminum foil (0.25 mm thick, 99.997% Al, Puratronic[®], Alfa Aesar) was cut into the desired shape and degreased in acetone. Degreased Al foil was electropolished in HClO₄:EtOH mixture (1:8) using platinum foil as a counter electrode. The electropolishing current was 2.7 A and the time was 2 min 15 s. The foil was rinsed with deionized water.

The back-side of the dry and electropolished aluminum foil was protected against anodization with nail polish (Maybel-line). Anodization was carried out at constant 40 V voltage in 0.3 M oxalic acid, at 3 °C for 10 or 24 h.

After anodization the nail polish on the back side was removed with acetone, and the anodized side, now with nanoporous structure, was covered with nail polish to protect it during removal of the unreacted aluminum and barrier layer. The native oxide layer was removed from the aluminum surface with 10% NaOH, after which the unreacted aluminum was removed with 0.5 M CuCl₂ solution by rubbing with a cotton stick. Addition of two or three drops of HCl to the CuCl₂ facilitated the removal. The barrier layer was removed by soaking the AAO membrane in 5% H₃PO₄ solution at 30 °C for 80 min. After barrier layer removal the nail polish was removed with acetone and the membrane was soaked in deionized water for 30 min to prevent corrosion of the pore walls.

For achieving combined micro- and nanometer-sized structures, the aluminum foil was microstructured before anodization. Microstructure was imprinted on the foil by a hydraulic press (COMPAC EP 40-1) with steel mesh (ISO 3310-1 AISI314L, Cemic Ltd.) of size 40 μm. After leveling of the mesh with a pressure of 48 MPa for 4 s, it was imprinted on the electropolished aluminum with a pressure of 190 MPa for about 13 s. The mesh was removed and the microstructured aluminum was anodized as described above.

AAO masks used in polymer patterning were fabricated by gluing the AAO membrane onto a 0.5-mm thick steel plate with thermostable epoxy glue (Duralco 4703, Cotronics). The side from which the barrier layer was removed and where the structure was more ordered was facing upwards.

2.2. Fabrication of patterned polymer samples

PVC (S-98, Dynea) and 3 wt.% liquid stabilizer (Therm-Chek[®] 7500L, Ferro) were blended in a Henschel mixer (FM 10 L, 800726). When the temperature had been raised to 60 °C, 20 wt.% plasticizer (Benzoflex[®] 2160, Velsicol or Hexamol[®] DINCH, BASF) was added gradually. Mixing was continued until the temperature rose to 80–90 °C and the blend was allowed to cool to room temperature.

PVC-stabilizer-plasticizer blends were granulated with a DSM Midi2000 extruder and a grainer. Granulated blends were injection molded with an Arburg Allrounder 270S 350-150 injection molding system to achieve smooth PVC samples.

Smooth and patterned COC (Topas 5013X5 FS, Ticona) samples and patterned PVC samples were prepared by injection molding with a DSM Midi2000 extruder—microinjection molding system. In the case of the patterned samples, AAO

Table 1
Injection molding parameters for polymer samples

Sample	Screw temperature (°C)	Melt temperature (°C)	Feed temperature (°C)	Mold temperature (°C)	Screw speed (rpm)
Patterned PVC	175	163	163	40–55	65
Smooth COC	265	241	240	95	80
Patterned COC	283	259	260	95	80

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