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Superhydrophobic elastomer surfaces with nanostructured micronails

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ABSTRACT

New approaches to the fabrication of microstructures of special shape were developed for polymers. Unusual superhydrophobic surface structures were achieved with the use of flexible polymers and hierarchical molds. Flexible polyurethane—acrylate coatings were patterned with microstructures with use of microstructured aluminum mold in a controlled UV-curing process. Electron microscope images of the UV-cured coatings on polymethylmethacrylate (PMMA) substrates revealed micropillars that were significantly higher than the corresponding depressions of the mold (even 47 vs. 35 μm). The elongation was achieved by detaching the mold from the flexible, partially cured acrylate surface and then further curing the separated microstructure. The modified acrylate surface is superhydrophobic with a water contact angle of 156° and sliding angle of <10°.

Acrylic thermoplastic elastomers (TPE) were patterned with micro—nanostructured aluminum oxide molds through injection molding. The hierarchical surface of the elastomer showed elongated micropillars (57 μm) with nail-head tops covered with nanograss. Comparison with a reference microstructure of the same material (35 μm) indicated that the nanopores of the micro—nanomold assisted the formation of the nail-shaped micropillars. The elasticity of the TPE materials evidently plays a role in the elongation because similar elongation has not been found in hierarchically structured thermoplastic surfaces. The hierarchical micronail structure supports a high water contact angle (164°), representing an increase of 88° relative to the smooth TPE surface. The sliding angle was close to zero degrees, indicating the Cassie–Baxter state.

1. Introduction

The wettability of a solid surface is related to the surface energy of the material and surface roughness on micro- and nanometer scale [1,2]. High surface roughness of a hydrophobic material enhances the water repellency, while hierarchical roughness may even create a superhydrophobic surface, with the self-cleaning effect of the lotus plant [3–5]. Hydrophobicity is usually explained by the theories of Wenzel and Cassie—Baxter, which describe relations between a rough hydrophobic surface and the water contact angle (CA). According to Wenzel, a water droplet completely fills the structure cavities of a solid surface, while the Cassie—Baxter model proposes that the water rests on the structured air/solid interface [6,7]. Thus, on a superhydrophobic surface, hierarchical micro—nanoscale structure has a great influence on the water contact angle (>150°), producing a low sliding angle (<10) and the self-cleaning effect [8,9].

The design and fabrication of an artificial superhydrophobic surface is important in many industrial applications. One of the most popular and successful strategies for formulating nonwettable and self-cleaning surfaces is the structuring of polymer surfaces. Many reports describe the fabrication of structured surfaces with high hydrophobicity on UV-curable [10–13] and thermoplastic [14–21] polymers.

Among the several UV-curable oligomers suitable for UV coatings, urethane acrylate is commonly used for applications where protective, hydrophobic, and clean coatings are required. Aliphatic urethane acrylates containing soft and hard segments are preferred because of their properties of non-yellowing, low shrinkage, and heat, abrasion, and chemical resistance [22–24]. UV molding is useful technique for high-volume fabrication of submicron features with high accuracy [25–27]. In previous work [26], we have shown that application of a solvent- and heat-assisted UV replication process to prepolymer improves the filling of the pyramidal structure of molds, especially in the case of high-viscosity polymer.

Thermoplastic elastomers (TPE) are a large class of materials with many potential candidates for manufacturing nonwettable and self-cleaning surfaces. Owing to the content of their hard and soft segments, these copolymers (ABA) offer a wide range of processing characteristics and physical properties lying in between those of thermoplastics and elastomers [28–31]. Recently, commercial thermoplastic elastomers such as all-acrylic and urethane polymers, with a variety of surface properties [32–34], have become available. The micro—nano injection molding of thermoplastic elastomers is a relatively new area of research, and little attention has been given

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to such molded materials. Alabran et al. [35] report processing conditions for the injection molding of sub-micron features on elastomeric surfaces. Recently, Yoon et al. [36] reported that thermoplastic polyurethane elastomers are suitable for injection molding and can provide good replication and processability.

Injection molding is widely used in the creation of high hydrophobic surfaces for polymers [15–17,27,37–42]. For instance, in earlier investigations [15–17,40–42] we demonstrated the formation of highly controlled micro- and nanostructures on surfaces of various thermoplastics by injection molding using microstructured aluminum and micro—nanostructured aluminum oxide molds. The polymer surfaces produced with the micro—nanomolds were highly superhydrophobic.

Advances in nanofabrication techniques have led to the creation of micro- and nanostructures of novel shape in hard nonpolymeric materials [9,43–47,52]. To date, the structural feature giving best contact angles for water, and also for organic solvents, is a nail-shaped structure where the high overhang angle plays an essential role. Recently, the research group of Krupenkin [44,45] created nanonails consisting of a silicon stem and SiO_2 nail-head, which under the influence of electrical voltage change from superhydrophobic to superhydrophilic. This reversible transition approach allows producing tunable nanostructured surfaces that can exhibit contact angles (CAs) as high as 150° and can even repel ethanol and methanol. Tuteja et al. [46,47] demonstrated two different approaches for fabricating surfaces possessing a re-entrant texture that can support the Cassie state with water ($\gamma_{lv}=72.1$ mN/m) and with various low surface tension liquids ($\gamma_{lv}=15.7$–23.8 mN/m). These controlled surfaces display contact angles greater that 150° and low contact angle hysteresis under both polar and nonpolar liquids. Also recent works by Marmur [48] and Nosonovsky [49] suggested that a surface with special multiscale roughness, leading to a heterogeneous interface, can stabilize the Cassie–Baxter state even in the case of hydrophilic materials. They and other researchers [50,51] pointed out that for the low contact angle hysteresis a heterogeneous interface having minimized adhesion force between the liquid droplet is needed. More recently, Karlsson et al. [52] have reported that in order to have superhydrophobic surface with a hydrogen-terminated diamond surface a nail-head-shaped pillar design was required. These investigations, and many examples in nature [5,53], confirm that special surface topography plays a crucial role in the creation of superhydrophobicity.

There are several methods (e.g., etching, electron beam lithography) to fabricate elaborate surface structures in hard materials. Corresponding methods to produce elaborate surface structures on polymers have not, however, been presented. Nail-shaped surface structures have not yet been reported for polymers. The aim of this work is to develop new controlled approaches for the fabrication of superhydrophobic surfaces in soft materials. With use of thermoplastic elastomers, micro- and nanosized surface features can be created and replicated. We show how, in a single step, at micro- and nanoscales, hydrophilic elastomeric polymers can be patterned with and shaped into superhydrophobic surfaces.

2. Experimental

2.1. Materials

UV-curable urethane, silicone, and fluoro acrylates were kindly supplied by Cytec, U.S. The acrylates are described in Table 1. Ebecryl 4830 and Ebecryl 8405 urethane acrylates were chosen for their good flexibility and low shrinkage, which were expected to impart elasticity to the coating. Ebecryl 350 and Ebecryl 381 contain acrylates with siloxane and fluoro groups, respectively. The reactive diluent trimethylolpropane triacrylate (TMPTA) and the two radical photoinitiators (1-hydroxy-cyclohexyl-phenyl-ketone, Irgacure 184, and 2-hydroxy-2-methyl-1-phenyl-propan-1-one, Darocur 1173) were purchased from Aldrich. Prepolymers and monomers were used as received. Two UV-curable liquid mixtures (ES and EF) were prepared with different concentrations of the acrylates (Table 2).

Table 1
Description of the acrylates.

Acrylates	Properties	Viscosity (mPa)	Density (g/cm^3)	Functionality	T_g (°C)
Ebecryl 8301 aliphatic urethane	High reactivity	150–550 (65.5 °C)	1.16	6	63
Ebecryl 4830 aliphatic urethane	Imparts flexibility and toughness	2500–4500 (60 °C)	1.12	2	42
Ebecryl 8405 aliphatic urethane	Enhances flexibility and hardness	4500 (60 °C)	1.13	4	30
Ebecryl 350 silicone diacrylate	Improves substrate wetting and slip	200–500 (25 °C)	1.05	2	–
Ebecryl 381 fluoro triacrylate	Provides excellent substrate wetting	330–525 (25 °C)	1.10	3	–
TMPTA	Acts as solvent	100	1.06	3	62

Two thermoplastic elastomers (TPE1 and TPE2), commercial (Kuraray Co. LTD., Japan) all-acrylic triblock copolymer elastomers for injection molding, were selected for study. The elastomers differed in content of hard blocks of polymethylmethacrylate (PMMA) and soft blocks of poly-n-butyl-acrylate (PnBA). Shore hardness was 65A for TPE1 and 95A for TPE2.

2.2. Fabrication of micro, nano, and hierarchical micro—nano molds

Micro molds (M-molds) were prepared by structuring electropolished aluminum foil (0.25 mm thick, 99.997% Al, Puratronic®, Alfa Aesar) with a microworking robot [15] (RP-1AH) from Mitsubishi Electric. Similar M-molds were used for the UV molding and injection molding. The structured area of the M-mold for UV molding possessing periodic micro depressions in the square symmetry was 25 × 25 mm and the diameter of the structured M-mold for injection molding was 25 mm. For both M-molds, the diameter of the micro depressions was 19 μm, the interdepression distance of the microstructures was 41 μm, and the depth of microdepressions was 35 μm.

For the nanostructured mold (N-mold), electropolished aluminum foil was anodized at constant voltage of 40 V in 0.3 M oxalic acid, at 3 °C for 24 h. The diameter of the structured N-mold was 25 mm. A hierarchical micro—nano mold (MN-mold) was fabricated by anodizing the microstructured aluminum foil. A detailed description of the micropatterning and anodization has been given earlier [40]. The unreacted aluminum and the barrier layer were not removed after anodization. On the side on which the anodization was done, the nanopores were opened by immersion in 5%

Table 2
Components and compositions of UV-curable coating mixtures.

Components		Compositions (wt-%)	
		ES[a]	EF[b]
Oligomers:	Ebecryl 8301	50	45
	Ebecryl 4830	5	5
	Ebecryl 8405	25	30
	Ebecryl 350	1.5	–
	Ebecryl 381	–	1.5
Monomer:	TMPTA	14.5	14.5
Photoinitiators:	Irgacure 184	2	2
	Darocur 1173	2	2

[a] Mixture containing a silicone acrylate component.
[b] Mixture containing a fluorinated acrylate component.