Applied Surface Science 458 (2018) 619–628

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Direct replication of micro-nanostructures in the fabrication of superhydrophobic silicone rubber surfaces by compression molding

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ARTICLE INFO

Keywords:
Superhydrophobicity
Silicone rubber
Micro-nanostructures
Direct replication
Self-cleaning properties
Compression molding

ABSTRACT

We describe a simple method for fabricating superhydrophobic high temperature vulcanized (HTV) silicone rubber surfaces by direct replication using a compression molding system. The resulting rubber samples possessed micro-nanostructures on the surface. This micro- and nano-scale roughness produced a water contact angle of > 160° and a contact angle hysteresis of < 3°. The roughness patterns on chemically etched aluminum surfaces, which served as templates, were successfully replicated on the rubber surfaces. An antistiction coating applied to the template surface ensured that the rubber was completely removed during demolding and that the replicated micro-nanostructures on the silicone surface were preserved. Surface roughness of the aluminum templates was optimized at HCl concentrations of 15 wt.%, with a lower roughness value observed at acid concentrations above and below this value. The developed HTV silicone rubber surfaces also demonstrated a freezing delay and a self-cleaning capacity.

1. Introduction

Due to its hydrophobic properties, silicone rubber has attracted much attention for application as high-voltage outdoor insulation [1]. Silicone rubber used in high-voltage outdoor insulation can be divided into three main subcategories: high temperature vulcanized (HTV) silicon rubber, room temperature vulcanized (RTV) silicone rubber and liquid silicone rubber (LSR). HTV rubber cured at high temperature and pressure and catalyzed with peroxide or a noble metal, such as platinum, possesses an inherent hydrophobicity as well as superior electrical and mechanical properties [2,3]. Given that the accumulation of ice and pollution is responsible for numerous electrical and mechanical issues involving insulators exposed to these harsh environmental conditions, outdoor insulators should ideally have superhydrophobic and self-cleaning properties [2,4].

Silicone rubber, due to its hydrophobic nature, causes water droplets to form on its surface rather than allowing water to immediately flow over the surface or to form a continuous water film [5]. The water contact angle (WCA) of its smooth surface is < 120° [6–8]. However, adding surface roughness can increase the WCA without altering surface chemistry. Superhydrophobic surfaces having a WCA > 150° and a contact angle hysteresis (CAH) < 10° can be created through a combination of low surface energy materials and a micro- and nanostructured surface topography [9,10]. When water droplets roll off a superhydrophobic surface, they also carry away hydrophilic contaminants adhered to the surface [11]. Due to surface tension, the adhesion of a contaminant particle to a water droplet is stronger than the particles' adhesion to the solid surface. Thus, superhydrophobic surfaces can be considered as self-cleaning surfaces [4].

Surfaces with micro-nanostructures have been used for a range of applications including antireflection coatings, bioinspired non-reflective coatings, antipollution and self-cleaning surfaces, cell culturing and differentiation, microlenses, dry adhesion surfaces and superhydrophobic surfaces [12]. Many methods have been used to create such surfaces including self-assembly, layer-by-layer methods, plasma treatments, chemical vapor deposition, sol-gel methods, lithography, spray coating, dip coating, electrostatic spinning and electrochemical deposition [9,13]. There are several problems and challenges associated with the use of these methods including complex engineering procedures, long fabrication times, expensive facilities, environmental concerns and less than optimal robustness when the methods are applied to real-world settings [9,14]. Consequently, a simple approach, such as the use of templates to create replicates having surficial micro-nanostructures, is preferable for reducing fabrication time and costs, applying to a wide range of materials, being easy to use and being reproducible. Moreover, using templates as replica to create micro-nanostructured surfaces favors mass production and is a method that is widely acceptable to industry. In addition, direct replication creates a

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https://doi.org/10.1016/j.apsusc.2018.07.099
Received 24 April 2018; Received in revised form 9 July 2018; Accepted 12 July 2018

superhydrophobic surface out of the bulk material, while the aforementioned techniques create an additional layer on the parent material.

Use of templates or direct replication has been widely used for making micro-nanostructures on the surface of polymeric materials [14,15]. A variety of materials can be used to fabricate such templates or inserts: nickel, steel, BMG (bulk metallic glass) and aluminum [12]. Considering the ease of creating patterns through mechanical machining, chemical etching and electroforming on metals, they represent materials that offer a high potential as templates. Moreover, there are numerous ways to create an aluminum surface having micro and/or nanostructures including chemical etching [16,17], anodization [18–21], boiling water [22,23], plasma treatment [22,24,25], laser ablation [26–28] and lithography [29–31]. Various solutions have been used for chemically etching aluminum surfaces. Hydrochloric acid—at various concentrations—is one of the most common chemical etchants used for this purpose [32–34].

These structured templates can then be used in a wide range of polymer processing techniques, such as injection molding [12,35–37], injection compression molding [38–40], compression molding [41–43] and hot embossing [44–48], to produce micro-nanostructured polymer surfaces via replication. Liu et al. [14] produced superhydrophobic polymeric surfaces using Al and Al_2O_3 replicas obtained via the anodization technique. Weng et al. [49] achieved a superhydrophobic electro-active epoxy coating by direct replication of fresh plant leaves, while Bhagat et al. [50] fabricated superhydrophobic polycarbonates (PC) using silicon wafer templates via a hot embossing process. Through femtosecond laser ablation and a hot embossing system, Toosi et al. [51] imprinted topographical stainless steel (SS) micro-nanostructured patterns onto the surface of thermoplastic polymers that included high-density polyethylene (HDPE), polylactic acid (PLA) and medical PVC. Cao et al. [52] fabricated superhydrophobic high-density polyethylene (HDPE) surfaces via a nanoinjection molding technique using a template of porous anodic aluminum (PAA) having pore diameters of 200 nm. Injection-molded superhydrophobic polypropylene (PP) surfaces with microstructures and hierarchical anisotropic micro-nanostructures (dual structures) have also been studied [53,54]. The fabrication of microstructured inserts, produced using a micro-working robot on aluminum foil, and micro-nanostructured inserts, obtained by anodizing aluminum foil, demonstrated that microstructures can, in some cases, produce superhydrophobic surfaces, while dual surfaces (i.e. surfaces with micro-nanostructures) always lead to a superhydrophobic surface having a WCA of $> 150^\circ$.

Most studies involving the fabrication of superhydrophobic polymeric surfaces have used thermoplastics as the matrix. Some studies have also used poly(dimethylsiloxane) (PDMS) [55,56] and LSR [15,57] for producing structured superhydrophobic surfaces. However, few studies have employed HTV rubber materials to create textured superhydrophobic surfaces [4], and thus there is a need for further investigation using this material.

Here, we present an efficient and simple method for fabricating micro-nanostructured rubber surfaces using a compression molding system. Compression molding is one of the most common methods for producing high volume polymer parts and components. Unlike conventional means for making superhydrophobic HTV silicone surfaces that rely mainly on coating techniques [1,58–60], we produce a micro-nanostructured template using simple chemical etching and subsequent direct replication of micro-nanostructures on the HTV silicone during its vulcanization process. Consequently, no additional coating is required to achieve a WCA of $> 160^\circ$. Replication quality depends greatly on having a well-structured and durable template that can be used repeatedly without considerable loss of roughness and having a technique to detach the mold without damage to the produced surface nor to the original template.

2. Materials and methods

All samples were made of HTV silicone rubber composites supplied by K-Line Insulators Limited (Canada) consist of two main parts, a matrix of long-chain silicone rubbers and fillers like alumina trihydrate ($Al_2O_3{\cdot}3H_2O$) and silicon oxide (SiO_2). The direct replication method was used to fabricate samples marked by micro-nanostructures (Fig. 1).

2.1. Equipment

A press machine (Carver Inc., USA) was used in the compression molding process to fabricate micro-nanostructured rubber surfaces. Minimum and maximum clamp capacities of the machine are 3 kN and 194 kN. The machine has two temperature-controllable platens.

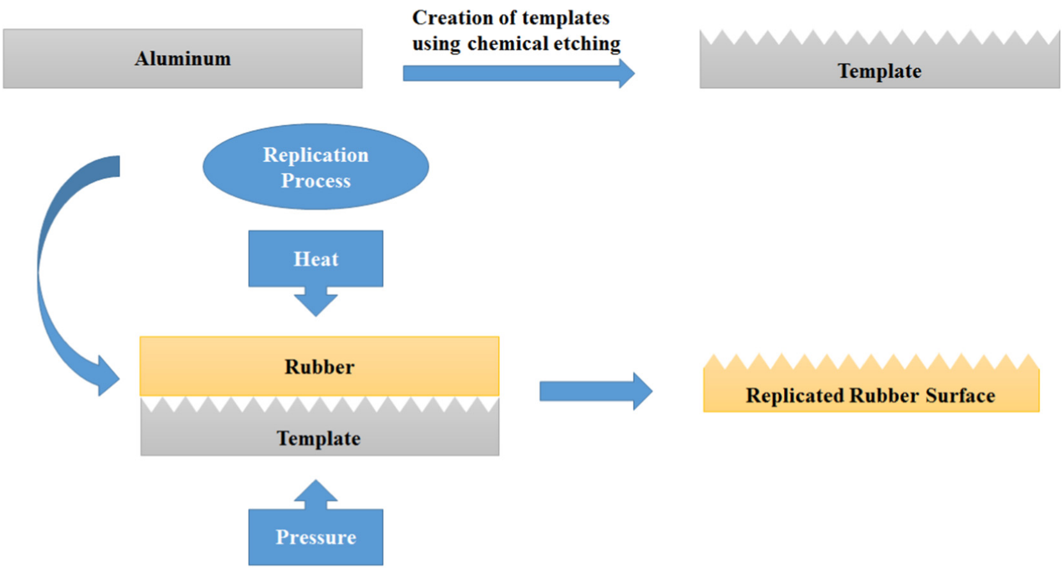

Fig. 1. Schema of the replication of micro-nanostructures on the surface of HTV silicone rubber from chemically etched aluminum templates to illustrate the replication of patterns on the template through curing under pressure and heat.