



Superhydrophobic microtextured polycarbonate surfaces



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ABSTRACT

A novel approach for fabrication of superhydrophobic polycarbonate (PC) surfaces has been developed based on purely physical process. Unlike the classical routes, which heavily rely on the surface chemical modification, the present route involves fabrication of microtextured Si master using high power pulsed laser and subsequent thermal replication of microtexture onto PC surface. The water droplet beads up on the microtextured PC in a Cassie–Baxter state exhibiting superhydrophobic nature of the surface. Average height of the micro-pillars formed on replicated PC surfaces played a crucial role in governing the superhydrophobic properties of the resulting microtextured surfaces. The water contact angle could be tailored over a wide range, from 82° for smooth PC surface to 155°, with an increase in average height of the micro-pillars from 1.34 μm to 6.68 μm . The infrared (IR) spectroscopy analysis revealed that the PC surface does not undergo any chemical change during thermal replication and further implied that the resulting superhydrophobic behavior was solely due to the physical modification of the surface. Moreover, the microtextured PC has been shown to be a perfect master for replication of microtexture onto other type of polymers such as polydimethylsiloxane (PDMS) in bulk and in thin film forms. Given the facile nature of the present technique and ease of fabrication, we believe that the present route is quite promising for large-scale production of PC based superhydrophobic surfaces. These surfaces find several potential applications such as anti-corrosive, anti-icing and self-cleaning surfaces, coatings inside of water pipes for frictionless flow and so on.

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1. Introduction

Polycarbonate (PC) has been replacing glass and several other types of polymers such as polydimethylsiloxane (PDMS), polymethylmethacrylate (PMMA), polystyrene, cyclic olefin copolymer (COC) and polyimide plastic resin, in many applications owing to their low cost, high impact resistance and good machining properties [1–4]. In addition, PC exhibits high optical transmission in the visible range, high modulus of elasticity and good mechanical strength which makes it ideal candidate for various applications such as microfluidic devices, CDs and DVDs, optical lenses and sports equipment [5–8]. Despite these advantages, as produced PC surface exhibits low water contact angle ($\sim 84^\circ$) and thereby suffers from the difficulty of partial wetting of the surface by aqueous solutions which severely limits its wide-scale exploitation in various applications where the water repellency is of paramount importance. Several attempts have been devoted to transform hydrophilic PC into hydrophobic material (contact angle, $> 90^\circ$) using various approaches such as ion beam irradiation, plasma treatment, phase separation and chemical treatments [9–13]. For example, Palumbo et al. recently reported fabrication of superhydrophobic PC

by tailoring chemistry and nano-structure using plasma processing and resulting PC show contact angle as high as 162° [14]. Garstecki et al. reported an interesting strategy for surface chemical modification of PC using dodecylamine which readily reacts with carbonate groups of PC to render it hydrophobic with contact angle of 132° [15]. Xu et al. obtained hydrophobic PC by modifying the surface roughness using spray treatment of aqueous solution of acetone [10]. Hydrophobic PC finds additional applications as self-cleaning surfaces, fluid drag reduction, anti-icing and anti-corrosive materials. Nevertheless, all synthetic approaches reported to date for hydrophobic PC involve either chemical treatments and or use of vacuum during plasma processing, which makes these processes difficult and costly.

It is a well-established fact that for a material to demonstrate hydrophobic behavior it must have non-polar groups on its surface. Further, it is not possible to achieve contact angles $> 120^\circ$ using purely chemical processes and the physical effect of the surface roughness needs to be considered to achieve contact angles in superhydrophobic regime ($> 150^\circ$) [16,17]. Depending on the interplay between these two parameters (i.e. chemical composition and surface roughness) generally two distinct wetting behaviors exist. The first wetting behavior refers to a scenario where the surface roughness is such that water droplet penetrates and engulfs the surface features. This is termed as “Wenzel state” type of wetting [18]. Secondly, on some of the surfaces water droplet rests on top of the roughness features with air pockets trapped underneath. This is referred to the “Cassie–Baxter state” [19].

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Superhydrophobic behavior is exclusively associated with the Cassie state of wetting: in this regime, water droplet maintains more or less spherical shape and exhibit high mobility and low sliding angles ($<10^\circ$).

Polycarbonate backbone intrinsically carries hydrophobic groups (such as $-\text{CH}_3$) as can be seen from its chemical structure shown in Fig. 1. However, water droplets placed on PC surface exhibit contact angle of 84° which does not fall in the hydrophobic regime ($>90^\circ$). This might be due to the fact that in most cases these materials are produced in such a form that their surfaces end up being optically smooth. So the question arises here that whether or not it would be possible to obtain superhydrophobic PC by simply modifying the surface roughness by some means? One of the most commonly used techniques to increase the surface roughness is high power laser texturing of surfaces with which unique microtexture, that mimics the lotus-leaf like morphology, can be realized [20–22].

Recently we reported an approach for superhydrophobic PDMS by replication of micro/nano-structures fabricated by ultra-fast microtexturing [21]. This approach of microtexture replication works only for thermoset polymers and cannot be applied for thermoplastic type of polymers such as polycarbonate. Therefore, in the present studies, an entirely new approach for replication of microtexture onto thermoplastics has been developed. Although both replication approaches are thermally driven, the actual protocols and mechanisms involved in these processes differ quite significantly. In the former, the heat energy is utilized to cure the polymer and it has no effect on the height of the replicated microtexture. On the other hand, in the present approach, heat is used to soften the thermoplastic polymer so that microtexture impressions can be made on the surface. Here the temperature of replication has significant impact on the height of the replicated microtexture which advantageously allows fabrication of PC surfaces with a wide variation in their wetting properties using the same master. The present studies were aimed to achieve the Cassie–Baxter type PC surfaces through pulsed laser microtexturing of silicon wafer and its replication on PC surface without any chemical modification. To the best of our knowledge, this is the first report on development of purely

physical strategy that enables fabrication of superhydrophobic PC surface. This technique offers several advantages such as it bypasses use of chemicals, multi-step processing and plasma processing which utilizes vacuum and thus making the present route industrially viable for large scale production of superhydrophobic PC.

2. Experimental

The overall experimental procedure to fabricate superhydrophobic PC has been depicted in the schematic diagram (Fig. 1). It involves two major steps as described below.

2.1. Microtexturing of silicon wafer

Optically smooth single crystal silicon wafers (Diameter ~ 10 cm and thickness ~ 525 μm) were purchased from Silicon Quest International. The wafers were first cleaned with acetone followed by methanol and final rinsing with deionized water to remove any impurities from the polished surface. The wafers were then dried by blowing dry air before they were used for laser microtexturing. Silicon substrates were obtained by cleavage of 3 in. diameter Si wafer into square sheets ($2\text{ cm} \times 2\text{ cm}$) and the cut samples were cleaned thoroughly as described above. The samples were then mounted onto a high precision computer controlled X–Y stage and were exposed to ~ 8 μJ pulses of green laser (532 nm wavelength Photonics fiber laser, model – IPG GLP 10). Large area scans (~ 3 in. diameter) were realized by scanning the laser beam with the help of X–Y stage in combination with the galvanometer scanner with an accuracy of ± 0.2 μm .

2.2. Replication of microtexture on polycarbonate

For microtexture replication, polycarbonate sheets ($2\text{ cm} \times 2\text{ cm}$) were cut out of CD discs purchased from Verbatim Americas, LLC. The rear side of the disc, which usually has printed matter on it, was utilized for the microtexture replication. The printed layer was peeled off using

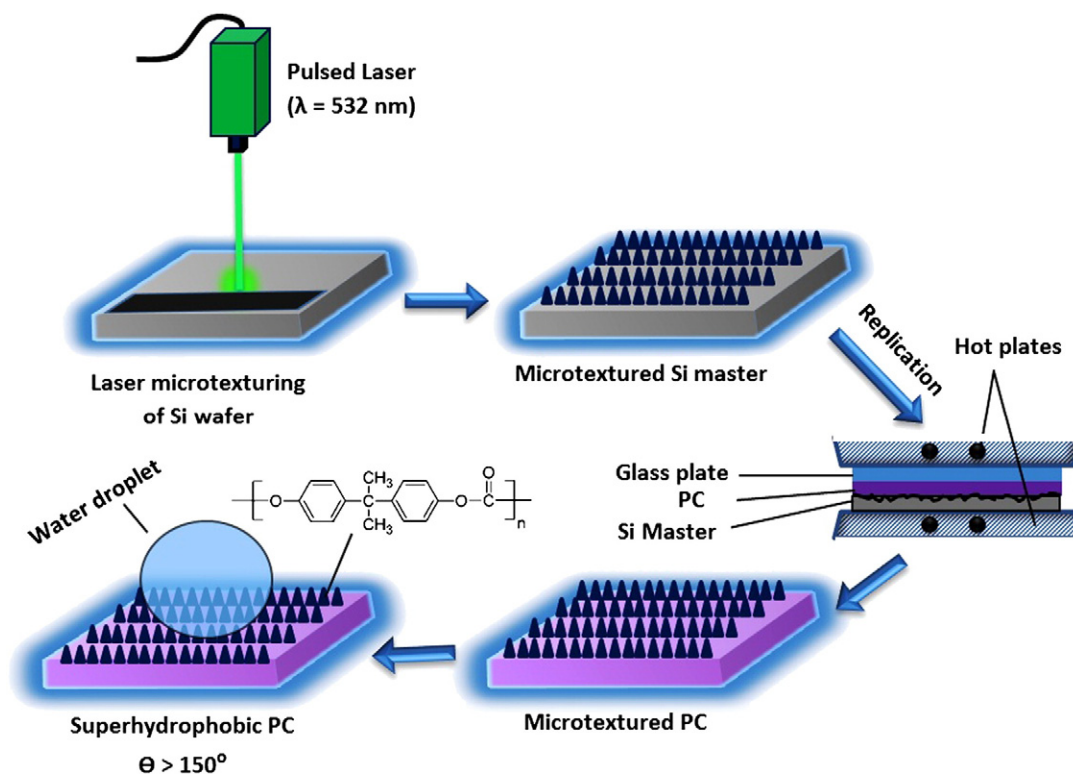


Fig. 1. Schematic depicting overall process for fabrication of superhydrophobic polycarbonate (PC) through ultra-fast laser microtexturing of Si wafer and its subsequent replication. The chemical structure of the PC, carrying two methyl groups per repeat unit, has been shown in the schematic.

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