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Thermal stability of micro–nano structures and superhydrophobicity of polytetrafluoroethylene films formed by hot embossing via a picosecond laser ablated template

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ABSTRACT

We report here a simple and efficient hot embossing process capable of mass fabricating superhydrophobic and self-cleaning polytetrafluoroethylene (PTFE) film surfaces. Adding superhydrophobicity to hydrophobic polytetrafluoroethylene (PTFE) significantly enhances their application potential in industry as well as in daily life. We applied a picosecond laser to fabricate regular array of micro-holes companied with submicron structures on high strength steel substrate to form a lotus-leaf-like template. Then the hot embossing process was performed on flat PTFE films to introduce a dual-scale structure composed of the micro-scale protrusions and nano-scale fibril structures on the top of protrusions. The hot embossing parameters such as the embossing pressure and time were optimized to achieve required micro- and nano-scale dual structure on PTFE film very closed to the similar dual structure of the lotus leaf surface. The PTFE films then exhibited superhydrophobicity with contact angle up to 154.6° and sliding angle of as low as 5.5°. The thermal stability of the superhydrophobic PTFE films was investigated from room temperature up to 430 °C. We demonstrate that the micro–nano dual structure on PTFE films and their superhydrophobicity is thermally stable up to 340 °C. The micro-scale protrusions will collapse and the superhydrophobicity will lose when the temperate is over 370 °C.

1. Introduction

After millennia of evolution, many plants and animals have developed superhydrophobic properties [1–6] signified by the static contact angle (SCA) of over 150° between water droplet and corresponding surface. The nelumbo nucifera leaf (lotus leaf) is a popular example [1,2]. In addition to a large SCA, lotus leaf has a low sliding angle (SA) at the same time, Consequently, water droplets easily roll off of the surfaces of lotus leaves, resulting in a "self-cleaning" function. Superhydrophobicity on lotus leaf is realized by its particular micro-scale protrusions as well as nano-scale wax tubers on the protrusions and other parts of surface [1]. The surface hierarchical structure and low surface energy are well known as two main factors for surface superhydrophobicity [7,8]. Hence, fabricating superhydrophobic surfaces typically follows two principles [9–14]: firstly forming the micro or nano structures to enhance the surface roughness, then decreasing the samples surface free energy by simply covering a low surface free energy membrane or directly choosing a low surface energy material, the latter was much easier to achieve. Herein, formation of surface micro–nano structures attracts more attentions in superhydrophobic surface research and fabrication.

Nowadays polymers are widely used due to their good functionality, flexibility, transparency and chemical stability. Polytetrafluoroethylene (also called Teflon or PTFE) is a typical sample with additional thermal stability, which make it an ideal choice for many industry applications. Moreover, PTFE possesses a low free surface energy [15], the contact angle measured on its flat surface is about 110°, making PTFE a good candidate for superhydrophobicity, which could significantly enlarge its application areas like potential "self-cleaning" windows, anti-icing, reduction of fluid resistance, etc. In recent years, some approaches have been reported to obtain a superhydrophobic polymer by packing of grains (sol–gel) [16,17], spraying [18,19], pressing (template) [20–23], etching [12,24,25], etc. Among these proposed methods, templating is an attractive approach to realize superhydrophobic PTFE for its capacity in high efficiency and potential mass fabrication. Victor et al. [20] used a nickel template to press a superhydrophobic PTFE surface with

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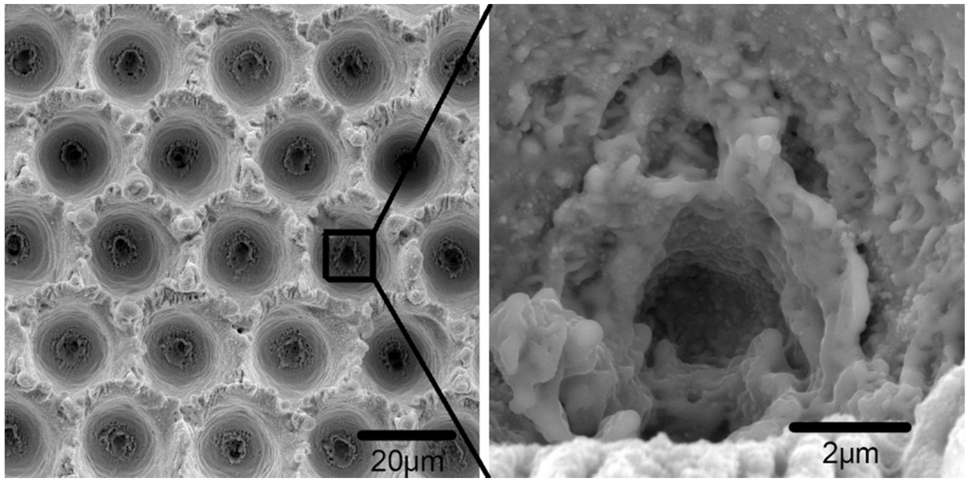

Fig. 1. SEM image for H13 mold steel template with negative lotus-leaf-like array.

a SCA of 166. Kim et al. [21] fabricated a superhydrophobic PTFE surface with a SCA of 165 by replicating the microstructures of an anodic aluminum oxide template.

Jucius et al. [22] presented a hot embossing method toward hydrophobic surface by using a Ni and a chrome template in generating the micro–nano structures on PTFE surfaces. The Ni template was fabricated by optical lithography with 2D micro-scale array of square pits and chessboard-like pattern. The chrome template was ablated by a 10 ns Nd:YAG laser in pit array with a periodicity of about 100 μm. Noh et al. [23] applied a Nd:YVO4 laser with a pulse width of 12 ps to ablate a NAK80 mold steel to form a template in conical spike array with a size of 10 μm. The microstructure on the mold surface was replicated onto poly(dimethylsiloxane) (PDMS) using the polymer casting method to fabricate superhydrophobic surfaces with micro–nano structures similar to a lotus leaf, the water contact angle reached to 157°.

The as-reported publications demonstrate that laser ablation is an effective approach to form templates with lotus-leaf like micro–nano structures and then the embossing with aforementioned templates can be a viable approach to mass produce hydrophobic polymer surfaces. However, one important issue-the stability of the micro–nano structures on polymer surfaces and the corresponding superhydrophobicity of the superhydrophobic polymer have caught little attention up to date. The thermal stability of superhydrophobicity defines the application capability and range of the superhydrophobic polymers. It is also of scientific interest to investigate the evolution of the micro–nano structures and the superhydrophobicity behavior of superhydrophobic polymer after being heated to elevated temperature.

In this paper, we applied a picosecond laser to ablate the H13 mold steel surface to form lotus-leaf-like micro–nano structures as the template. Then we reprinted this kind of micro–nano structures onto the PTFE film via a hot-embossing process to achieve superhydrophobic PTFE films by optimizing the embossing parameters like pressure and time. The focus was placed on the thermal stability of the micro–nano structures and the superhydrophobicity by keeping the superhydrophobic PTFE films for a period of time at different temperatures from room temperature up to 430 °C. We demonstrate that the superhydrophobicity of the PTFE film is thermally stable up to 340 °C.

2. Experimental procedure

H13 mold steel template substrates with size of 25 mm × 25 mm × 5 mm were mechanically polished for smooth surface and ultrasonically cleaned in ethanol. These H13 samples were then treated by laser ablation point by point using an Edgewave picosecond pulse laser source (with 1064 nm wavelength, pulse width about 10 ps). The focused spot diameter of the laser beam, which is $1/e^2$ of the maximum intensity of the Gaussian profile, was approximately 24 μm. The laser parameters applied on H13 surfaces were: repetition rate of 100 kHz, laser fluence of 6.63 J/cm^2, 70 pulses in each point, repeat 10 times for the same parameters above, and 24 μm between two adjacent points.

Commercial PTFE films with size of 25 mm × 25 mm × 1 mm were used. These films were rinsed by absolute ethyl alcohol then dried before the following experiments. The hot-embossing was performed on a CARVER hot-embossing equipment. The embossing pressure was modestly varied from 55 MPa to 85 MPa; the embossing time was changed from 2 min to 15 min, and the heating temperature was chosen around the glass transition temperature of PTFE to be 130 °C.

Scanning electron microscopy (SEM) was used to characterize surface morphology, the samples were previously coated a conductive gold layer by an electron beam evaporator. In observing the microstructure of the samples, the plate was horizontally placed to obtain the planar array image, then the plate was inclined to 30° to present the height of protrusions on treated samples. The surface superhydrophobicity was tested on an optical contact angle system 15 (OCA15) by measuring the droplet static contact angle (SCA) on the surface as well as the surface sliding angle (SA) for droplet to roll off, the deionized water volume for measuring static SCA and SA was 4 μL, respectively. A tube furnace was used for analyzing the thermal stability of superhydrophobic PTFE surfaces.

3. Results and discussions

3.1. Laser ablated H13 mold steel for lotus-leaf-like template

Fig. 1 shows the morphology of the micro-scale regular hexagonal array holes ablated by the picosecond pulse laser, which was similar to a negative structure of the micro-scale epicuticle protrusions on lotus leaf. The diameter of these holes was about 24 μm, which was nearly equal to the distance between centers of two adjacent holes. At the bottom of each hole, some submicron waves and particles were observed, with the size varying from 100 nm to 700 nm, due to the characteristics of ultra-fast laser ablation. The morphology feature of the micro hole array with submicron structures mimics well the lotus leaf structure, while the intrinsic high strength of the H13 substrate make this lotus-leaf-like template