

Communication

Control of Polydimethylsiloxane Surface Hydrophobicity by Plasma Polymerized Hexamethyldisilazane Deposition

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Abstract: The properties of a polydimethylsiloxane (PDMS) surface were modified by a one-step deposition of plasma polymerized hexamethyldisilazane (pp-HMDS) by the arc discharge method. Scanning electron microscopy, atomic force microscopy, and Fourier-transform infrared spectroscopy analytical techniques were employed for morphological, structural, and chemical characterization of the pp-HMDS modified PDMS surface. The changes in PDMS substrate wetting properties were evaluated by means of contact angle measurements. The unmodified PDMS surface is hydrophobic with a contact angle of 122°, while, after pp-HMDS film deposition, a dual-scale roughness PDMS surface with contact angle values as high as 170° was obtained. It was found that the value of the contact angle depends on the plasma processing time. Chemically, the pp-HMDS presents methyl moieties, rendering it hydrophobic and making it an attractive material for creating a superhydrophobic surface, and eliminating the need for complex chemical routes. The presented approach may open up new avenues in design and fabrication of superhydrophobic and flexible organosilicon materials with a self-cleaning function.

Keywords: polydimethylsiloxane; superhydrophobicity; hexamethyldisilazane; plasma polymerization

1. Introduction

Polydimethylsiloxanes (PMDS) are the most widely used silicon-based organic polymers, commonly referred to as silicones. Because of easy fabrication, non-toxicity, biocompatibility and biodurability they have found potential applications in various fields. The surface of PDMS is naturally hydrophobic, but a number of efforts have been made to modify PDMS and further enhance its hydrophobicity [1,2]. PDMS hydrophobicity plays an important role in diverse applications e.g., self-cleaning surfaces [3], microfluidics [4], microelectromechanical systems [5], and biomedical applications [6].

Superhydrophobic PDMS surfaces can be fabricated by pulsed laser irradiation resulting in surface modification with a static contact angle (CA) value of 170° [7]. However, the whole irradiation procedure is highly time-consuming, thus limiting the scalability of this method. A more reliable and effective practice includes the deposition/formation of a thin film on the surface of the material to obtain the desired functionality. Plasma treatment is attractive as the processing time is short, the process involves low temperature, and procedures are relatively simple. Importantly, a single-step technique is desired for obtaining superhydrophobic and self-cleaning surface functionalities.

In this contribution, we fabricated a superhydrophobic PDMS surface via plasma polymerized hexamethyldisilazane (pp-HMDS) thin film deposition by arc discharge. To the best of our knowledge,

the technique adopted here has been not reported for the fabrication of superhydrophobic PDMS surface using hexamethyldisilazane monomer as a precursor. HMDS is well known as being widely used for hydrophobic coatings on various hydroxyl-bearing surfaces [8,9]. HMDS chemical activity derives from the presence of a highly reactive nitrogen atom within the compound. The presented one step deposition of in situ polymerized hexamethyldisilazane is simple and scalable, and thus can provide a new strategy for the large scale fabrication of superhydrophobic surfaces with a self-cleaning function on flexible substrates.

2. Materials and Methods

The addition-curing silicone rubber Elastosil RT 601 A/B with a viscosity of 3500 mPa·s at 23 °C (Wacker Chemie AG, München, Germany) was used as received for flexible films fabrication. HMDS of analytical grade ($\geq 99\%$, Sigma-Aldrich, Saint Louis, MO, USA) was used as received.

The experimental setup of arc plasma reactor and technological conditions have been reported previously [10]. Briefly, a rod-shaped graphite anode and cathode were placed at the center of the discharge chamber. A quartz cuvette containing HMDS solution was positioned 20 mm from the anode, and PDMS substrate was placed at a distance of 15 mm from the electrodes. The chamber was connected to a vacuum line backed by a rotary pump. Arc-discharge was generated between anode and cathode using a DC transferred arc process using ~ 4.3 mA current and ~ 25 kV voltage. The deposition time was varied up to 60 s.

A FEI Quanta 200 scanning electron microscope (SEM, Thermo Fisher Scientific, Waltham, MA, USA) was used to collect micrographs of the investigated surface. The samples were imaged at an accelerating voltage of 30 kV. Atomic force microscopy (AFM) experiments were carried out with NT-206 (Microtestmachines, New Taipei City, Taiwan) in air at room temperature (22 ± 1 °C) using a V-shaped silicon cantilever operating in contact mode. The surface morphology of the resulting films was evaluated based on the AFM surface topography images and roughness parameters. Vertex 70 Fourier transform infrared (FTIR) spectrometer (Bruker Optics Inc., Billerica, MA, USA) equipped with a 30Spec (Pike Technologies, Madison, IA, USA) specular reflectance accessory having a fixed 30° angle of incidence was used for the chemical characterization of the modified PMDS surface.

CA measurements were performed at room temperature using the sessile drop method. A droplet of deionized water (5 μ L) was deposited onto the investigated surface. Optical images of the droplet were recorded with a PC-connected digital camera after 10 s of dropping and CA measurements were carried out using an active contour method based on B-spline snakes (active contours) [11]. The contact angle hysteresis was measured as the difference between the advancing and receding contact angle of a sliding droplet. The test was performed by setting a droplet on a sample, which was placed on a horizontal plate. The plate was tilted slowly until the water drop began to slide along the surface; at this point the camera shutter was activated. The advancing and receding contact angles were then measured.

3. Results

The morphology of unmodified and plasma polymerized HMDS (pp-HMDS) modified flexible PDMS substrate and water droplets on the PDMS surface before and after pp-HMDS film deposition at different times are compared in Figure 1. Cured PDMS is produced spontaneously forming wavy structures on the surface with micro-scale amplitude and periodicity of 128 nm. SEM images of the resulting pp-HDMS thin film surface for deposition times of 30 and 60 s are presented in Figure 1b,c, respectively. The deposition resulted in a highly branched and crosslinked pp-HMDS structures composed of quasi-spherical nanoparticles with size in the range of 15–60 nm. Growth in three-dimensional assemblies and formation of large nanoparticles aggregates were observed as the deposition time increased.

These morphological alterations change the wetting properties of the PDMS surface (Figure 1). The unmodified PDMS surface exhibits hydrophobic behavior with a static CA value not higher than 122°.

A considerable improvement in non-wetting characteristics of pp-HMDS film functionalized surfaces was observed. After 30 s of deposition, the nanostructured pp-HMDS film exhibited superhydrophobic properties with static CA values of 169° – 170° . In this case the low value of CA hysteresis (2°), defined as the difference between the CA at the front of the droplet (advancing CA) and at the back of the droplet (receding CA), was obtained. The increase of deposition times up to 60 s results in lower CA values, i.e., CA = 159° – 161° .

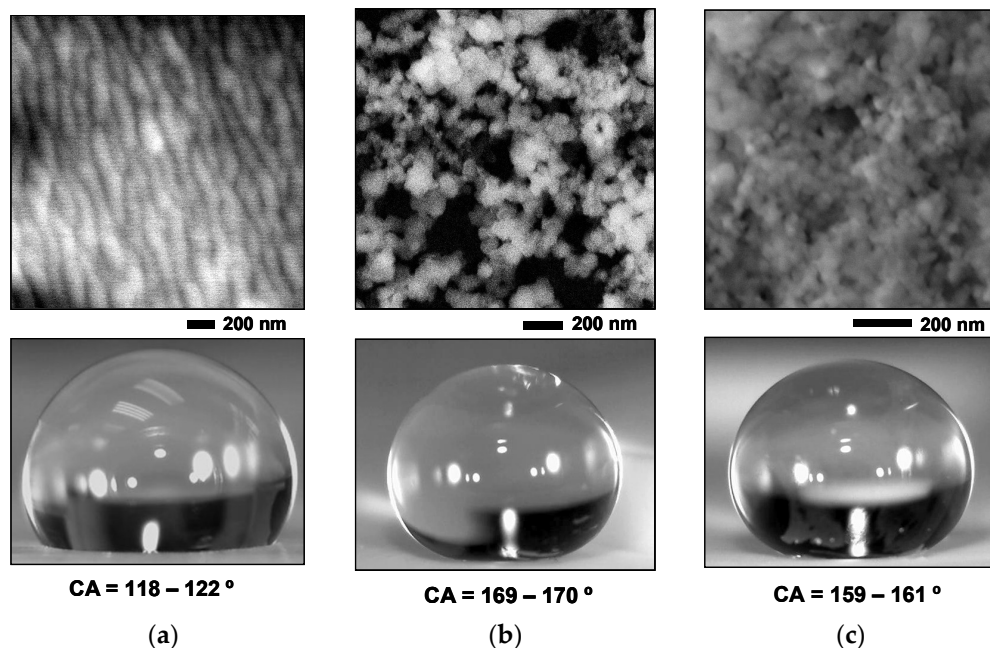


Figure 1. SEM image of unmodified (a) and pp-HMDS film modified PDMS surfaces (b,c) and water droplets on PDMS surface before and after pp-HMDS film deposition at different times: (a) 0; (b) 30 s; (c) 60 s.

The presence of nanostructures in the form of quasi-spherical nanoparticles and interconnection caused by the formation of large aggregates at longer pp-HMDS deposition time (60 s) was confirmed using characteristic AFM topographical and surface profile images shown in Figure 2. In this case dual-scale roughness of the surface was maintained, the pp-HMDS film surface was found to be rough with the root-mean square roughness having a value of 96.11 nm. However, the spiky surface morphology changes into a bumpy one and the negative surface skewness parameter value (-0.2) indicates predominance of valleys.

As can be seen from Figure 3a, in the FTIR absorbance spectrum of unmodified PDMS the bands at 2965 and 2906 cm^{-1} are assigned to asymmetric and symmetric stretching of CH_3 groups, respectively [12]. The asymmetric and symmetric bending vibrations of CH_3 groups are also observed at 1410 and 1258 cm^{-1} , respectively. The bands at 1072 and 1007 cm^{-1} are characteristic of Si–O–Si asymmetric and symmetric stretching vibrations, respectively. Asymmetric rocking at 864 cm^{-1} and stretching at 785 cm^{-1} vibrations can be attributed to the Si– CH_3 group [12].

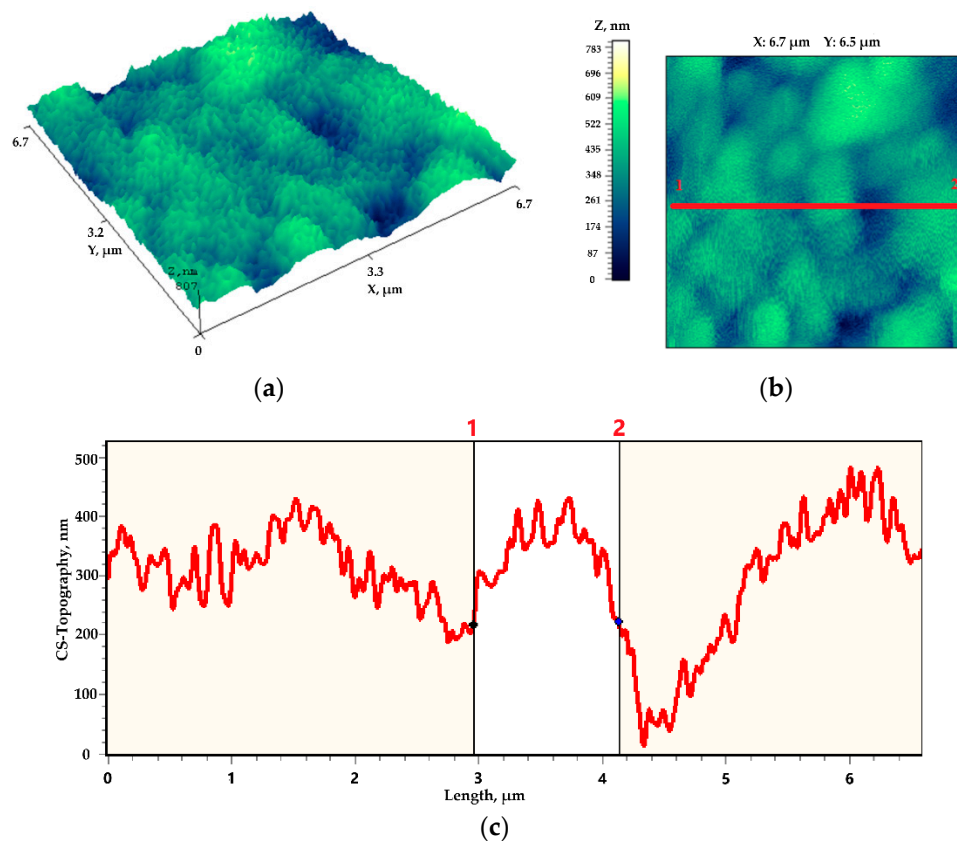


Figure 2. AFM image of 3D (a) and 2D (b) topography with normalized Z (nm scale), and profilogram of pp-HMDS film at deposition time of 60 s (c).

The deposition of polymerized pp-HMDS film leads to the obvious PDMS surface functional group changes (Figure 3b). The broad band between 3400 and 3700 cm^{-1} is related to O–H stretching in Si–OH bonds of hydrophilic silanol groups [13]. The absorbance at 3350 cm^{-1} is characteristic for stretching of the N–H bond, while the doublet at 2350 cm^{-1} is attributed to CO_2 species [10]. As in the case of unmodified PDMS, the presence of methyl moieties in the modified surface is confirmed by an absorption band at 1410 cm^{-1} , related to CH_3 asymmetric bending in Si– CH_3 bonds, and 2965 and 2906 cm^{-1} bands, which are characteristic for asymmetric stretching and symmetric stretching of the CH_3 group, respectively [14,15]. A low intensity band at 1454 cm^{-1} is assigned to the asymmetric bending vibrations of the CH_2 group in the Si– CH_2 – CH_2 –Si link that play a substantial role in the cross-linking process during HMDS polymerization [15]. The band located at 2250 cm^{-1} corresponds to Si–H stretching vibration [16], while the band at 1629 cm^{-1} can be assigned to stretching of C=O [17]. Some oxygen related functional groups could arise from free radical (possibly trapped in the film structure) reaction with the atmosphere, when the samples are removed from the reactor [18].

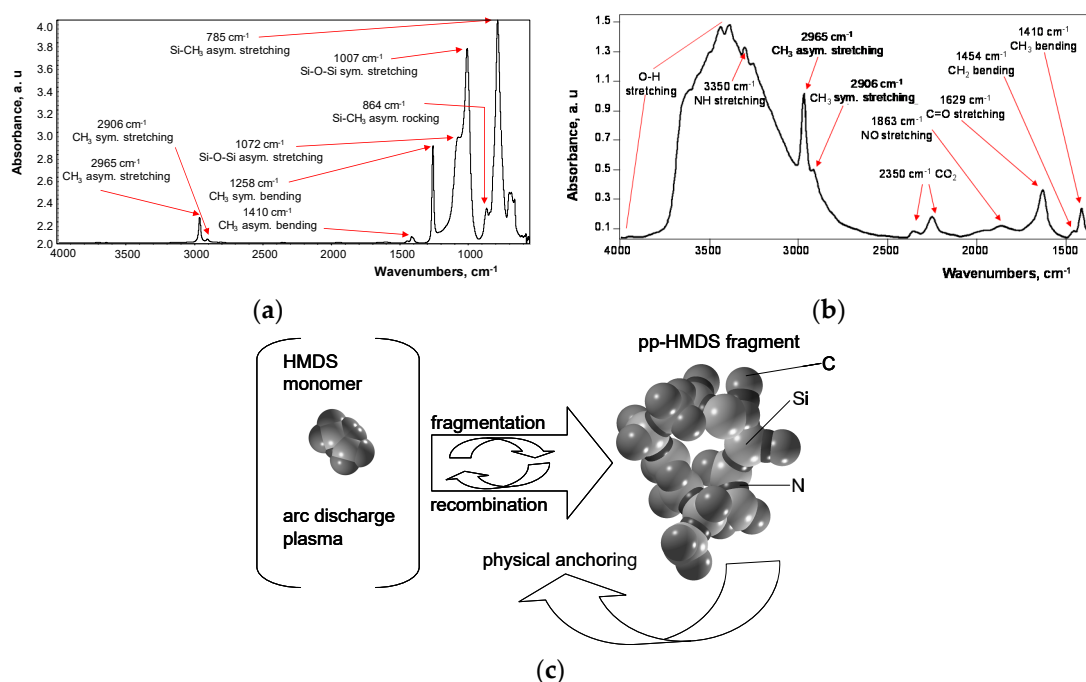


Figure 3. FTIR absorbance spectra of flexible PDMS substrate (a) and pp-HMDS (b) with functional groups assigned and schematic diagram of probable deposition mechanism (c); HMDS monomer and pp-HMDS network fragment are shown in van der Waal's-based representation.

4. Discussions

Generally, the hydrophobic properties of films are determined by the kind and amount of grafted hydrophobic groups and surface roughness parameters. One step coating by in situ HMDS deposition and polymerization is an easy and rapid method to impart non-wetting properties to the PDMS surface. The plasma polymerization process of HMDS monomers resulted in highly branched and crosslinked structures composed of quasi-spherical nanoparticles. After pp-HMDS film deposition, the PDMS surface shows superhydrophobic characteristics with a CA value close to 170°. High hydrophobicity of pp-HMDS originates from the high amount of CH₃ species and specific film surface morphology. The pp-HMDS film functionalized surfaces exhibited Cassie–Baxter state with a “lotus effect” observable and a low CA hysteresis of 2°, suggesting that a water droplet is not able to wet the spaces between surface morphological features allowing air pockets to remain at the interface. The increase of pp-HMDS film deposition time influences the decrease of CA value. It can be attributed to a higher solid fraction of surface morphological features in contact with the water droplet, which decreases the concentration of air pockets trapped at the interface of pp-HMDS with the droplet.

Based on the SEM, FTIR data, and surface wetting studies, it is suggested that the HMDS monomer molecules passing to the arc plasma region during the operational process are fragmented with partial retention and formation of new chemical bonds. The corresponding repetition of fragmentation and recombination reactions of HMDS monomers in arc plasma leads to the deposition of a randomly crosslinked network structure of pp-HMDS (Figure 3c) and forms a heterogeneous surface with a high fraction of methyl moieties retained, thus providing superhydrophobic characteristics with a self-cleaning function.

Thus, FTIR investigations reveal multiple non-covalent interaction achieved by in situ HMDS polymerization with physical anchoring on the polymer surface [19]. Such an interaction can be recognized as the driving force for constructing and fabrication of superhydrophobic and flexible organosilicon materials with a self-cleaning function.

5. Conclusions

Herein, we successfully enhanced the non-wetting properties of a flexible polydimethylsiloxane substrate surface via plasma polymerized hexamethyldisilazane thin film deposition by the arc discharge method. Such a film is composed of quasi-spherical nanoparticles stacked together, which form a branched network. The deposited nanostructured plasma polymerized hexamethyldisilazane film exhibits superhydrophobic properties with static contact angle values as high as 170° and a low contact angle hysteresis of 2°. The PDMS surface undergoes self-cleaning and non-wetting behavior due to the multiple non-covalent interactions attended by the incorporation in the surface layer of methyl groups and a nano-rough surface formation. This is a facile and effective method that can provide a new strategy for the large scale fabrication of superhydrophobic surfaces with a self-cleaning function on flexible substrates.

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