Superhydrophobic electrosprayed PTFE

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Abstract

This paper shows the deposition of superhydrophobic PTFE (polytetrafluoroethylene) films on FTO (fluorine doped tin oxide) coated glass slides, employing the electrospray technique, using a commercial PTFE particle suspension in water. Water contact angles as high as 167° were measured on the PTFE surface. Water drop sliding angles at 2° show a very low contact angle hysteresis. Scanning electron and atomic force microscopy images show the typical rough micro/nanostructure required for superhydrophobicity.

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1. Introduction

Superhydrophobic surfaces are attracting the attention of many researchers worldwide. The specialized literature shows a wealth of papers on the topic, especially since Barthlot and Nienhuis published their findings on the self-cleaning properties of superhydrophobic Lotus leaves [1]. The area is interesting per se but has strong impacts on technology, in particular on microfluidics [2].

It is now generally acknowledged that the superhydrophobic surface is formed by the additive action of two basic conditions: a low polarity or low energy surface material composition, together with a particular surface roughness [3]. The contact angle on apolar solids is typically in the 90–120° range. Zisman [4] reports that the surface energy of polymers decreases as the predominant bonds show a composition going from CH\textsubscript{2}→CH\textsubscript{3}→CF\textsubscript{2}→CF\textsubscript{3} bonds. Many different materials present a non-polar behaviour and there are many examples of surface treatments which lead to a low-energy surface finishing. Regarding the surface roughness, it is still not clear which are the best conditions leading to contact angles above 150°. Nano and micro roughness profiles have shown superhydrophobicity [5], as well as fractal surface patterns [6]. Recently improved understanding to this topic has been added by Xiu et al. [7] who experimentally mimicked biological hierarchical structures by combining colloidal self-assembled particles with thin film sputter deposition. A detailed account on superhydrophobicity or “non-sticking drops” can be found in the review of Quéré [8]. The synthesis of transparent superhydrophobic polyethylene surfaces modified by a CF\textsubscript{4} plasma treatment with contact angles above 160° has also been accomplished [9]. Transparency is wanted for optical applications.

According to the Cassie-Baxter theory, superhydrophobic properties appear when a sessile drop sits mostly on an air cushion [10], and the macroscopic contact angle is an apparent angle. Typically the contact angle is an average between the contact angle on air and on the solid.

Polymeric PTFE (polytetrafluoroethylene) surfaces show hydrophobic and oleophobic characteristics. Water contact angles on smooth PTFE are found between 98 and 112° [11] and are widely used in kitchenware and in low-friction engineering components, with good mechanical properties. The hydrophobic properties of PTFE are caused by the fluorination of the carbon bonds.

Several different approaches were tried successfully to change PTFE surfaces towards a superhydrophobic behaviour. Superhydrophobic CF\textsubscript{x} coatings deposited via in-line atmospheric RF plasma of He/CF\textsubscript{4}/H\textsubscript{2} gas mixtures have been reported [12]. Fluorocarbon coatings, deposited starting with tetrafluoroethylene...
using modulated RF glow-discharges, have shown superhydrophobic properties [13]. Plasma treatment of polyethylene using SF6/Ar plasma also led to superhydrophobic behaviour of the surface [14], mainly due to fluorination of plasma generated dangling bonds. Stelmachuk et al. [15] report on sputtered PTFE films, deposited under various argon pressures, reaching 146° water contact angles. Busscher et al. [16] studied the adhesion of human fibroblasts on superhydrophobic FEP-PTFE, prepared by ion-etching, followed by an oxygen glow-discharge treatment. Superhydrophobic carbon nanotube forests, coated with PTFE, using a hot filament chemical vapor deposition process, have shown advancing and receding water contact angles of respectively 170 and 160° [17].

Recently an interesting precision spraying technique has been described to generate hydrophobic PTFE patterns for living cell adhesion control [18]. Here the interest is in the reduction of process complexity and not in the generation of superhydrophobic surfaces, enabling rapid and flexible micropatterning of surfaces in two easy steps. Acatay [19] showed that the electrospinning of a polycrilonitrile polymer, with the addition of a fluorinated hydroxyl-ended oligomer, presented strong superhydrophobic characteristics. In this same context we report on a new, different, easy and successful way to form superhydrophobic PTFE, using the electrospray method.

2. Experimental section

Electrospinning is a well known technique to deposit polymers electrostatically [20] on conducting substrates. We used the same technique to deposit PTFE, but since we have no evidence of PTFE fiber formation, we call the technique electrospraying. The electrospray technique has been reported since 1902 [21,22].

Our basic ingredient for fluoropolymer electrospray deposition is an aqueous dispersion of the polymer produced by DuPont under the brand name Teflon® PTFE 30. This product, according to the company, is a fluoropolymer suspension containing 60% by weight of polytetrafluoroethylene with particles ranging from 0.05 to 0.5 μm, suspended in distilled water, together with a 6% by weight nonionic wetting agent and stabilizer. According to the manufacturer, the product after processing has to be heated to 115 °C to remove water, and later on, typically to 290 °C, to
remove the wetting agents, with a final cure of the polymer at 337 °C [23].

Electrospraying was done using a 0.7 mm rectified chirurgical injection needle attached to a 3 ml syringe. A DC-motor advanced the syringe piston to feed the spray at 10 μl/min. The injection needle was positioned 5 cm from the substrate and attached to a high voltage supply at 6 KV. As substrates we used conducting fluorine doped tin oxide (FTO) coated glass slides with a 15 Ω/□ resistance produced by Flexitec [24], fixed to a hot plate at 150 °C. Normally, in electrospinning or electrospraying of polymers, the solvent evaporates from the needle to the substrate, but here the hot substrate is essential for this particular suspension, since most of the water evaporates upon impact. We used several deposition times to study the microstructure of the deposits per se, together with their hydrophobic character. Typical deposition times ranged from 30 s to 20 min in the particular configuration reported here. The as-deposited samples are hydrophilic, wet easily and the coating starts to float on the substrate upon wetting. We found out experimentally that the heat treatment of the sprayed coatings in air at 265 °C already removes the wetting agents and we used this temperature in the results reported below.

The SEM images were obtained, after coating the PTFE samples with a gold film, using JEOL JSM 6360-LV equipment operating at 15 kV. The surface characterizations were done with a Shimadzu SPM-9500J3 atomic force microscope (AFM) operating in the dynamic mode using the same gold coated samples. The surface topography was obtained from the AFM scanning experiments. The microscope software uses the scanning tip positions to calculate Rms roughness, arithmetic mean roughness Ra, distance between the average cross line and the maximum peak Rp and distance between the average cross line and the minimum valley Rv of the chosen scanned area. The fractal dimension of the scanned surface can be calculated also by the proprietary AFM software. The calculation employs the well established box counting technique (see e.g. Ref. [6]).

The contact angle measurements were done on a Ramé-Hart 100 goniometer. This conventional equipment uses 1 μl distilled water drops which are deposited by a syringe on the surface. The projection of this sessile drop is captured by a CCD camera and the contact angle is calculated using the goniometer software. Several measurements are done to improve the calculated mean contact angle measurement. The equipment measures the advancing contact angle.

The sliding angle measurements were obtained using a mechanical level goniometer, recording the angle when the deposited water drop starts to move. For superhydrophobic surfaces the stabilization of the drop on the leveled surface is not an easy task, since the drop dances and moves upon deposition.

3. Results

Fig. 1 shows the scanning electron microscopy image of PTFE which was electrosprayed with a 30 s deposition time. The image shows that the technique for this suspension produces droplets, which form spherical solid particles uniformly distributed on the substrate surface. An image analysis using
Image Tool software [25] of Fig. 1 on the size distribution of the particles reveals the characteristics shown in Fig. 2. Particles below two pixels (about 200 nm) where not counted to avoid picture noise. The distribution is skewed with a maximum counting of particles at 350 nm. The calculated particle surface coverage for this particular image is of 11.1%.

The analysis of SEM images of as-deposited and heat treated electrosprayed PTFE coatings revealed no visual differences, which means that the heat treatment to remove wetting agents does not alter the original electrosprayed morphology. No melting, sintering or bottleneck forming was found.

Figs. 3 and 4 show scanning electron micrographs of a complete 10 min deposit of electrosprayed and cured PTFE. The picture shows a fairly uniform coating of PTFE particles which are deposited randomly on top of particles which arrived and solidified earlier, generating a random network of spheres with different diameters with a very high porosity, leading to a rough surface structure. A detail of this interesting structure is shown in Fig. 5, where spherical particles on top of other spherical particles can be clearly seen.

Fig. 6 shows an AFM scan on an area of 3.75 × 3.75 μm² of a sample electrosprayed for 10 min. The image seen in two, and repeated in three dimensions shows clearly several structures which can be broadly classified in micro and nano, but basically resembles a cauliflower structure. The AFM software performed the surface topological analysis. The root mean square roughness Rms of sample was measured at 114 nm. The maximum peak relative to the average crossline Rp was found at 394 nm and the minimum valley of Fig. 6 was calculated at 332 nm. Additionally, the fractal dimension of this sample was calculated at $D = 2.1$, using the AFM equipment software.

Fig. 7 shows a picture of the drop with highest advancing water contact angle (167°) obtained in this work.

Fig. 8 shows the measured water advancing contact angles on thermally treated electrosprayed PTFE coatings. Mean calculated contact angles are plotted versus deposition time. The contact angles start at hydrophilic values on the FTO substrate as expected. After a PTFE deposition time of 1 min the contact angle already rises to typical PTFE values. Our experiments demonstrate that for this deposition time typically 22% of the FTO surface is covered with PTFE particles. This is in accord with earlier reports where fairly low coverages lead to profound contact angle changes [26]. After 5 min deposition time the cured samples already display superhydrophobic characteristics. Our results indicate that a complete coverage is necessary to reach superhydrophobicity.

The drop sliding angles on the 20 min electrosprayed superhydrophobic PTFE surface were measured at $(2.1 \pm 0.5)°$.

4. Discussion and conclusions

It is well known that fluorine containing groups are preferentially concentrated at the polymer-air interface and thus small amounts of fluorine containing groups can lower the surface energy [27]. This property has been used many times to turn surfaces hydrophobic. Fluorine has a very small atomic radius and the highest electronegativity of the periodic table, forming strong covalent bonds with carbon, significantly lowering the surface energy. Especially CF₃ bonds display the lowest surface energy of any solid [28]. In the case of PTFE, the polymer is formed by CF₂ monomers and the low energy surface will be formed naturally.

Several conditions are necessary to produce superhydrophobic surfaces which are technologically useful. Despite mandatory water contact angles above 150° a very low contact angle hysteresis is necessary. The low hysteresis is wanted for many applications, like self-cleaning properties and electrowetting performance, since the water drop mobility depends strongly on the difference of advancing and receding contact angles. Besides, good mechanical properties of superhydrophobic surfaces are desirable, such as: superior adhesion in the case of coatings and wear and compression resistance. Chemical inertness of the superhydrophobic surface element would also widen its applicability. Several of these conditions are met by the electrosprayed PTFE coatings reported here.

Scanning electron and atomic force microscopy results show that electrospraying a water soluble PTFE suspension on hot conducting substrates leads to a nanostructured coating. Wetting agent removal by heat treatment at 265 °C easily leads to hydrophobic or superhydrophobic coatings, depending on coverage. We found out, that the heat treatment can be lowered to 190 °C in vacuum to reach the same results.
The contact angle measurements show that the technique leads easily to superhydrophobic PTFE deposits with water contact angles above 160°.

The sliding angle measurements at around 2° show that electrospayed PTFE has minimal advancing and receding contact angle hysteresis, which is essential to characterize superhydrophobic behaviour with excellent water mobility for device applications.

PTFE by itself is chemically inert and the superhydrophobic electrospayed coating will resist environmental exposure, being friendly to the environment. Further processing of this inert coating for device applications is clearly possible, specially considering the fairly low heat treatment temperatures.

The remaining drawbacks of this superhydrophobic coating are the mechanical properties such as wear and adhesion in tribological applications. Work is in progress to solve also these issues. In our opinion this technology reported here to produce superhydrophobicity is by far the simplest we found in the literature, to the best of our knowledge.

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