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Superhydrophobic polytetrafluoroethylene surfaces with leaf-like micro-protrusions through Ar + O_2 plasma etching process

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ABSTRACT

Polytetrafluoroethylene (PTFE/Teflon) is an excellent material in applications demanding high thermal and chemical stability. Imparting water repellency in such materials can be an advantage when they are used for biomedical and electric insulation applications. Using Ar + O_2 plasma treatment superhydrophobic PTFE surfaces were prepared. The plasma treated PTFE samples exhibited a change in the surface morphology showing 'leaf-like' micro-protrusions in the field emission scanning electron microscopy (FESEM) analysis. 3D Profilometry results showed an increase in the average surface roughness until a treatment time of 4 h. The highest value of the water contact angle was obtained at the maximum average surface roughness for 4 h treatment. Chemical analysis by micro-Raman and X-ray photoelectron spectroscopy for the untreated and Ar + O_2 plasma treated PTFE samples did not show much variation in their chemical structures. The report asserts that a change in the surface roughness is sufficient enough to create superhydrophobic surfaces of PTFE.

1. Introduction

Superhydrophobicity is becoming a desired surface property, as its applications are reaching out to several different fields such as green energy technologies, antifouling in underwater applications, self-cleaning surfaces, glass windows, anti-icing coatings on aircrafts and antennas, stain-resistant textiles, drag reduction, etc. [1–3]. Popular ways of introducing superhydrophobicity on various surfaces involve the achievement of water contact angles that are higher than 150°, because they are usually accompanied by a low contact angle hysteresis and hence, a low tilt (roll-off) angle. Wenzel [4] and Cassie–Baxter [5] theories have described the different wetting regimes a droplet can assume when the surface roughness is modified. If the surface free energy (SFE) of the material involved is sufficiently low, such that the smooth surface itself demonstrates hydrophobic nature, it becomes fairly easy to attain superhydrophobicity by merely increasing the surface roughness. In our present work, we have used Polytetrafluoroethylene (PTFE), a low SFE material for exactly this reason.

PTFE, popularly known by the brand name 'Teflon', is a fluoro polymer which possesses very useful physical properties such as high thermal stability, good electrical insulation, lubricity, corrosion resistance and biocompatibility. It is a helical structured polymer with high symmetry and crystallinity which makes it an important practical candidate for various applications [6]. Due to small atomic radius and high electronegativity of fluorine atoms, PTFE contains strong CF bonds and thus demonstrates low surface free energy ($\sim$20 mN/m at 20 °C), along with water and oil resistance. For this reason, PTFE coatings have found widespread usage in nonstick cookware. According to Wenzel, a water repelling solid surface can be made more repelling when it is made to possess more roughness [4]. So a method that produces sufficient amount of surface roughness can help in achieving superhydrophobicity. Sputter deposition [7], etching with gas plasma and lasers [8–10], electro spraying [11], simple sand blasting and cleaning [12], lithographic patterning [13,14] and others [15] are some of the commonly used methods for making superhydrophobic PTFE surfaces. Among them, reactive plasma etching has proven to be an effective, environment friendly and versatile way of modifying surface properties of a material. Surface modification is achieved by the bombardment of excited ions, which are generated from the plasma, on the substrate. This process is capable of producing significant physical (surface roughness) and/or chemical modifications of a few monolayers of the surface without changing the properties of the bulk material [16]. Moreover, consistency and the control of surface chemistry can be achieved easily in the plasma process.

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Our present analysis involves the usage of reactive plasma, generated from Ar and O_2 mixture, to incur physicochemical modifications on PTFE surfaces. We have used the same plasma in our earlier experiments for other polymeric materials like Kapton® [17] to obtain superhydrophobicity. For the case of PTFE, chemical analyses have shown that after plasma treatment, the chemical nature of the material remains intact. Plasma treatment, in earlier studies, have also been used to alter the wetting properties of PTFE surfaces [8,18–20]. These studies have demonstrated the effects of various gas plasmas (Ar, O_2, N_2 and CF_4) to reduce the surface hydrophobicity or, in some cases, to achieve superhydrophobicity. The use of only Ar plasma has shown to decrease hydrophobicity and also alters the chemical identity of the surface [19]. Using Ar + O_2 plasma, we were able to produce superhydrophobic PTFE surfaces with high durability even after several months of storage. Using Ar + O_2 plasma, we were able to produce superhydrophobic PTFE surfaces that retained their properties even after several months of storage (nearly 10 months). We hereby present a comprehensive study which reports our findings after various characterization procedures, and focuses on the superhydrophobicity of the PTFE surfaces.

2. Experimental details

Commercial PTFE samples (25 mm diameter and 2 mm thickness) were polished, and then cleaned with acetone and isopropyl alcohol in succession. The substrates were dried with dry nitrogen and loaded into a plasma reactor. The details of the plasma reactor are described in our earlier paper [21]. The PTFE samples were treated with Ar + O_2 plasma for durations of 1–5 h (labeled as TF1 to TF5). In addition, one untreated sample was used to serve as a control sample (TF0). Ar and O_2 flow rates were maintained at 20 and 12 sccm (standard cubic centimeters per minute), respectively. A pulsed bias power supply (Huttinger, PBP-3) was used to create the plasma. A DC bias of -1000 V was used to generate the Ar + O_2 plasma at room temperature at approximately 1.46 Pa pressure. Under these conditions the plasma current was ~290 mA and the power was 289 W. The temperature of the sample measured using a chromel–alumel thermocouple was 40 °C. After the plasma treatment, the samples were tested for superhydrophobicity by measuring there static water contact angles in a Phoenix-300 plus (Surface Electro Optics, Korea) contact angle goniometer using the sessile drop method. The CA measurements were made at three different locations per sample and the average values were reported. The morphology of the untreated and plasma treated samples were studied using Field Emission Scanning Electron Microscopy (FESEM, Supra 40VP, Carl Zeiss). To determine the average surface roughness of the untreated and plasma treated PTFE samples, 3-D surface profiles of the samples were taken using a surface profiler (model: Nanoprobe 500 LS; scan area = 230 × 230 μm and resolution = 1 μm). Surfaces of the samples were scanned at three different regions and the average roughness was calculated for each to check the consistency in the results. In order to analyze the change in the surface chemistry due to plasma treatment, micro-Raman spectra (with DILOR-JOBIN-YVON-SPEX integrated micro-Raman spectrometer) were recorded in the wave number range between 100 and 1800 cm^{-1}. Detailed analysis of the chemical nature of the surface layer was also performed by X-ray photoelectron spectroscopy (XPS) using SpecsLab2 (Version 2.57-r18860) with monochromatic Al K_α radiation (1486.6 eV) operated at 12 kV and 12.5 mA X-ray source. The binding energies reported here were calculated with reference to C 1s peak at a binding energy of 284.6 eV. For each sample, several batches were prepared using the same conditions and the same results were reproduced without any significant error.

3. Results and discussion

Fig. 1 shows the photographs of an untreated and a plasma treated PTFE sample. The droplets on the surface indicate the change in the wetting behavior of PTFE upon plasma treatment. The smooth (untreated) PTFE substrate is hydrophobic because of its low SFE, so droplets are seen to exhibit an obtuse contact angle. Whereas for the plasma treated PTFE sample the droplets are nearly spherical, displaying the superhydrophobic ability of the sample. Macroscopically, the two samples seem similar and any evidence of surface roughness is not apparent. The surfaces were closely observed for morphological changes using FESEM.

Modifications in the smooth surface of the PTFE substrates are observed through FESEM upon Ar + O_2 plasma treatment. Fig. 2(a)–(d) shows the surface micrographs of TF0, TF2, TF4 and TF5 samples, respectively. The fine lines in Fig. 2(a) for the untreated sample (TF0) are a result of the polishing process. The morphology of the samples TF1 and TF2 (Fig. 2(b)) demonstrate non-uniform 'leaf-like' protrusions. These protrusions become more pronounced in samples TF3 and TF4 (Fig. 2(c)). The samples treated for 5 h (TF5) or more display visible deterioration in the protrusions which is possible due to re-sputtering of the protrusions (Fig. 2(d)). Plasma treatment generally facilitates two kinds of changes in the polymer substrate such as modification of the surface by introducing new functional groups through surface reactions and production of low molecular weight degradation products. The latter originates from chemical reactions and physical etching effects. This process roughens the surface and at the same time most of the degradation products are pumped out of the system [22]. Fig. 3 shows a schematic representation of the plasma etching process and the changes it brought to the PTFE surface.

Kitamura et al. [23] have investigated in detail the mechanism of protrusion formation in PTFE upon plasma treatment. Their analysis suggests that the protrusions form as a result of stretching due to the reduction in heat conduction path and overlapping of heated areas (as plasma collision results in temperature elevation) on the edges of the structure. They established that the growth in the size of protrusions is not due to sputter deposition of defluorinated products. A closer inspection of the nature of these protrusions was carried out by using higher magnification FESEM data at various locations for the sample TF4. The micrographs for the data obtained are shown in Fig. 4. The leaf like structure of protrusions is clearly observed in Fig. 4(a) and (b). Fig. 4(c) gives a detailed view of the tip region of one of the protrusions. Presence of nanoscale roughness is observed in the form of nano-wrinkles and nano-folds which may be caused due to the stretching of PTFE (Fig. 4(d)). Presence of

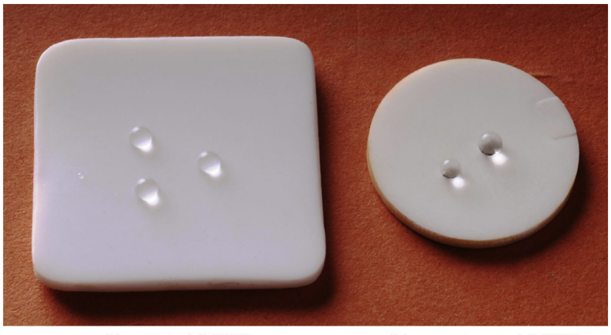

Fig. 1. Sample photographs showing the untreated (TF0) and 4 h plasma treated (TF4) PTFE samples.