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Non-equilibrium hybrid organic plasma processing for superhydrophobic PTFE surface towards potential bio-interface applications

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ABSTRACT

Superhydrophobic surfaces have gained increased attention due to the high water-repellency and self-cleaning capabilities of these surfaces. In the present study, we explored a novel hybrid method of fabricating superhydrophobic poly(tetrafluoroethylene) (PTFE) surfaces by combining the physical etching capability of oxygen plasma with the plasma-induced polymerization of a organic monomer methyl methacrylate (MMA). This novel hybrid combination of oxygen-MMA plasma has resulted in the generation of superhydrophobic PTFE surfaces with contact angle of 154°. We hypothesized that the generation of superhydrophobicity may be attributed to the generation of fluorinated poly(methyl methacrylate) (PMMA) moieties formed by the combined effects of physical etching causing de-fluorination of PTFE and the subsequent plasma polymerization of MMA. The plasma treated PTFE surfaces were then systematically characterized via XPS, FTIR, XRD, DSC and SEM analyses. The results have clearly shown a synergistic effect of the oxygen/MMA combination in comparison with either the oxygen plasma alone or MMA vapors alone. Furthermore, the reported new hybrid combination of Oxygen-MMA plasma has been demonstrated to achieve superhydrophobicity at lower power and short time scales than previously reported methods in the literature. Hence the reported novel hybrid strategy of fabricating superhydrophobic PTFE surfaces could have futuristic potential towards biointerface applications.

1. Introduction

Superhydrophobic surfaces are used for a wide range of applications such as self-cleaning, antifogging, and anti-icing surfaces [1–3]. Additionally, the self-cleaning properties of these surfaces make them useful for a wide range of industrial and biological applications such as anti-biofouling paints, self-cleaning wind shields, and stain resistant textiles [4–6]. Some of the naturally occurring superhydrophobic surfaces are lotus leaf, water striders' legs, and *cicada ornis* wings [7–9]. Owing to the high water repellency, water droplets will roll off the surfaces and remove possible contaminants or impurities from the surface (self-cleaning). The morphological features on superhydrophobic surfaces consist of asperities in the micro or nano length scale. Water droplets usually suspend above these asperities which gives a high contact angle (> 150°). The methodologies for preparation of superhydrophobic surfaces can be classified into either top-down or bottom-up approaches [10]. The top-down approach involves lithographic or template methods and plasma treatment [11,12]. The template method involves molding and replication where as the plasma treatment involves anisotropic etching of the surfaces. In contrast, the bottom-up approach involves self-organization and self-assembly. Chemical vapor deposition/polymerization and electrochemical deposition/polymerization are some of the important bottom-up approaches used to fabricate superhydrophobic surfaces [13–15]. In chemical vapor deposition the product deposits and self-assembles over the surface and modifies the surface properties of the substrate.

Poly(tetrafluoroethylene) (PTFE) is a fluoropolymer which is employed in a wide variety of applications such as nonstick coatings, insulators, seals, gaskets and others. PTFE also has an important role as a material in fabricating various medical devices. The high strength and chemical resistance of carbon-fluorine (C—F) bonds present in this polymer endow it with long term biocompatibility. It is one of the most widely used synthetic polymers to fabricate vascular grafts. The chemical inertness of PTFE makes it ideal for blood-contact devices. Plasma

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surface modification is one of the widely explored techniques to modify the surface properties of PTFE [16,17]. Plasma modification can introduce oxygen rich functional groups which can modify the surface properties of PTFE including wettability and surface energy [18]. As an alternative approach, hybrid surface modification processes for PTFE, which combines both plasma modification with polymerization, were also reported [19,20]. The hybrid processes were found to result in both stable and durable surface modifications.

Recently, it was reported that superhydrophobic PTFE surfaces are widely used for a variety of blood-contact devices [21]. Plasma based surface etching, which causes surface roughness in the nanoscale, was responsible for the observed phenomenon of superhydrophobicity in PTFE. Ryu et al. [22] have reported superhydrophobic PTFE surfaces using an Ar-O_2 plasma treatment; however, the study by Ryu showed that superhydrophobic surfaces were only observed at high plasma power and exposure time (> 100 W, > 150 min) [22]. Hence, hybrid processes which combine top-down and bottom-up approaches can greatly improve the efficiency in fabricating superhydrophobic surfaces [23–27]. In the realm of chemical vapor deposition, organic plasma processing (OPP) is a recent area, which has gained significant attention in the literature for surface modification of polymers [28,29]. In this technique, the monomers (organic precursors) deposit and polymerize on the surface of the substrate using plasma processing. The reduced pressure and the presence of radio frequency (RF) energy inside the plasma chamber cause the monomer to ionize, and subsequently polymerize, and get deposited over the surface of the substrate. Recent results for organic plasma polymerized coatings based on acrylate monomers have been reported for modifying the surface properties of biomaterials to be favorable for cell growth, proliferation and differentiation [30,31].

In the present work we have attempted to design a hybrid process which combines the etching capability of oxygen plasma (top-down approach) with the plasma polymerization capability of the organic monomer MMA (bottom-up approach) to fabricate a superhydrophobic PTFE surface. It was expected that this process can access superhydrophobic PTFE surfaces at lower RF power and shorter timescales than previously reported. To the best of our knowledge there are no reports, in this regard, of fabricating a superhydrophobic PTFE surface through the hybrid process of plasma etching and plasma enhanced organic chemical vapor deposition.

2. Materials and methods

PTFE substrate used for the plasma modification (Mil SPEC T-27730A. 100% pure PTFE tape) was purchased from KH industrial sales New York, USA. Harrick Plasma chamber (PDC-001-HP) used for the plasma surface modification was purchased from Harrick Plasma, New York, USA. The reagents used for the experiments such as methyl methacrylate and acetone were purchased from Sigma Aldrich.

2.1. Oxygen plasma enhanced organic chemical vapor modification of PTFE

The PTFE tapes were cut into 3 cm × 1.2 cm (0.2 mm thickness) pieces for plasma treatment. Briefly, the samples were washed with acetone for 30 min. before the plasma treatment to remove adsorbed impurities (if any) from the surface. The PTFE samples were then placed inside a Harrick Plasma chamber (PDC-001-HP) and a radiofrequency (13.56 MHz, 45 W) were used for plasma treatment. In order to combine oxygen plasma etching with chemical vapor deposition, we have used a combination of methyl methacrylate-oxygen system inside the plasma chamber. 1 mL of methyl methacrylate (MMA) was placed on a glass slide adjacent to the PTFE samples inside the chamber, followed by applying a constant oxygen gas flow rate of 40 SCCM inside the chamber. The reduced pressure (500 mTorr inside the chamber) facilitates the formation of MMA vapors. Different plasma treatment times were used ranging from 10 min. to 1 h for the surface modification. Comparison experiments were also carried out using both MMA only and oxygen only plasmas to modify the surface of PTFE.

2.2. Characterizations

Fourier-transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) were employed to elucidate the surface chemistry. The Bruker alpha FTIR spectrometer with ATR mode was used to acquire IR-absorption spectrum (ranging from 4000 to 400 cm-1). XPS spectra of plasma treated samples were obtained using a Phi 5000 Versaprobe made by Phi Electronics, Inc. (Chanhassen, WI USA). The X-ray source of this instrument is a monochromatic, focused, Al K-alpha source (E = 1486.6 eV) at 25 W with a 100 μm spot size. The Mg anode (λ = 1253.6 eV) was used at 300 W and a barium oxide neutralizer eliminated charging. The survey scans (4 scans averaged per analysis) were obtained using pass energy of 187.5 eV with a step size of 0.5 eV. The high resolution scans (8 scans average per analysis) were obtained with pass energy of 23.5 eV and a step size of 0.1 eV.

To Measure the static contact angle, the samples (n = 3) and were mounted onto a glass slide. Contact angles were measured using the sessile drop method as reported previously at the room temperature [32]. The water droplet size was 5 μL. Image *J*software was used to accurately measure the contact angle of the water droplets on the surface. The dynamic contact angle measurements were done through actively adding and withdrawing a liquid drop with a pump, VWR International (Radnor, PA, USA) a fixed rate (1.0 μL s^{-1}), connected to a 25 G needle. Different fixed volumes of water (2, 4, 6, 8 and 10 μL) were employed to calibrate the flow rate. The angles were then calculated from the average of six measurements taken for each time point. Image J software was used to accurately measure the advancing and receding contact angle of the water droplets on the surface.

The differential scanning calorimetry (DSC) analysis of the PTFE was performed on the range -50 to 400 °C at a rate of 10 °C/min were conducted to determine the melting temperature and enthalpy of melting employing a Q-100 DSC with external chiller (TA Instruments, Delaware, USA). The x-ray diffraction (XRD) experiments were performed on an Empyrean x-ray diffractometer (Malvern Panalytical, UK) equipped with a Cu LFF HR x-ray tube at 30 kV tension and 10 mA current. The spectrum was recorded for the range of 2θ from 10 to 100. The optical emission spectroscopy of the MMA plasma plume was characterized using an Ocean Optics USB4000 (Florida, USA) optical spectrometer.

The structure and morphology of the plasma treated and untreated control PTFE tapes were characterized scanning electron microscopy (SEM) after sputter-coated with Au-Pd and observed using a FE-SEM (Quanta FEG 650 from FEI, Hillsboro, OR) and images were taken at different magnifications.

3. Results and discussion

Methylmethacrylate (MMA) can be polymerized and deposited over the surface using the assistance of organic plasma processing (OPP); however, the polymer surface coating will not exactly exhibit the characteristics of a conventional wet chemistry derived poly(methyl methacrylate) PMMA polymers [33]. In the present study we selected MMA as the monomer, and our hypothesis was that combining oxygen plasma and MMA would exploit the synergistic effects of both to produce a superhydrophobic surface. We propose the possible mechanism is that during this process, due to the surface etching, the fluorine is abstracted from the surface of the PTFE and combines with the highly energetic MMA radicals during the chemical vapor deposition. As a result of the combination of fluorine and methyl methacrylate radicals during the OPP, it can form fluorinated poly (methyl methacrylate) (F-PMMA) and deposit over the surface of PTFE as depicted in Fig. 1a. It is already reported that the F-PMMA has high chemical and thermal stability and it has low surface energy which gives surface hydrophobicity

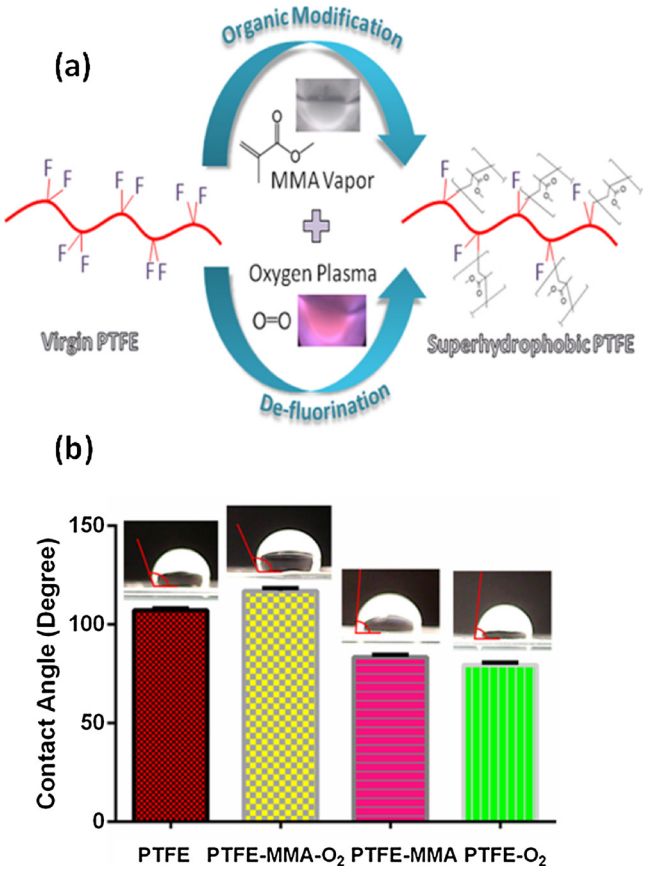

Fig. 1. Illustration of the plasma surface modification of PTFE surface using the non equilibrium organic plasma processing (a), Comparison of the wetting behavior of PTFE surface using oxygen plasma, MMA plasma and oxygen-MMA plasma for 10 min plasma exposure time (b).

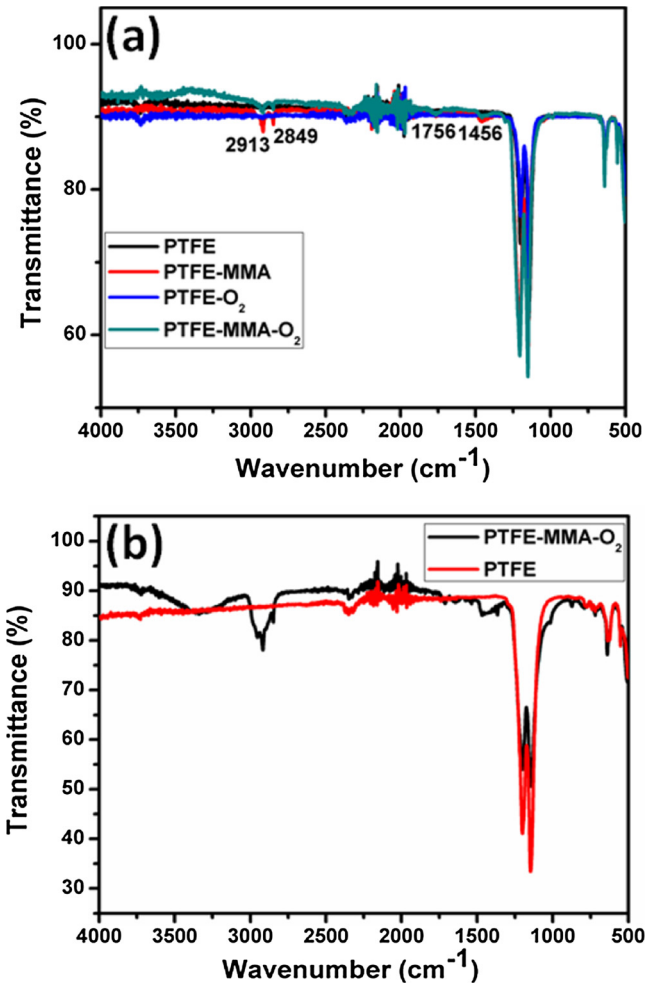

Fig. 2. FTIR spectral analysis comparison of pristine PTFE, PTFE-MMA, PTFE-O2 and PTFE-MMA-O2 after 10 min plasma exposure (a), FTIR spectral analysis comparison of pristine PTFE with PTFE treated with MMA and oxygen plasma system after one hour exposure time (b).

and may explained our observed results [34]. To test the hypothesis, we investigated the effect of three different plasma systems (oxygen, MMA and oxygen-MMA combination) at constant RF power and constant exposure time (45 W, 10 min). It was found that the oxygen plasma treatment for 10 min on the PTFE surfaces resulted in a decrease of the contact angle from 108 to 80° (Fig. 1b). The MMA plasma exposure was also observed to decrease the contact angle from 108 to 84°. The observed decrease in the contact angle for the oxygen plasma treatment was consistent with the previous literature. It was reported that with lower power, less than 50 W, the oxygen plasma treatment causes more surface functionalization with polar functional groups which increases the wettability of the PTFE surfaces; therefore, hydrophobicity is not accessible with oxygen alone at lower power/time [35]. The observed similar trend of lowering the contact angle of PTFE using the MMA plasma system can be attributed to the polymerization of MMA and subsequent deposition over the surface of PTFE with a PMMA layer. Interestingly, when we used the oxygen-MMA combination plasma treatment for the same conditions, it had significantly increased the contact angle of the PTFE from 108 to 120°. Thus, we surmise the oxygen-MMA combined system can form low surface energy bearing F-PMMA which can decrease the wettability of the PTFE surface and, subsequently, increase the contact angle.

The optical emission for each system was observed to be different (Fig. 1). Further, we utilized FTIR spectroscopy to identify the functionalizations taking placing on the PTFE surface. Both pristine and oxygen plasma treated samples have exhibited the characteristic stretching vibrations of -CF_2 at 1153 cm^{-1} and 1210 cm^{-1} and rolling vibrations of -CF_2 groups at 635 cm^{-1} (Fig. 2a). However, when we used MMA vapor, in addition to the characteristics peaks of PTFE, we observed some additional peaks. The peaks at 2913, cm^{-1}, 2849 cm^{-1}, respectively which correspond to the −CH stretching vibrations of $-CH_2$and C−H_3 groups of MMA, and peaks at 1756 cm^{-1} and 1456 cm-1 which correspond to stretching vibrations of the carbonyl groups of MMA. This result was indicating the possible formation of PMMA over the surface of PTFE through the OPP method. The oxygen-MMA plasma treated PTFE has also exhibited similar bands in the FTIR spectrum to that of MMA modified PTFE. On close examination of the bands of the C−F_2 stretching vibrations of the MMA and MMA-oxygen modified PTFE samples there was a clear and distinct change from pristine PTFE (Fig. 2). The characteristic C−F_2 stretching vibrations of pristine PTFE was found to be at 1197 and 1143 cm^{-1} respectively. However, the MMA treated and oxygen-MMA treated PTFE have shown peak shifts for C−F_2 stretching vibrations (1204 and 1197 cm^{-1} respectively) in compared to the pristine PTFE C−F_2 stretching vibrations (1197 and 1143 cm^{-1} respectively). The presence of additional bands and peak shifting indicates the OPP process was successful. We increased the exposure time of oxygen-MMA combined system on PTFE to one hour to see the effect on surface functionalization at longer exposure time. It was found that at one hour exposure time, in comparison with the pristine PTFE, the modified sample has clearly shown a high degree of surface functionalization as the peaks attributed to OPP products were prominent (Fig. 2b).

Optical emission spectroscopy (OES) was utilized to get more insight regarding the plasma inside the system (Fig. S3). We have placed

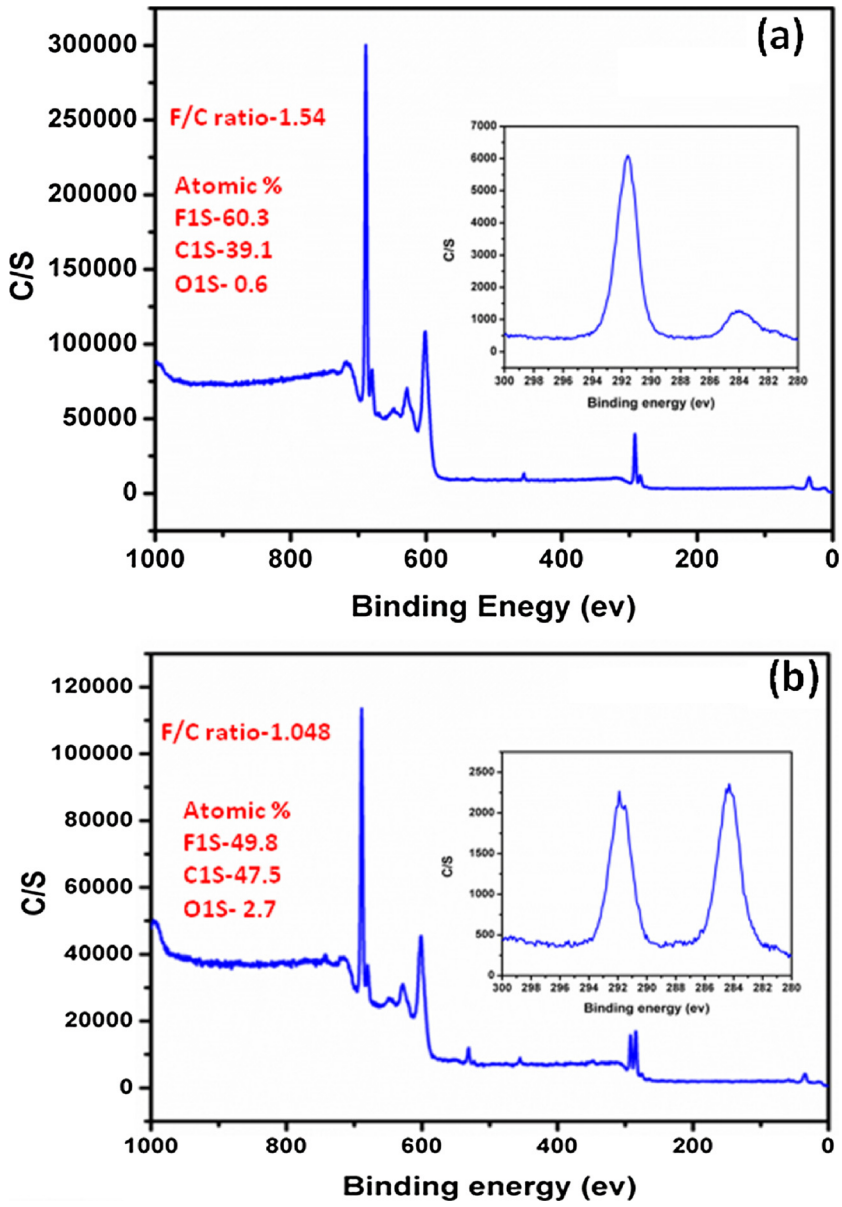

Fig. 3. XPS spectral analysis of pristine PTFE (a), XPS spectral analysis of PTFE modified with oxygen-MMA combination plasma for 1 h (b). The inset of the pictures shows the magnified spectral region from 300 to 280 eV.

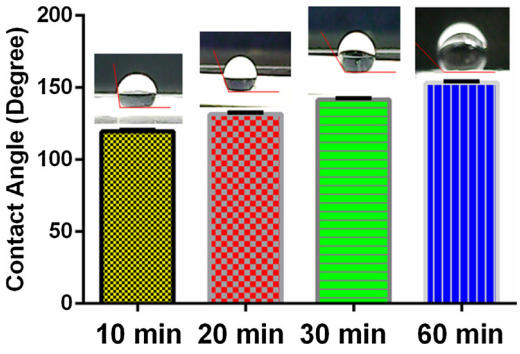

Fig. 4. Time dependent increase in the contact angle of PTFE treated with oxygen-MMA plasma.

different volumes of MMA inside the plasma chamber for the analysis such as 0.25, 0.5, 0.75 and 1 mL. The OES spectrum has shown major peaks at 426,784 and 870 nm respectively. The peaks at 784 nm and 870 nm can be attributed to the oxygen atom transition O (3p5P → 3s5S) and O (3p3P → 3s3S) present in the MMA vapor. The peak at 426 nm corresponds to the CH groups present in the MMA vapor. It was also found that when the concentration of MMA increased to 1 mL, a more pronounced peak at 650 nm appeared which can be attributed to the Hα peaks of MMA. Hence it was clear that the MMA vapor plasma was composed of mainly oxygen, carbon, and hydrogen based chemical species which was consistent with respect to the structure of MMA and the excitations from various transitions show a variety of excited states contributing to the OPP process.

X-ray photoelectron spectroscopy (XPS) analysis of the pristine PTFE was exhibiting a fluorine to carbon ratio (F/C) of 1.76 with only carbon and fluorine found at the surface (Fig. S4a(i)). The PTFE treated with oxygen plasma was exhibiting fluorine/carbon ratio of 1.69 with carbon, fluorine and oxygen (as an additional element) found at the surface (Fig. S4a(ii)). Interestingly, the PTFE treated with the MMA plasma has clearly shown a difference in the F/C ratio making it to 1.41 (Fig. S4b(i)). The oxygen-MMA combination plasma treated PTFE was also exhibiting a difference in F/C ratio of 1.60 (Fig. S4b(ii)). These

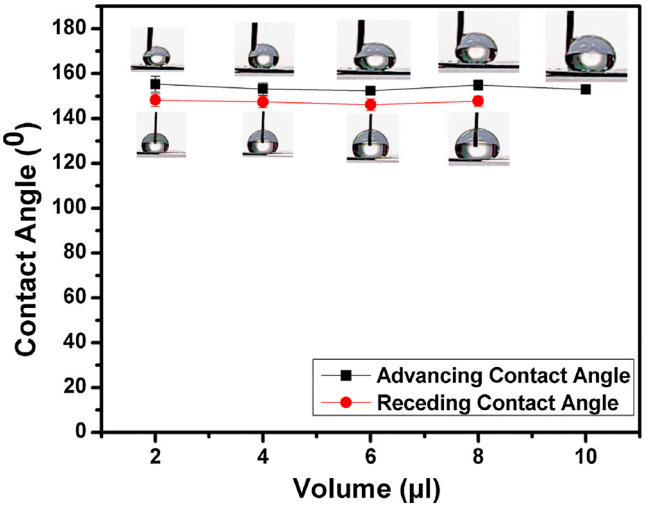

Fig. 5. Dynamic contact angle measurements on superhydrophobic PTFE (PTFE-MMA-O_2).

results indicated the clear changes in the surface chemistry of PTFE in the presence of MMA, oxygen, and oxygen-MMA plasmas. In order to get more insight regarding the surface chemical environment of carbon atoms attached to other groups, the high resolution C1s XPS spectra of the plasma treated samples were measured. The high resolution C1s XPS spectra (after deconvolution) has shown two peaks for the pristine PTFE at 291.81 and 23.45 corresponding to the C—F and CC— chemical bonds respectively (Fig. S5 ai). The oxygen plasma treated PTFE was exhibiting peaks at the similar region to that of the pristine PTFE (Fig. S5 aii). This indicates that oxygen plasma alone was not imparting a significant surface chemistry change; however, the PTFE treated with the MMA plasma has shown a difference in peak distribution. As the peak at 291 eV (due to C—F bond) decreased for the MMA modified PTFE, there observed an increase in the peak at 284 eV (due to C—C bond) (Fig. S5 bi). The high resolution spectra of PTFE treated with oxygen-MMA plasma was also exhibiting almost similar trend with the MMA treated PTFE surface (Fig. S5 bii). XPS spectra showed the drastically reduced F/C ratio of 1.04 in the long exposure time treated (1 h) PTFE surfaces (Fig. 3a and b). The high resolution C1s spectrum has also shown a difference in peak distribution between the pristine and 1 h treated PTFE. In the pristine PTFE, the C—F bonds (at 291 eV) were more predominant than the C—C bonds; however, in the case of 1 h treated PTFE surface, it was found to be the reverse. The C—F bonding was found to be decreasing and became almost half of the C—C bonds indicating the possible de-fluorination and surface functionalization with oxygen-MMA plasma system (Figs. S6a and S6b).

Furthermore, we have systematically studied the influence on the contact angle (CA) of PTFE at different time intervals using the oxygen-MMA system ranging from 10 min to 1 h. It was found that the contact angle increased with respect to increase in plasma exposure time (Fig. 4). Finally, a duration of 1 h exposure has resulted in super hydrophobic PTFE surface with a water contact angle of 154° (super-hydrophobic defined as CA > 150°). The time-dependent increase in the CA can be attributed to the increased surface content of our proposed F-PMMA moieties which explains the steady decrease in wettability of the PTFE surfaces. Thus, it was evident that the combined oxygen-MMA plasma was successful in the formation of a super-hydrophobic PTFE surface. The water-repellency of the superhydrophobic surface was evaluated by dropping water (with added fluorescein) droplets on pristine PTFE and PTFE-MMA on an inclined position. It was found that the treated surface has exhibited high water repellency and the entire droplets slide off the surface immediately after dropping (Fig. S7) However, in the case of untreated PTFE the water droplets stayed on the surface without rolling off. This clearly suggests the high water-repellency of the prepared super-hydrophobic surfaces.

We have also studied the effects of the treatment on the dynamic contact angle for both advancing and receding water drops. The advancing contact angle was found to be 156 ± 3.54° while the receding angle was found to be 148 ± 2.87° which is shown in Fig. 5. Thus, the overall contact angle hysteresis was found to be approximately 8° which is comparatively low and provides evidence of producing a Cassie-Baxter state on the surface. A hysteresis would be considered significant on superhydrophobic surfaces, if the difference in contact angle were greater, such as 20° or more [36]. Furthermore, we conducted an experiment to compare the effect of dropping liquid from a fixed height and found that the untreated surface retained the drops, whereas, the treated surface dramatically repelled the drop and rolled directly to glass surface (SI: Supplementary video).

In addition, we have compared the x-ray diffraction (XRD) analysis of the superhydrophobic PTFE surface with pristine PTFE. It was found that both pristine PTFE and superhydrophobic PTFE has exhibited major peak at 2θ of 17.8 (Fig. 6a). It was found that the superhydrophobic PTFE has exhibited a slight peak broadening in comparison with the pristine PTFE. The observed peak broadening can be attributed to the fact that the OPP deposition of MMA and surface etching of PTFE using oxygen plasma can possibly form F-PMMA over the surface of PTFE which can impart a slight amorphous characteristic to the PTFE [34]. Pristine PTFE is a crystalline polymer with long range of order in their crystal structure, but in the super-hydrophobic PTFE surface this crystallinity is reduced or compromised.

Further, we have compared differential scanning calorimetry (DSC) analysis on pristine and superhydrophobic PTFE. It was found that there was a shift in the melting peak of superhydrophobic PTFE from 328 to 334 °C in comparison with the pristine PTFE, and there was a reduction in the crystalline nature of superhydrophobic PTFE (Fig. 6b). Crystallinity, calculated based on the ratio of enthalpy of fusion determined from the endothermal melting peak of sample to the enthalpy of fusion of 100% crystalline PTFE material, indicated a decrease in crystallinity from 34.4% to 19% (approximately) due to OPP deposition, adopting a value of 82 J/g for 100% crystalline PTFE as per the reference found elsewhere [37]. The reduction in crystalline nature observed through DSC was consistent with the results obtained through the XRD measurements.

The wetting behavior of any surface is greatly depends on the surface roughness, in the case of super hydrophobic surfaces, the surface roughness lies in the nanometer range. More specifically for PTFE, the surface protrusions in the nanometer range were found to be a contributing reason for the phenomenon of super-hydrophobicity [22]. In the present system, the oxygen plasma used in combination with MMA was expected to physically etch the surface and causing defluorination, and creation of nanoscale roughness. Hence, we have compared the surface topography of super-hydrophobic PTFE and pristine PTFE. It was found that the pristine PTFE was exhibiting irregular surface roughness. However, as expected the superhydrophobic PTFE surface was exhibiting a regular roughness pattern that lies in the 500 nm range (Fig. 7). This observation was clearly pointing out the surface-etching phenomenon, which is taking place on PTFE during the OPP process. Previously, the XPS data has shown a drastic decrease in the carbon to fluorine ratio from 1.74 to 1.04 indicating strong defluorination. This observed trend of a defluorination process on PTFE was clearly supported by the nano-level surfaces protrusions which we observed through SEM analysis.

The data have strongly supported our hypothesis that accessing super-hydrophobic PTFE surfaces requires the synergistic combination of oxygen plasma (to physically etch the surface of PTFE to cause defluorination) and MMA (which may undergo polymerization at the same time to form F-PMMA). It has been reported that prolonged O_2 plasma treatment produces nano-roughness that increases the hydrophobicity on the surface of PTFE due to chemical ablation process [38]. Recently, Superhydrophobic PTFE surfaces were fabricated through the

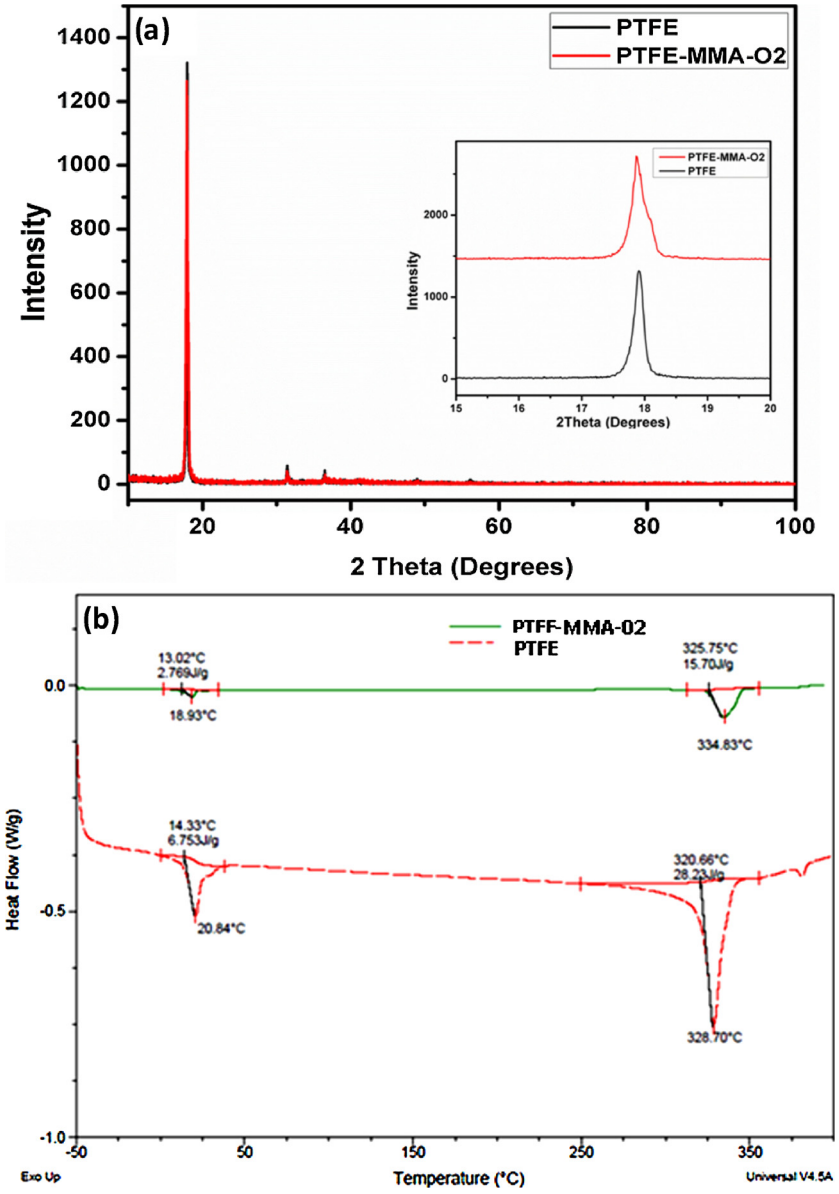

Fig. 6. XRD spectral pristine PTFE and superhydrophobic PTFE (PTFE-MMA-O_2) (a), Modulated DSC spectral analysis of pristine PTFE and superhydrophobic PTFE (PTFE-MMA-O_2) (b).

combined use of an oxygen-argon etching process. This process was found to require long treatment time around 4 h and high plasma power (289 W) to endow the property of super-hydrophobicity [39]. However, the presently reported oxygen-MMA hybrid strategy was able to generate a superhydrophobic surface modification on PTFE using the low power (45 W) and shorter exposure time (1 h) as compared to the previously reported methodology [39]. Furthermore, to compare the efficiency of this hybrid process with respect the conventional oxygen plasma etching strategy, we have compared the effect of plasma exposure time on the hydrophobicity over the surface of PTFE with the data from Lee et al (please see Supplementary information Fig. S7) [38]. It was evident that the oxygen plasma alone gradually increased the hydrophobicity of PTFE with respect to time and reaches saturation (120^0) around 30 min of plasma treatment (Fig. S8). Afterwards, the oxygen plasma treatment was found to be decreasing the hydrophobicity of PTFE. In contrast, this new hybrid strategy steadily increased the hydrophobicity of the PTFE surface and after reaching one hour, super-hydrophobicity was found to be achieved. Therefore, this oxygen-MMA hybrid system is hereby demonstrated to be more efficient with respect to time/power for generating super-hydrophobic surfaces and potentially accessing the Cassie-Baxter state [40].

This novel method of the combination of top-down (plasma etching) and bottom-up (chemical vapor modification) represents an improvement in the design of superhydrophobic PTFE surfaces and we anticipate there are several potential biointerface applications worthy of future study. In general, polymeric materials have good utility for blood contact applications [41]. More specifically, PTFE surfaces have been already explored by different groups for blood contact applications. Milionis et al has systematically studied the dynamic wetting behavior of human blood and plasma with rough PTFE surfaces. The study has shown that the rough PTFE surfaces has exhibited small roll-off angle of 18^0 and 14^0 with blood and plasma contact [42]. The superhydrophobic PTFE was also explored to use as small diameter vascular grafts as a blood repellent surface to prevent thrombosis [43]. However, the results of this study were not found to be promising to use superhydrophobic PTFE material for small diameter vascular graft. Surface properties of PTFE were modified to exhibit favorable responses for other purposes such as to confer an antifouling nature for blood contact

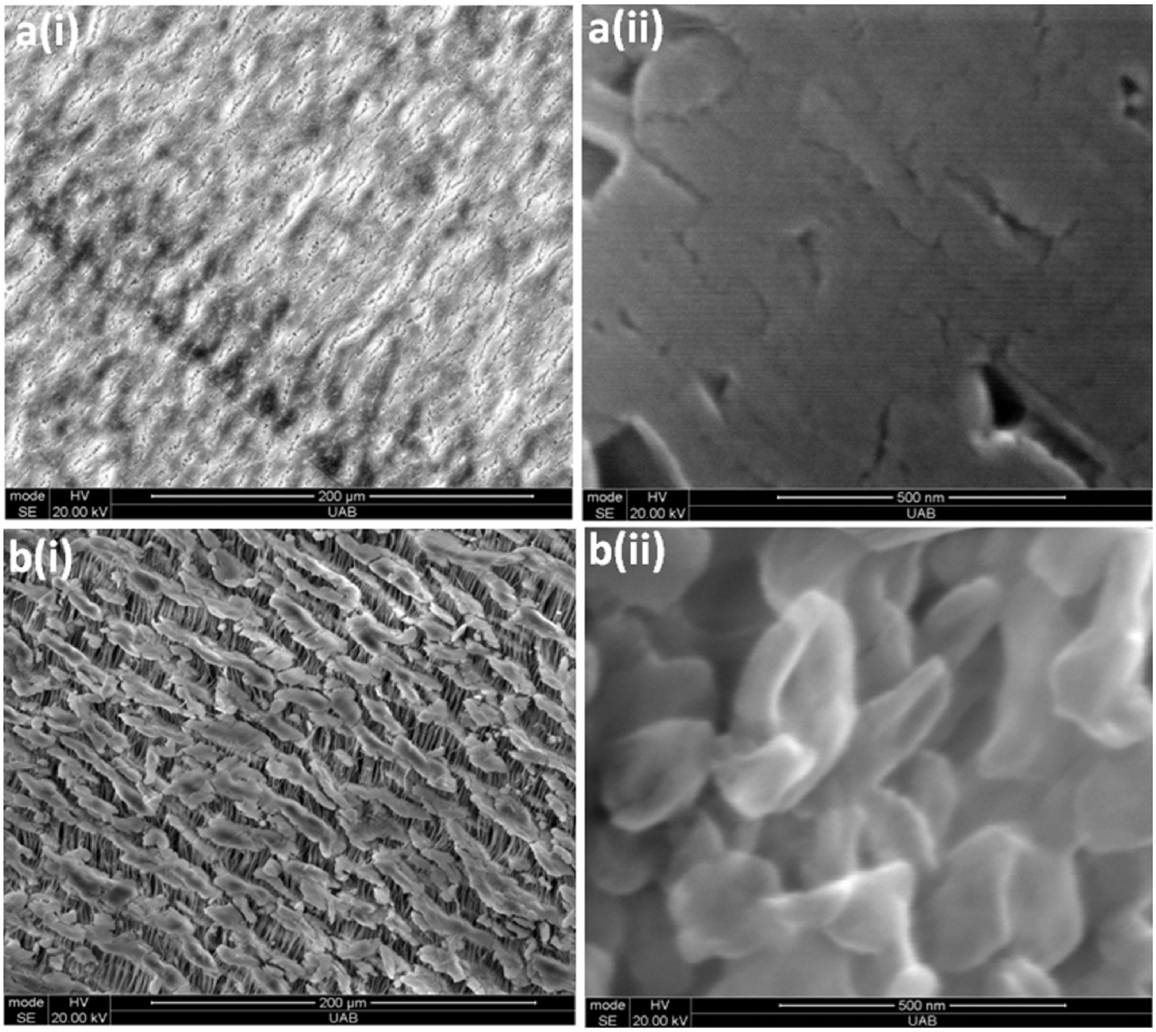

Fig. 7. SEM analysis of pristine PTFE at two different magnifications (a(i)&a(ii)), SEM analysis of Superhydrophobic PTFE (PTFE-MMA-O_2) at two different magnifications (b(i)&b(ii)).

applications [44]. Some of the other possible future applications of the current superhydrophobic PTFE surfaces are in restorative dentistry as a barrier membrane against microbes [45]. Also, we are planning to extend this study with an atmospheric pressure plasma system with additional polymers, other than PTFE, similar to a previously reported system for modifying the inner surface of polymeric tubes to potentially give superhydrophobic properties [32].

4. Conclusions

In conclusion, we explored a new hybrid process comprising of oxygen and methyl methacrylate (O_2/MMA) as precursors for organic plasma processing (OPP) to generate superhydrophobic PTFE surfaces with contact angle of 154°. The observed phenomenon of superhydrophobicity can be attributed to physical etching of surface of PTFE by oxygen plasma and the subsequent O_2/MMA combined plasma mediated surface chemical modification/deposition. Our data has strongly supported the hypothesis regarding the formation of superhydrophobic PTFE surfaces via this hybrid plasma process. More importantly, the low power (45 W) and shorter exposure time (1 h) was able to generate a superhydrophobic surface modification on PTFE more efficiently than the previously reported methodology.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.colsurfb.2019.110463.

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