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Stability of the hydrophilic and superhydrophobic properties of oxygen plasma-treated poly(tetrafluoroethylene) surfaces

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ABSTRACT

Poly(tetrafluoroethylene) (PTFE) materials were exposed to low and high-energy oxygen plasma, and the stability of the materials' surface was evaluated using contact angle, surface roughness, and surface chemistry characterizations. Lower-energy oxygen plasma treatments exhibited hydrophilic behavior with contact angles as low as 87°, and the higher-energy oxygen plasma treatments exhibited superhydrophobic behavior with contact angles as high as 151°. The wettability of all the treated samples as stored in air and in water was found to be stable in time as evidenced by the statistically insignificant differences in the advancing, receding, and hysteresis contact angles. Low contact angle hysteresis ($\theta_H < 5^\circ$) and low sliding angle ($\alpha \approx 4^\circ$) were exhibited by the superhydrophobic surface. The surface morphology was found to be responsible for the changes in the wettability of the PTFE samples since (1) there was an increase in the surface rms roughness as the plasma discharge energy was increased, and (2) there were no significant changes in the observed group frequencies of the FT-IR spectra of the treated PTFE.

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1. Introduction

The use of poly(tetrafluoroethylene)(PTFE) materials in modern technology has been extensively studied because of its excellent and adaptable properties, such as high thermal, and chemical stability. Because of its flexibility, various surface treatments using flame, chemical, grafting, corona discharge, low-pressure plasma, and UV exposure have been developed to aid in improving its properties for a wide range of applications in electronics, food processing and packaging, biomedical, agricultural, and aeronautical industries [1–4].

Plasma treatment of PTFE is becoming the primary method in changing its surface wettability [3–8]. In general, the wettability of a surface can be changed by altering the surface chemical functionalities and/or the surface roughness [8–17]. Since plasmas contain different active species such as ions, radicals, and electrons, its ability to change the wettability of a surface is promising because it has etching and activation effects [17–18]. The change in the PTFE's hydrophobic surface to either hydrophilic or superhydrophobic is a key indicator of its possible use. Since there are no permanent surface modifications using plasma treatment, it is important to know

the stability as a function of time of surfaces, especially for hydrophilic surfaces, because they undergo hydrophobic recovery [19].

This work presents the synthesis of stable hydrophilic and superhydrophobic PTFE surfaces by altering the plasma discharge energy while maintaining the use of the same discharge gas. The stability as a function of time of the plasma-treated PTFE surfaces is explained by the changes in the wettability, surface morphology, and surface chemistry.

2. Experimental procedures

2.1. Materials and plasma treatment

Tecaflon[®] poly(tetrafluoroethylene) (PTFE) samples of size $2 \text{ cm} \times 2 \text{ cm}$ were used in the experiment. The PTFE samples were cleaned ultrasonically with ethanol followed by distilled water. The cleaned and dried samples were exposed to oxygen plasma using varying discharge powers (from 100 W to 400 W) and plasma exposure times (from 30 min to 90 min), which represents plasma discharge energies ranging from 180 kJ to 2160 kJ. Table 1 shows the summary of the experimental parameters.

The plasma was produced using a BSET EQ NT-1 plasma device (Digit Concept Microelectronics and High Tech Equipment) operating at an excitation frequency of 13.56 MHz. The power and ground electrodes were placed parallel to each other at 50 mm distance,



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Table 1

Summary of the experimental parameters in relation to the water contact angle and surface rms roughness of oxygen plasma-treated PTFE materials.

Power (W)	Time (s)	Energy (kJ)	Contact angle (°)	$R_{\rm q}$ (µm)
	Untreated		119.0	1.79
100	1800	180	87.3	1.15
100	3600	360	100.0	1.29
100	5400	540	108.4	1.95
400	1800	720	127.4	2.53
400	3600	1440	130.0	2.75
400	5400	2160	151.3	2.98

and the samples were placed at the ground electrode. The system was evacuated by a $20 \text{ m}^3/\text{h}$ rotary pump, and the base pressure was set at 100 mTorr. Oxygen discharge gas was fed into the chamber at a rate of 20 sccm.

2.2. Characterizations

2.2.1. Contact angle measurements

A DSA-10 goniometer (Krüss GmbH) was used to study the changes in the wettability. The sessile drop method was used to determine the static contact angles. About 2 μ L of deionized water was dropped vertically onto the samples using a motorized syringe mechanism; a drop shape analysis software was used to measure the contact angles. For each sample, contact angles were measured at five different sites, and the standard deviation of the contact angles measurements at different sites were all statistically the same. The contact angles were measured as a function of time right after plasma treatment until after 552 h. All contact angle measurements were recorded at 21 °C ± 1 °C.

To study the stability of the surfaces after plasma treatment, the samples were stored in air and in water. The advancing (θ_A), receding (θ_R), and hysteresis (θ_H) contact angles were measured as a function of storage time from 3 h until 144 h. θ_A and θ_R were determined by increasing and decreasing the water drop volume (ranging from 1 µL to 6 µL) using the motorized syringe mechanism.

2.2.2. Surface roughness

A Wyko NT1100 Optical Profiling System (Veeco) was used to measure the surface roughness. The experiment was carried out at VSI mode using a 50× objective lens and a 0.5× field of view lens. The effective field of view was 0.240 mm × 0.182 mm. The

surface roughness was reported as root-mean-squared (rms) roughness calculated over the entire measured array.

2.2.3. FT-IR characterization

A Spectrum 100 FT-IR spectrometer (Perkin Elmer) with a diamond ATR top plate was used to determine the changes in the surface chemical functionalities. The samples were scanned 4 times at 4 cm^{-1} spectral resolution.

3. Results and discussion

Fig. 1 shows the changes in the contact angles as a function of time after exposure to oxygen plasma. Table 1 also shows the contact angle values of PTFE samples just right after plasma treatment. The untreated PTFE samples were found to have a contact angle of 119°. Plasma treatment using the lowest discharge energy exhibited hydrophilic behavior as indicated by a contact angle of 87°, while the plasma treatment using the highest discharge energy exhibited superhydrophobic behavior as indicated by a contact angle of 151°. Fig. 2 shows the images of a water droplet on the PTFE's surface of (a) an untreated PTFE, (b) a PTFE treated with low discharge energy, and (c) a PTFE treated with high discharge energy.

In general, as the plasma discharge energy is increased, the water contact angle also increases. There is a general trend that when after 24 h exposure to air, the contact angles decreased, and it increases from 48 h up to 552 h. The differences in the increase or the decrease in the contact angles as a function of time of most samples are found to be statistically insignificant (p > 0.1). For the 180 kJ and360 kJ plasma discharge energies, there is a significant decrease in the contact angle after 24 h exposure to air. Further experiments revealed that within the 5-min period after exposure to air, the contact angle decreases faster until it reached a more stable contact angle. It can be assumed that within this period, the effect of plasma activation in the surface is greater than the etching effect of the plasma.

Figs. 3–5 show the effects of the exposure of PTFE samples to air on the advancing, receding, and hysteresis water contact angle at various times after oxygen plasma treatment, respectively. The θ_A and θ_R increases as a function of time, but the increase in values is statistically insignificant (p > 0.1).

The $\theta_{\rm H}$ values were higher for the low plasma discharge energies, and it was lower for the highest plasma discharge energy (2160 kJ). For the superhydrophobic surface, $\theta_{\rm H}$ was found to be less than 5° as a function of time, and it is interesting to note that



Fig. 1. Changes in the contact angles as a function of time after exposure to oxygen plasma.



Fig. 2. A water droplet on the PTFE's surface; (a) untreated PTFE showing a contact angle of 119°; (b) 180 kJ oxygen plasma-treated PTFE with a contact angle of 87°; and (c) 2160 kJ oxygen plasma-treated PTFE with a contact angle of 151°.



Fig. 3. The effect of the exposure of PTFE samples to air on advancing water contact angles at various times after oxygen plasma treatment.



Fig. 4. The effect of the exposure of PTFE samples to air on receding water contact angles at various times after oxygen plasma treatment.

the sliding angle (α) for this surface is approximately equal to 4°. The differences in the hysteresis contact angle were also found to be statistically insignificant (p > 0.05).

Figs. 6–8 show the effects of the exposure of PTFE samples to water on the advancing, receding, and hysteresis water contact angle at various times after oxygen plasma treatment, respectively.

The θ_A increases as a function of time, but the increase in values is statistically insignificant (p > 0.1). However, θ_R decreases as a function of time, but the decrease in values is also found to be statistically insignificant (p > 0.1).

For samples stored in water, the $\theta_{\rm H}$ values were also higher for the low plasma discharge energies, and it was lower for the highest



Fig. 5. The effect of the exposure of PTFE samples to air on hysteresis water contact angles at various times after oxygen plasma treatment.



Fig. 6. The effect of the exposure of PTFE samples to water on advancing water contact angles at various times after oxygen plasma treatment.



Fig. 7. The effect of the exposure of PTFE samples to water on receding water contact angles at various times after oxygen plasma treatment.

plasma discharge energy (2160 kJ). For the superhydrophobic surface, $\theta_{\rm H}$ was found to approximately equal to 5° and increases to approximately 10° as a function of time. There is a slightly signif-

icant increase in the hysteresis contact angles (p < 0.05) as a function of time. This result leads us to assume that the PTFE surface is slightly more stable when it is stored in air than in water.



Fig. 8. The effect of the exposure of PTFE samples to water on hysteresis water contact angles at various times after oxygen plasma treatment.

Table 1 show the relationship of the experimental parameters to the water contact angle and surface rms roughness. In general, there is an increase in the surface rms roughness as the plasma discharge energy is increased. Morra et al. [5] explained that the increase in the θ_A also gives rise to the increase in the surface roughness, and their findings are consistent with the increase in θ_A for PTFE samples stored both in air and in water. Fig. 9 shows the 3D surface profile of the (a) untreated; (b) 180 kJ oxygen plasma-treated; (c) 720 kJ oxygen plasma-treated; and (d) 2160 kJ oxygen plasma-treated PTFE samples. It can be observed that the untreated sample has a higher surface rms roughness than the samples treated with lower plasma discharge energies. As established from the work of Takahashi et al. [3], the plasma treatment using oxygen discharge gas has a higher etching rate than other discharge gases, this means that higher chain scission reactions occurs at the surface of the PTFE and that new surfaces continually appear during the etching process. Ryan et al. [16] and Vandencasteele et al. [20] explained in detail the polymer radical formations when the ions, photons, and electrons contained in the O_2 plasma reacts with PTFE; the polymer radicals that reacts with the O_2 atoms inhibit cross-linking that leads to chain scissions in the polymer backbone. The effects of the low plasma discharge energy on the new surfaces that appears during etching give a smoother surface than the surface of the untreated samples.

For the superhydrophobic surface, the extremely low $\theta_{\rm H}$, low α , and high surface rms roughness can be a sign of air trapping in the surface [8–9,11]; based on this, we can assume that the Cassie–Baxter state is predominant in the surface.



Fig. 9. 3D surface profile of the (a) untreated; (b) 180 kJ oxygen plasma-treated; (c) 720 kJ oxygen plasma-treated; and (d) 2160 kJ oxygen plasma-treated PTFE samples.



Fig. 10. FTIR-spectra of untreated and oxygen-treated PTFE samples; the spectra of the oxygen-treated PTFE samples represent low and high plasma discharge energies.

Fig. 10 shows the FTIR-spectra of the untreated and the oxygentreated PTFE samples; the spectra of the oxygen-treated PTFE samples represent low and high plasma discharge energies. The existence of CF₂ bonds on all the samples verifies that they are all PTFE materials. Asymmetric and symmetric stretches of $-CF_2$ groups were observed from the high absorbance peaks at group frequencies of 1201 cm⁻¹ and 1146 cm⁻¹, respectively. Peaks with lower absorbance intensity at group frequencies of 639 cm⁻¹ and 626 cm⁻¹ represent the wagging modes and chain stretching of the $-CF_2$ groups, respectively. The bending and rocking modes of the $-CF_2$ groups were observed at group frequencies of 554 cm⁻¹ and 505 cm⁻¹, respectively.

There were no significant changes in the observed group frequencies of the FT-IR spectra of the treated samples from the untreated samples. The slight differences in the intensity value of the absorbance peaks were found to be statistically insignificant (p > 0.05) for all the samples. This means that the plasma discharge energies have no significant effects in the absorbance values. Since there is no change in the chemical nature of the PTFE samples after plasma treatment, we can assume that the plasma treatment is brought about only by the changes in the surface morphology as also observed from the changes in the surface rms roughness. Several studies also showed that surface modification of PTFE can only be morphological in nature and not chemical [4,16].

4. Conclusions

After the exposure of poly(tetrafluoroethylene) (PTFE) materials to low and high-energy oxygen plasma, the stability of the materials' surface were evaluated using contact angle, surface roughness, and surface chemistry characterizations. It showed that

lower-energy oxygen plasma treatments exhibited hydrophilic behavior with contact angles as low as 87°, and the higher-energy oxygen plasma treatments exhibited superhydrophobic behavior with contact angles as high as 151°. The wettability of all the treated samples as stored in air and in water was found to be stable in time as evidenced by the statistically insignificant differences in the advancing, receding, and hysteresis contact angles. However, it was found that PTFE surface is slightly more stable when it is stored in air than in water. Low contact angle hysteresis ($\theta_{\rm H} < 5^{\circ}$) and low sliding angle ($\alpha \approx 4^{\circ}$) were exhibited by the superhydrophobic surface. The surface morphology was found to be responsible for the changes in the wettability of the PTFE samples since (1) there was an increase in the surface rms roughness as the plasma discharge energy was increased, and (2) there were no significant changes in the observed group frequencies of the FT-IR spectra of the treated PTFE from the untreated PTFE.

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