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Article

Surface Characterization of Polytetrafluoroethylene (PTFE) Substrate after Oxygenated Plasma Treatment towards Potential Food Processing Application

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Abstract: The spray drying process causes the buildup of an unspecified and unique pattern of wall deposits on the wall. The powder recovery of fruit juice by spray dryer is associated with stickiness problems because of the nature of food which contains low molecular weight sugars and organic acids, which have a low glass transition temperature (T_g). The surface properties of oxygen plasma treated-PTFE substrate were evaluated by using the different parameters of Plasma Enhanced Chemical Vapour Deposition (PECVD) prior to spray drying analysis. In this study, the fabrication method of nearly perfect superhydrophobic surfaces through plasma treatment with oxygen gas was generated and utilized. The plasma-treated PTFE were deposited from a fixed flow rate of oxygen gas with 30 cm^3/min by varying the deposition time from 1 to 15 minutes to induce the hydrophobic surface of the PTFE substrate. The characterization techniques used to determine the morphology and chemical bonding of the substrate were field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR), respectively. The hydrophobicity of the glass samples was determined by the water droplet contact angle. Sample prepared at radio frequency (RF) power of 90W for 15 minutes duration of treatment time showed porous and spongy like microstructure which correlates with the best performance of a good contact angle which creates the superhydrophobicity regime (171°). Surface morphology analysis using scanning electron microscopy (SEM) showed changes in its roughness in the surface-treated glass substrate. The success of this method produced a huge potential for solving most of the food processing issues which relate to biofouling (e.g., powder stickiness) that would otherwise struggle to improve high productivity and recovery.

Keywords: biofouling; deposition; hydrophobic; plasma treatment; PTFE; stickiness

1. Introduction

The consumption of fruit juices has significantly increased during last few years and it is growing remarkably since consumers are interested in a healthy product which are practical, ready to be consumed and prolong shelf-life (especially in the form of dried solid powdery) [1]. For that reason, recovery of the food-based powder especially by spray drying process is a major challenge in food processing industry. In the preliminary study, a borosilicate micro-slide was used to mimic and model the pilot scale spray drying chamber wall surface (which has the same material characteristics) prior to PTFE liquid surface coating [2]. Wall deposition (biofouling) has been thoroughly studied in co-current dryers, especially on foods (e.g., herbal extract or fruit juices) and this leads to several common main problem of reduction in yield and quality problems (shelf-life) [3, 4]. In the case of fruits, the presence of sugars and organic acids of low molecular weight in the composition, which has low glass transition temperatures may limit the spray drying process due to problems such as stickiness and high hygroscopicity [5]. Previous research conducted *in situ* stickiness tests on different wall materials and suggested that Teflon showed

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less adhesion than stainless steel and glass [6]. The findings agreed with the previous research, showing that Teflon has a comparatively lower propensity to form wall deposits in the middle chamber segment due to lower surface energy properties [7]. Design with glass components may be problematic and a metal design can be considered, but dryer may have windows built into its walls to allow visual inspection. Components may be made of metal and other materials and the walls may have a coating using low surface energy materials to minimize product sticking [8]. The highly useful plastic materials PTFE (polytetrafluoroethylene) were identified by name as Teflon is one of plastics group, called fluoropolymers [9]. PTFE is a polymerized tetrafluoroethylene form. Fluoro-based polymer coatings possess excellent anti-stick features but are also exposed to rather aggressive environments and extreme conditions of operation [10]. PTFE fulfilled all the qualities of alloys for bearing such as embedded ability, conformability, load efficiency, corrosion resistance, the strength of fatigue, compatibility, and robustness [11]. Prior work shows that polytetrafluoroethylene (PTFE) has hydrophobic features, oil resistance, self-lubrication, low adhesion, and stronger resistance to corrosion which could provide new thought and method [12]. In the foodservice industry, anti-adhesive components usually employ composite PTFE coatings to enhance wear resistance and improve cleanliness [13]. PTFE exhibits hydrophobic and oleophobic character at the same time [14]. When a liquid drop is placed on these surfaces, it does not stick to the surface and formulates in a nearly spherical shape [15].

For several fields of surface engineering, plasma can be artificially produced and implemented for three main purposes: surface alteration, surface etching, and surface coating [16]. 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 [17]. Plasma modification can introduce oxygen rich functional groups which can modify the surface properties of PTFE including wettability and surface energy [18]. Plasma treatment is a surface modification method based on a dry process and therefore this does not involve the use of a corrosive solution [19].

In general, plasmas can be subdivided into two categories based on the gas temperature: thermal and nonthermal (cold) plasmas [20]. These treatments include but are not limited to improving dyeability, printability, flammability, wettability, hydrophobicity, adhesive binding, and stain and soil resistance [21]. Moreover, this is an expensive approach, because of the high-cost requirement due to the gas flow, is acceptable for some biomedical applications, rather than food processing, in which cost is an important consideration [22]. Plasma processing modifies the food material to the desired characteristics, maintains texture and nutritional properties, and promotes microbial decontamination [23]. One of the main challenges in plasma surface treatments is the retainment of induced properties on the polymer surface.

Plasma treatment can mechanically or chemically change the characteristics of the materials or surfaces [24]. Among various surface modification techniques, we propose a low-pressure plasma polymerisation technique allowing a thin layer of polymer to be deposited that contains specific functional group depending on the monomer. This technique has various advantages such as room temperature process, nanoscale thickness; small amount of monomer, and does not produce any secondary waste with the distribution of polymers deposited on the surface is homogeneous on a large amount of area [25, 26]. For that reason, a polytetrafluoroethylene (PTFE) sheet was selected as a substrate material in this present studies. The important parameters in the plasma treatment are the total amount of gas, the gas flow rate ratio of oxygen gases, the RF power, and the plasma exposure time to fabricate superhydrophobic PTFE sheets. Based on the Taguchi method, the RF power was found to be the most influential factor, and plasma exposure time was the second important factor [17]. The properties and the sensitivity of plasma treated-PTFE films towards contact angle can be tailored by using appropriate precursor gases and deposition parameters of plasma-enhanced chemical vapor deposition (PEVCD).

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Thus, the main objective of this studies was to determine the efficacy of the plasma treatment (which was set at an optimal 90W power) that could potentially enhance the value of the contact angle of plasma treated PTFE and thus reduced the particulates adhesion on the spray dryer wall chamber by creating a superhydrophobicity surface that reduces the stickiness. Increase in hydrophobicity of the PTFE membrane could attribute to the powder stickiness reduction and the real spray drying (pilot scale) performance case scenario will be discussed in future studies once it is proven to be the best solution to increase the productivity and production yield.

2. Materials and Methods

2.1. Preparation of Hydrophobic Substrate

Microscope slides (Borosilicate, 76 mm x 26 mm x 1 mm) were obtained from Quasi-S Technology (M) Sdn. Bhd. and were used to mimic the chamber wall of a spray dryer. A commercial polytetrafluoroethylene (PTFE) tape manufactured by a chemical company (Hyunwoo Chemical, Korea) was selected as the material for surface modification via plasma treatment. The specimens were cut into 2.0 cm × 2.0 cm (0.2 mm in thickness) square-shaped samples for plasma treatment. They were cleaned using pure ethanol followed by pure isooctane (GR for analysis, Merck) before being introduced into the plasma chamber. The specimens were ultrasonically cleaned with acetone for 5 minutes followed by drying at room temperature for 2 hours before plasma treatment. This fluorocarbon-based polymer (PTFE) has a low surface free energy of 20 mNm^{-1} at 20 °C, which permits easy fabrication of superhydrophobicity [27].

2.2. Oxygen Plasma Treatment

The plasma polymerization of oxygen on PTFE substrate was carried out in a 7-inch diameter cylindrical quartz tube chamber, with a steel stainless-steel plate connected to an RF generator with a frequency of 13.56 MHz. A volumetric gas flow rate was set at 30 cm^3/min and controlled by means of a mass flow controller (MKS). Prior to depositing, the samples were exposed to air plasma treatment (30W, 150 mTorr) for 2 minutes to eliminate the contaminant on the membrane and to activate its surface. The gap between the two electrodes was 3 cm and the plasma was adjusted to occur in the space between the electrodes. The glass slide was placed on the lower electrode disc for the plasma treatment. After air plasma treatment, the pressure inside the chamber was again evacuated to reach 30 mTorr before allowing oxygen gas to flow inside the chamber at 300 mTorr pressure. The glass slides were treated in different conditions in which the duration of treatment and proportion of O_2 gas was kept constant and the effect on its physico-chemical properties was later evaluated. Four samples were produced by varying the deposition time at 1, 5, 10, and 15 minutes respectively. The plasma power for plasma treatment was kept constant at 90W.

2.3. Contact Angle Measurements

The water contact angle (WCA) was measured using an Automated Contact Angle Goniometer (Model 100) from Rame-Hart Inc. The contact angle measurement was carried out using a static contact angle technique (Drop Tensile Analyzer). To confirm the homogeneity of the treated samples, approximately of 0.5 ml deionized water was dropped at three separate points on the glass surface of the PTFE plasma treated and untreated slides (without PTFE film) [24]. The angles were then calculated from the average of six measurements taken for each time point ($n = 6$). Image J software was used to accurately measure the advancing and receding contact angle of the water droplets on the surface.

2.4. Surface characterization by FT-IR spectroscopy

To measure the change in intensity of the substrate surface spectrum, the Fourier Transform Infrared (FTIR) Spectrometer (Perkin Elmer model 1600 coupled with Attenuated Total Reflectance (ATR): PIKE Technologies, Madison, WI, USA) was used in the

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range of 4000 to 550 cm^{-1}. The exiting rays were gathered by sensors and the infrared spectrum was produced by the FTIR spectrometer [28].

2.5. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy Analysis (EDX)

The examination of samples was carried out, using a scanning electron microscope JSM-5800, made by JEOL, Japan and Energy Dispersive Spectroscopy Analysis (EDX). Each EDX spectrum is normalised by the counting rates (cts/s)N of the coupled EDX detectors and plotted against the keV scale. This method enables an expert to simultaneously observe the characteristic morphology and check its elemental content without prior damage of the sample/object. All samples were covered with a fine layer of carbon by sputtering in a vacuum sputter and automatically searches for particles of defined features by analysing the specimen surface divided into small areas depends on the set-up magnification. The program requires that the operator set up the layout of the stubs as well as the standard, establish the set of the expected chemical classes of the particles, set the limits of the particle size and define the lower and upper particle diameter in the analysed area [29].

3. Results and Discussion

3.1. Water Contact Angle (WCA) Profiles

Contact angle profiles shown in Figure 1 and Figure 2 proves that the immobilization of radicalized oxygen plasma on the surface of the PTFE membrane substrate can be increased to a certain degree of its hydrophobicity. Increasing in WCA has been reported for PTFE substrate exposed to air plasma treatment for 15 minutes; where the WCA values of plasma-treated PTFE registered at 171◦ (superhydrophobicity) in which superficially improved from 118◦ (untreated Teflon). PTFE is a hydrophobic surface with a static WCA of 111.4° ± 6.2 before isooctane cleaning and 103.6° ± 8.8 after cleaning [29] and the other reported values are ranging from 102.5 to 130.8◦ [15]. It is worth noting that the surface treatment homogeneity on both treated substrates (borosilicate and PTFE plate) was considered good as the angle variations was less than 2% (n = 6) (Table 1). In fact, the present work was manifestly adequate to exceed the hydrophobicity threshold by maintaining the WCA profiles as observed by FESEM and FTIR (Section 3.2 and 3.3) through its physical and chemical changes. The static WCA increased to about more than 90° when the surface was modified by radicalized O_2 plasma exposure for 1, 5, 10, 15 minutes under atmospheric pressure (Figure 1). Moreover, after the high-power oxygen plasma treatment, there was a significant increase of WCA as compared with borosilicate glass substrate (p<0.05), with values higher than 160° at high RF power (90W) (Figure 2). The rapid WCA increased (up to 171°) was due to a plasma induced polymerization process by means of introducing into radicalized and oxidized O_2 molecules at high exposure power (90W; 15 minutes) which eventually produced a superhydrophobicity regime.

Meanwhile, Table 1 shows the degradability profiles of WCA between borosilicate glass and PTFE-film surface samples after oxygen plasma treatment after 15 days of storage. The gradually changes of WCA from 118° (untreated PTFE) to 116.3° and 108.8° at 5 minutes and 1 minute of exposure respectively might be due to the hydrophobic recovery process (reorientation of functional groups) which is related to a decrease/increase in the value of surface free energy (SFE). The hydrophobic recovery mechanism depends on the processing, materials, and enthalpy-related factors such as precursor type, type of substrate, treatment conditions and aging micro-environment [30, 31]. A good sustainability of its superhydrophobic condition is one of the main concerns of maintaining the efficacy of the spray drying recovery (yield) throughout the process as it would be a cost-effective procedure for food manufacturing industry. The fundamental mechanism of this observation is presently being examined and will be reported in the future subsequent work.

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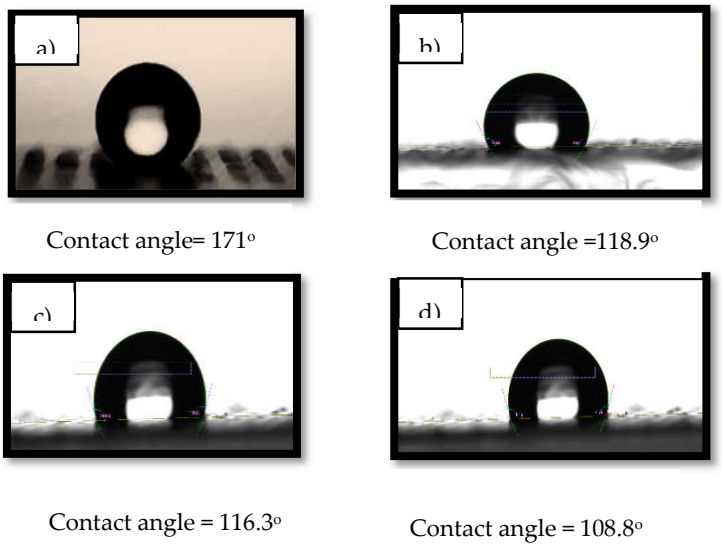

Figure 1. Contact angle images for the Teflon (PTFE) substrate sample treated with oxygen plasma with variation of exposure time a) 15; b) 10; c) 5; d) 1 minute.

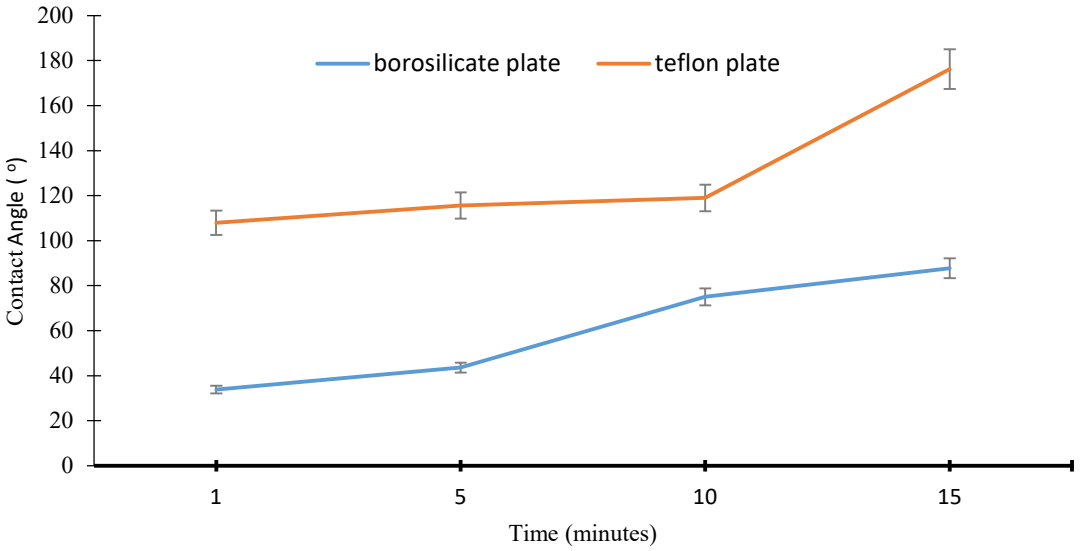

Figure 2. Water contact angle of PTFE- and borosilicate-substrates of various exposure period ranging from 1 to 15 minutes.

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Table 1. The water contact angle (WCA) degradability profiles of borosilicate glass and PTFE film substrates after oxygen plasma treatment as a function of treatment time.

Treatment Time (min)	*Initial exposure (°)	*After 15 days (°)
Untreated borosilicate glass	48.20 ± 0.7	47.10 ± 1.1
1	43.30 ± 0.2	39.10 ± 0.8
5	40.60 ± 0.7	38.60 ± 0.1
10	38.10 ± 0.3	33.40 ± 0.8
15	30.20 ± 1.2	28.40 ± 0.8
Untreated PTFE film	118.10 ± 0.5	106.10 ± 0.3
1	108.80 ± 0.6	107.10 ± 0.2
5	116.30 ± 0.7	116.10 ± 0.5
10	118.90 ± 1.4	117.31 ± 0.8
15	171.00 ± 0.1	170.20 ± 0.3

*The angles were calculated from the average of six measurements taken for each time point (n = 6)

3.2. Fourier-transform infrared spectroscopy (FTIR)

Figures 3 and 4 show the chemical composition of untreated and treated glass surfaces. For untreated glass, as expected, the glass composition such as Si-O bending and Si-OH stretching peaks were only observed as shown in Figure 5. Surface reducing agent such as sodium hydrate/benzophenone complex was used for chemical transformation of the carbon-flourine (C-F) bond into carbon-hydrogen (C-H) bonding to surfaces of PTFE [24]. Based on Figure 3, the main SiO_2 stretching vibration is at 945.6 cm^{-1} while the rocking vibration is at 781 cm^{-1}. Both of these peaks, subsequently can be used to quantify the amount of SiO_2 present in the oxide layer. In addition, ATR-FTIR studies indicate that the effect of the O_2 plasma is two-fold [32].

As shown in Figure 4, the absorption band at 1158-1200 cm^{-1} is due to C-C stretching while the other at 500-700 cm^{-1} is due to C-F stretching as a cause of the changing microstructure of the surface through chemical reactions such as dissociation and excitation in the plasma irradiation. Besides, a weak absorption band appear at about 2200-4000 cm^{-1}. FTIR analysis revealed the defluorination of PTFE modified by plasma due to the rupture of C-C and C-F bonds. Considering the main absorption bands of PTFE (i.e. -CF2-), it is observed that the ratio of the asymmetric and symmetric stretching bands intensity has been reversed and the absorption maxima have been shifted to higher wavenumbers. Usually, oxygen plasma treatment of polymers induces a decrease of the contact angle due to the grafting of new polar functionalities (-OH, -O, -OOH, etc.) onto the sample surface [33]. In cases where the gaseous plasma is rich in oxygen, the radiation that causes bond breaking between C and F atoms in PTFE arises effectively only from excited neutral oxygen atoms. The result is a formation of unstable fragments containing carbon, fluorine, and oxygen. Known fragments of such type include oxy (x = 1) and peroxy (x = 2) radicals of formulae CF_3x, $FC(O)Ox$, $CF_3C(O)Ox$ and $CF_3OC(O)Ox$ [34]. Such moieties desorb from the surface, which results in etching. The etching outcome is increased roughness, which in turn results in the super-hydrophobic surface finish. Additionally, the appearance of some new bands was observed to broadening the whole absorption area, for example from the defluorinated group, that may be attributed to the micro-surface changes [35]. These results of FTIR corroborate with those of the contact angle. In fact, short period and low positive pulses between longer and high negative pulses greatly increased the energetic positive O_2^+ ions species that cleaved C-C and C-F bonds, causing the CF_2 chain scission producing polymer radical segments as expressed by the following reactions [31];

$$-CF_2\text{-}CF_2- \rightarrow -CF_2\text{-}CF\cdot + F\cdot$$

$$-CF_2\text{-}CF_2- \rightarrow -CF_2\cdot + \cdot CF_2-$$

$$-CF_2\cdot + F\cdot \rightarrow -CF_3$$

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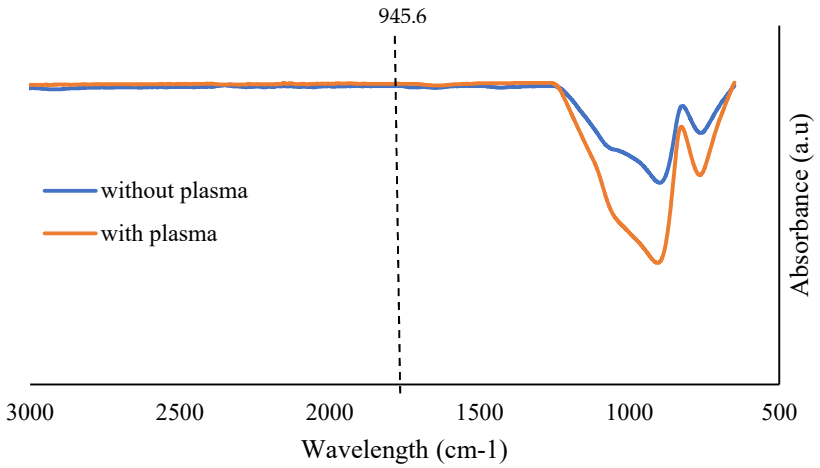

Figure 3. FTIR spectra analysis comparison of borosilicate substrate sample treated with oxygen plasma (a) after 15 minutes duration time and (b) without oxygen plasma .

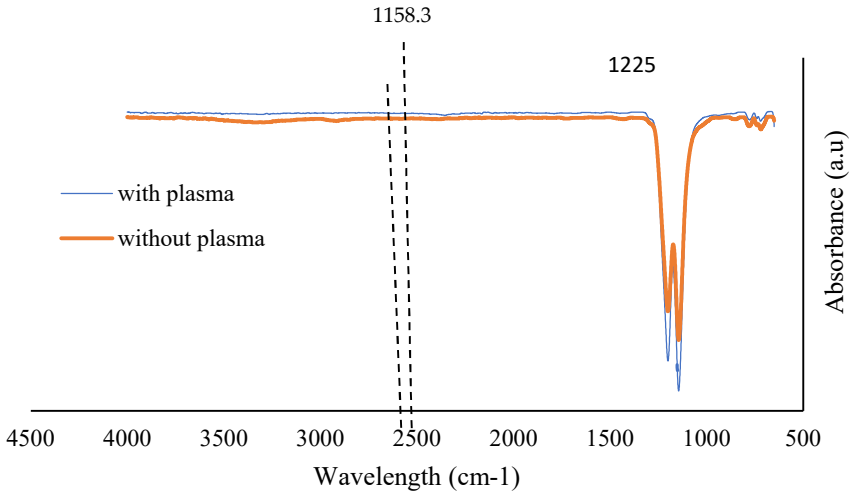

Figure 4. FTIR spectra analysis comparison of Teflon (PTFE) substrate sample treated with oxygen plasma (a) after 15 minutes duration time and (b) without oxygen plasma.

3.3. Surface Morphology by Scanning Electron Microscopy (SEM) and EDX

The surface roughness was intensely increased on the treated PTFE-glass surface (a) as compared with the untreated glass surface (b) where the increase in surface roughness may be due to the adsorption of radicalized oxygen ions on to the reorientated PTFE functional groups which reduces its wettability. Figure 5 shows the SEM images of PTFE samples and non-PTFE sample with PEVCD treatments in different duration treatment. By changing the plasma parameters (treatment time) the roughness and feature size of the PTFE surfaces can be systematically varied. Moreover, for longer treatment durations, there was a strong increase in the contact angle value due to the roughening of the surface.

Previous studies have also shown a significant reduction of molecular adhesion as the surface contact angle increases due to the improvement in the glass surface roughness after plasma treatment [36]. Among various surface treatment methods used to fabricate a superhydrophobic surface, the plasma-based dry etching method, which requires the use of reactive gases, was employed in previous study. Even different types of polymers are etched at different rates. The effect of composite etching is therefore a rough surface

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[37]. Figure 6 shows the differences of elemental species appear before and after oxygen plasma treatment by EDX. In the case of oxygen plasma treatment, two kinds of reaction are competing: the first is surface modification, leading to fluorine depletion and some oxygen introduction, while the second is etching, leading to a chemically PTFE-like (Figure 6) but morphologically spongy-like surface (Figure 5(f)). Surface modification is dominant at first and then is overwhelmed by etching. Based on the EDX result, with increasing of the F element content in PTFE, the hydrophobicity becomes stronger as reflected by the increased of contact angles [38]. A steady state is reached with a surface that is not chemically PTFE-like but clearly has more fluorine-containing components than at the beginning of the treatment. In fact, prolonged exposure produced a dynamic evolution of its micro-topography. Most of the glass surface, the presence of functional groups (non-polar) prevents the entry of water molecules in the polar bonds, thus contributing to the enhancement of its hydrophobic properties [39-42]. Based on Figure 6 profiles, PTFE surfaces contained up to 3.3% oxygen (before undergo oxygen plasma treatment), but this concentration decreases after exposure until zero detection of oxygen in the chamber occurred. Before oxygen plasma treatment, sample with borosilicate glass surface have an increment of oxygen (wt%) from 22.8 to 34.8. The readily chemical interaction of reactive oxygen species with the borosilicate glass surface causing spatial oxidation which decreases the WCA and resulting the surface cleaning. The differences of WCA as compared to other studies could be explained by differences in plasma conditions whereas prior work [44] used only 3W of plasma power instead of 90W with various duration time of treatment in the present work.

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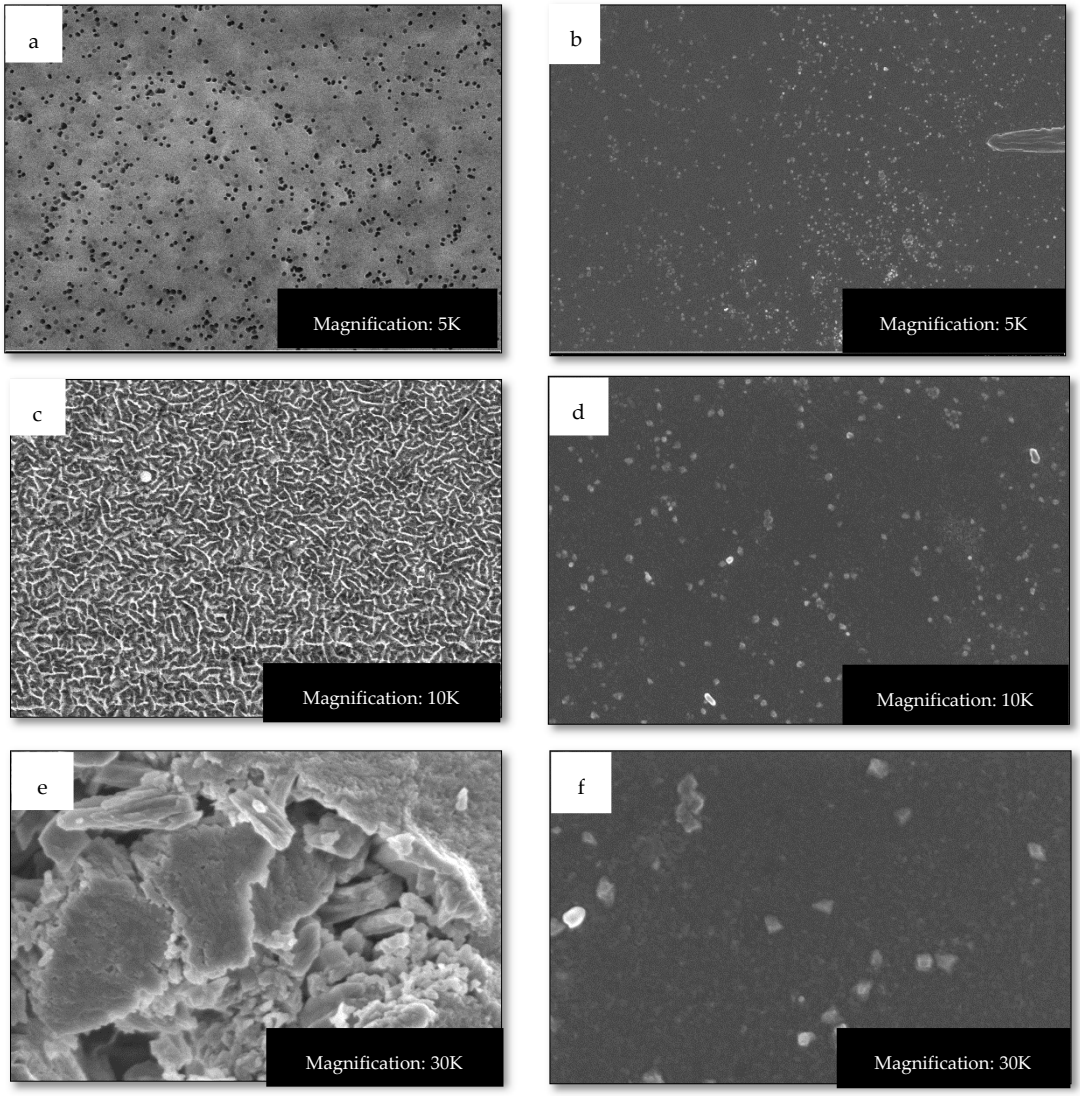

Figure 5. SEM images for the PTFE substrate sample (a, c, e) and borosilicate sample (b, d, f) treated with oxygen plasma at 90W for 15 minutes under magnification of 5K, 10K and 30K respectively.

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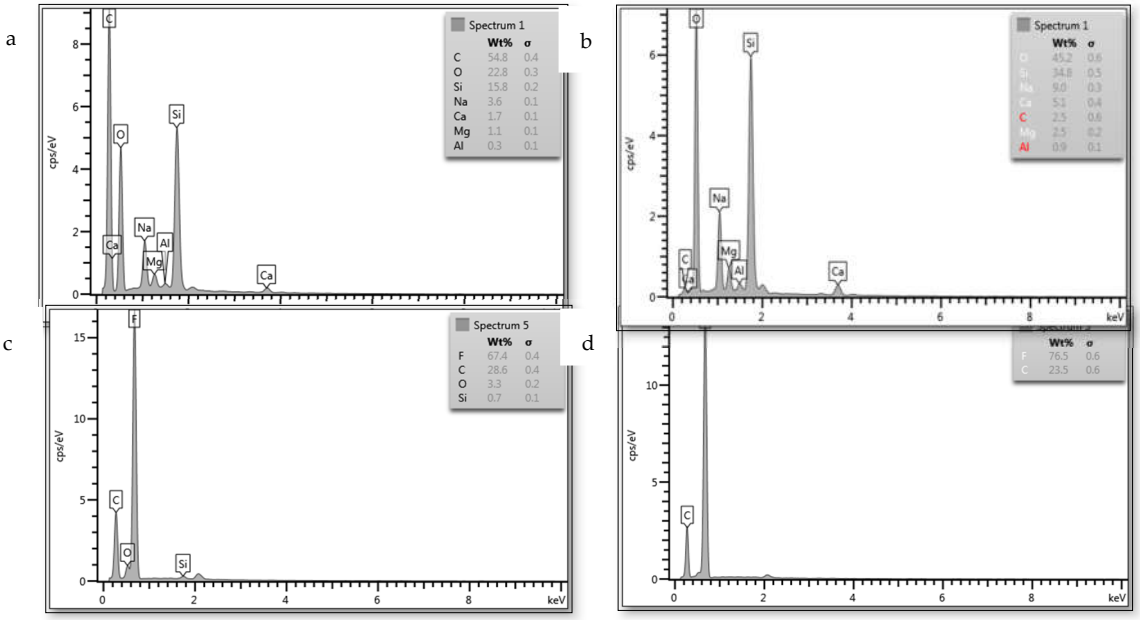

Figure 6. A labelling of EDX spectra elemental composition on borosilicate glass sample before oxygen plasma treatment (a, b) and PTFE film substrate after plasma treatment (c, d) at 15-minute duration of treatment and 90W (power).

4. Conclusion

As a conclusion, the method of modifying the chamber design was found promising for reduction wall deposition. SEM micrographs show a small variation in surface roughness and appearance of microcracks for high exposure times, although the data available was not enough for quantitative analysis. On the other hand, the samples exposed to oxygen plasma for longer times (15 minutes) showed a surface morphology different to that of the samples treated for shorter times. Hence, the present study aimed to establish a simplified model of spray drying based on the fundamental parameter concentrating on application in food industry. The development of this model allows the estimation of sustainability efficacy in maintaining its superhydrophobic condition that could potentially reduce biofouling or stickiness on the wall chamber surface throughout the spray drying process.

Data Availability Statement: No data were used elsewhere to support this study and it was entirely a new set of data.

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