Carbohydrate Polymers 86 (2011) 1031–1037

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

# Cold plasma treatment on starch foam reinforced with wood fiber for its surface hydrophobicity

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ARTICLE INFO

*Article history:*
Received 21 March 2011
Received in revised form 24 May 2011
Accepted 26 May 2011
Available online 12 June 2011

*Keywords:*
Cold plasma
Starch foam tray
Aspen wood fiber
Composite
Hydrophobicity
Fluorocarbon
Hexafluorosulfur
Surface modification

ABSTRACT

Tray samples of starch foam reinforced with aspen wood fiber were produced using a lab model-baking machine. Surfaces of the trays were treated with $CF_4$ and $SF_6$ plasma to get hydrophobic properties on surfaces. Fluorine compounds were found in XPS analysis of plasma treated samples. Due to the hydrophobic fluorine-rich surface, the contact angle was increased up to 150° with distilled water. RF power and gas pressure were varied to evaluate the effects of each parameter on fluorination of surfaces. The fluorine concentrations of treated sample surfaces were ranged from 46.8% to 60.2%. $CF_4$ treatment showed higher concentration of fluorine on surfaces than $SF_6$ treatment did. Water liquid and vapor uptake tests showed that the fluorine-rich surfaces restricted the permeability of water into the inner-layer of the treated samples.



## 1. Introduction

Starch-based products have prevailed all over the market, from packaging to the toy industry. One of the major applications is disposable trays that are used for food packaging. Due to the excellent biodegradable and eco-friendly properties of starch products, their market share has gradually increased (Shogren, Lawton, & Tiefenbacher, 1998). Thermoplastic starch has a low initial material cost and is readily available, thus many disposables are made of the starch materials (Whistler, 1984). However, only a few industrial applications have been adopted since there are limitations to the utilization of starch products in packaging applications because of their water sensitivity (Avérous, Fringantb, & Moro, 2002; Zobel, 1988). Especially in food packaging, the hydrophilic properties of starch have become an obstacle to expanded uses because wet products cannot be packed on the starch tray because of the low wet strength (Han, Manolache, Denes, & Rowell, 2010). To overcome this defect of biodegradable starch products in the food packaging, synthetic petroleum-based polymers with hydrophobic properties can be used to coat or laminate the surfaces of hydrophilic starch products (Glenn et al., 2007). The additional processing, however, requires extra costs for coating polymers, which leads to prohibitive manufacturing costs. Moreover, this coating process might decrease the biodegradability of starch products since the thickness of lamination or coating might be up to a few μm which would be thick enough to prevent microorganisms from penetrating the plastic layers decreasing the biodegradation rate. This is why a thin film coating or deposition is needed to prevent a decrease in biodegradability. To increase the wet strength of starch products, wood fiber can be used as a reinforcing filler. The stiffness of composites can increase with the addition of wood fiber (Kiziltas, Gardner, Han, & Yang, 2010; McHenry & Stachurski, 2003; Selkea & Wichman, 2004).

A cold plasma technique is optimal for this modification because the depth of deposition of plasma-induced treatments is t a few nanometers (Denes & Young, 1998). Many applications of cold plasma exist nowadays including: strengthening of tools, manufacturing of semiconductor integrated circuits, and coating for anti-corrosion, thermal and electrical improvements (Carrinoa, Moronib, & Polini, 2002). Moreover, it is strongly emphasized that

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doi:10.1016/j.carbpol.2011.05.056

**Table 1**
Surface elemental properties of foam tray samples treated with $CF_4$ and $SF_6$ plasma.

| | Control | Starch foam | Starch-Aspen foam | | |
|---|---|---|---|---|---|
| | Untreated | 350 mT–250 W[a] | 100 mT–100 W | 350 mT–100 W | 350 mT–250 W |
| $CF_4$ | | | | | |
| F[b] | 0.00 | 64.4 | 46.5 | 62.6 | 64.4 |
| O/C[c] | 0.54 | 0.43 | 0.19 | 0.37 | 0.26 |
| CA[d] | 68.3 | 149.0 | 141.2 | 140.9 | 152.7 |
| $SF_6$ | | | | | |
| F | 0.00 | 52.2 | 45.2 | 46.8 | 40.9 |
| O/C | 0.54 | 0.32 | 0.34 | 0.48 | 0.44 |
| CA | 68.3 | 140.7 | 150.8 | 130.2 | 152.3 |

[a] Parameters in plasma treatments [gas pressure in mTorr-RF power in Watts].
[b] Atomic concentration of fluorine.
[c] Atomic ratio of oxygen to carbon.
[d] Contact angle.

in a cold plasma treatment, neither high temperature nor large amounts of reagents are needed, which maximizes the advantages of natural products because of their comparatively low thermal degradation temperatures. The reaction time is relatively short (less than 10 min) and the processing is entirely dry producing no by-products. It is well known that gas deposited fluorocarbon coating creates a hydrophobic, chemically inert layer on metal and plastic surfaces (Limb, Labelle, Gleason, Edell, & Gleason, 1996; Riccardi et al., 1996; Sasaki, Furukawa, & Kadota, 2000; Wang, Chen, & Timmons, 1996). The benefits of the fluorocarbon treatments include the creation of non-stick surfaces, biocompatibility, and hydrophobicity. In this study, a coating is created by plasma enhanced chemical vapor deposition in a vacuum chamber at near room temperature using tetrafluoromethane ($CF_4$) and sulfur hexafluoride ($SF_6$) gases for the production of starch foam trays with hydrophobicity surfaces. In the plasma treatment with $CF_4$ and $SF_6$, four mechanisms are expected: functionalization (fluorination), deposition (by $CF_x$ and $SF_x$), etching, and stabilization (rearrangement of excited molecules including sample surfaces). These mechanisms can be affected by operating plasma parameters—reaction time, plasma gas pressure, and RF power.

In a previous study, it was found that a starch foam tray can be treated by $SF_6$ cold plasma for hydrophobic surfaces (Han et al., 2010). The objectives of this study are to create fluorocarbon barriers on a starch tray sample surfaces and to reinforce its strength by additions of aspen wood fiber. The dominant mechanism during plasma treatments will be studied for the operating parameters: species of plasma gas, pressure of the gases, radio frequency (RF) power, and reaction time.

## 2. Materials and methods

### 2.1. Materials

Starch, guar (1% based on starch weight) and magnesium stearate (2% based on starch weight) were mixed in the dry state using a mixer with wire whisk attachment. Guar was added to increase batter viscosity and therefore prevent starch from settling during preparation. Magnesium stearates were added to facilitate release of baked starch foams from the mold surfaces. Distilled water and aspen wood fibers (10 wt.% on starch weight) were then added to the starch and the batter was mixed at medium speed for 20 min. After mixing, the starch-aspen fiber mixtures were transformed into the baking machine. Foam trays were prepared using a lab-model baking machine (model LB TRO) supplied by Franz Haas Machinery of America. This machine consists of two heated steel molds, the top of which can be hydraulically lowered to connect with the bottom half for a set amount of time. Mold temperatures were set at 175–235 °C. Actual temperatures at the mold surface were approximately 10 °C lower as measured using a Temp-Sure Digital Pyrometer TS-200. The minimum amount of starch batter required to form a complete tray was added to the bottom half of the mold after which the top was closed. The solid content of starch was 33% in the batter. Baking times were the minimum required to avoid a soft or bubbled tray and depended strongly on the formulation. Sample trays were dried in a vacuum oven for 12 h at least.

### 2.2. Methods

Sample trays were then transferred into a reaction chamber of a parallel plasma reactor that is designed for treatments of flat substrates such like polymer films, metal or semi-conductor plates [Fig. 1]. Sulfur hexafluoride ($SF_6$) and tetrafluoro carbon ($CF_4$) gases were purchased from Aldrich Company with a purity of 99.9%. The plasma parameters of reaction time, gas pressure, and RF power were varied to evaluate the effects on surface treatment. Surfaces of the treated sample trays were then analyzed using an Electron Scanning for Chemical Analysis (ESCA or XPS), which informed the relative atomic concentrations of carbon, oxygen, and fluorine. Treated sample trays were measured for contact angle of the sample surfaces with distilled water to determine the hydrophobicity. A test of liquid water and water vapor uptake was performed to evaluate the water resistance. Untreated and plasma-

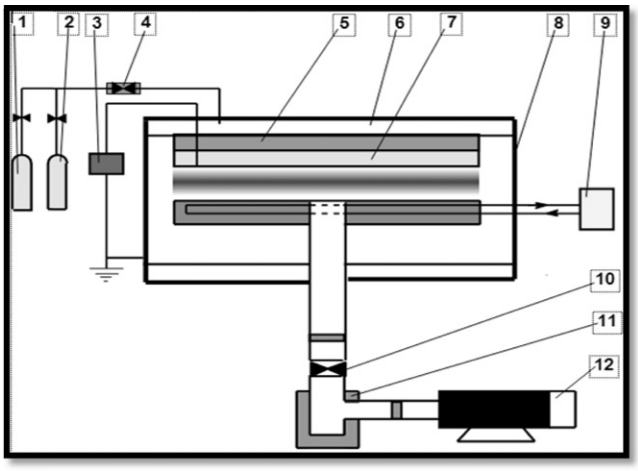


**Fig. 1.** The scheme of parallel plate reactor for plasma treatment [1. gas reservoir; 2. heated reservoir; 3. RF generator; 4. flow controller; 5. electric insulator disc; 6. gas mixing chamber; 7. drum type stainless upper electrode; 8. cylindrically shaped upper part of reactor; 9. temperature controller for the built-in electric heater of the lower electrode; 10. butterfly type valve; 11. stainless steel liquid nitrogen trap; 12. mechanical vacuum pump].

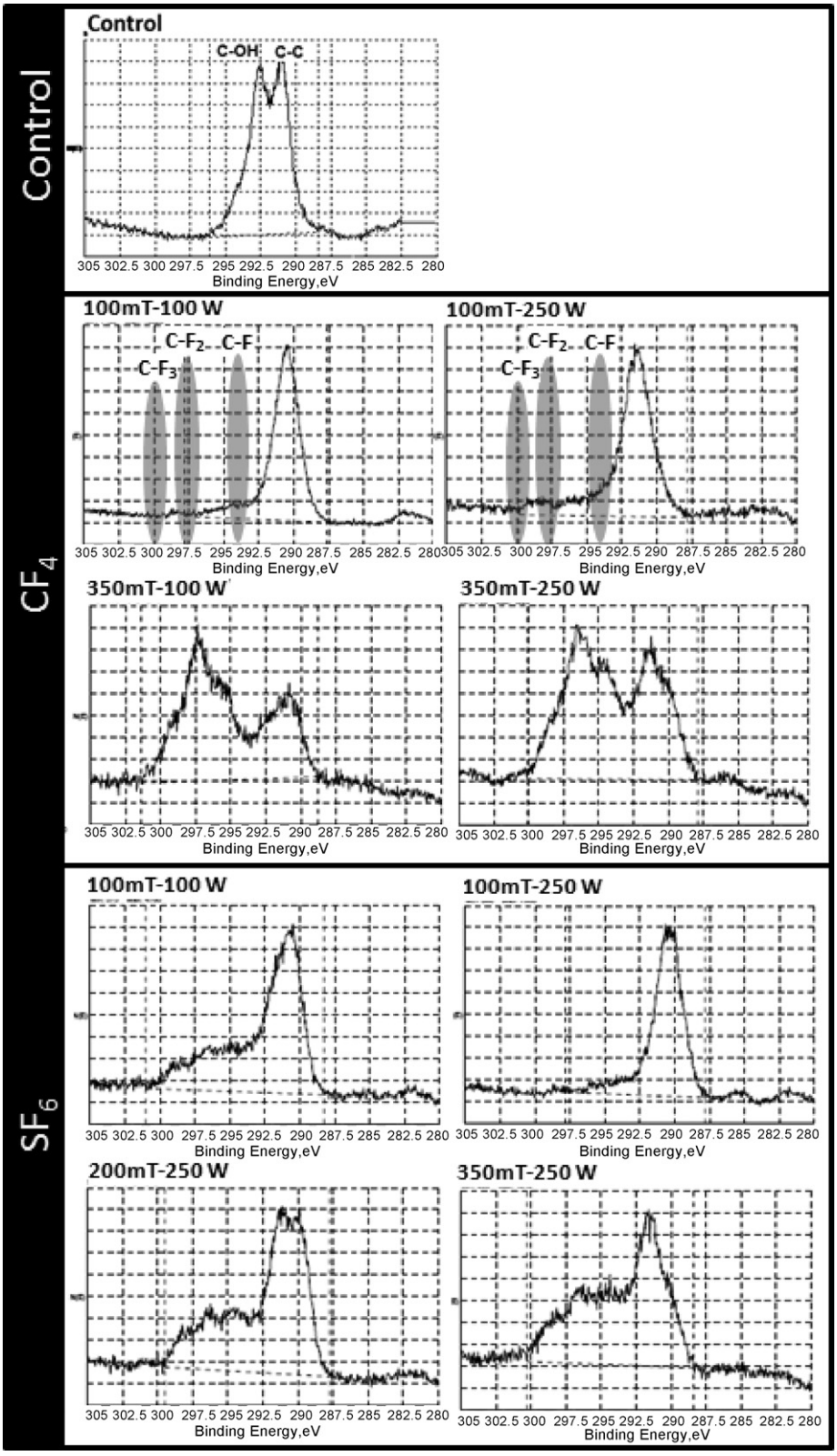


**Fig. 2.** High resolution surveys of carbon from $CF_4$ and $SF_6$ plasma-treated aspen-starch foam trays.

treated samples (2 cm × 2 cm) were exposed to wet cylindrical sponges (diameter = 1.5 cm, length = 1.8 cm). One sponge contains about 2.5 g of distilled water and will supply water continuously. Samples with wet sponges are placed at laboratory ambient conditions and sponges are regularly (every one hour) refilled with distilled water. For the test of water vapor uptake, distilled water (30 mL) was poured into a deep dish, and a rubber panel with an opening (8 mm diameter) in the center was placed on the dish. A square sample (2 cm × 2 cm) was placed over the hole of the rubber panel, and another dish covered the sample to prevent any loss

of moisture. The bottom dish was heated at 50 °C and kept for the entire experiments at that temperature. Dry sample weight and moisture gain after exposure to high humidity were recorded every 10 min.

## 3. Results and discussion

### 3.1. Fluorination

$CF_4$ and $SF_6$ plasma deposited fluorine compounds to the surface of sample trays. The atomic concentration of fluorine was ranged from 46.5% to 64.4% in $CF_4$ plasma treatment and 40.9% to 46.8% in $SF_6$ plasma treatment (Table 1). In ESCA from the $SF_6$ plasma treated samples, no sulfur was found at the surface of the sample trays, which might imply that $SF_x$ species did not significantly adhere to starch in fluorination. Otherwise, the deposition of $CF_x$ to the samples is expected in CF plasma treatment. The significant difference in the ratio of oxygen to carbon from two different gas plasma treatments would indicate that there was no other carbon source in the $SF_6$ plasma. The atomic concentration of fluorine does not show differences between sample trays of starch and starch-aspen trays, which does not significantly interact with surface properties of contact angles. It is clear that the plasma-aided fluorine deposition decreases the ratio of oxygen to carbon, which represents the degree of fluorine deposition. The high resolution surveys of carbon peaks in ESCA reveal the distinct differences between plasma gases [Fig. 2]. New peaks erode at the left of the original peaks (C–C and C–OH) from the untreated samples, which might represent fluoro-carbons ($CF_x$) in each plasma gas treatment. In terms of intensity of new peaks, the level of gas pressures is the more influential factor on the peak intensity rather than RF power. Different plasma gases create each unique shape of fluoro-carbon peaks

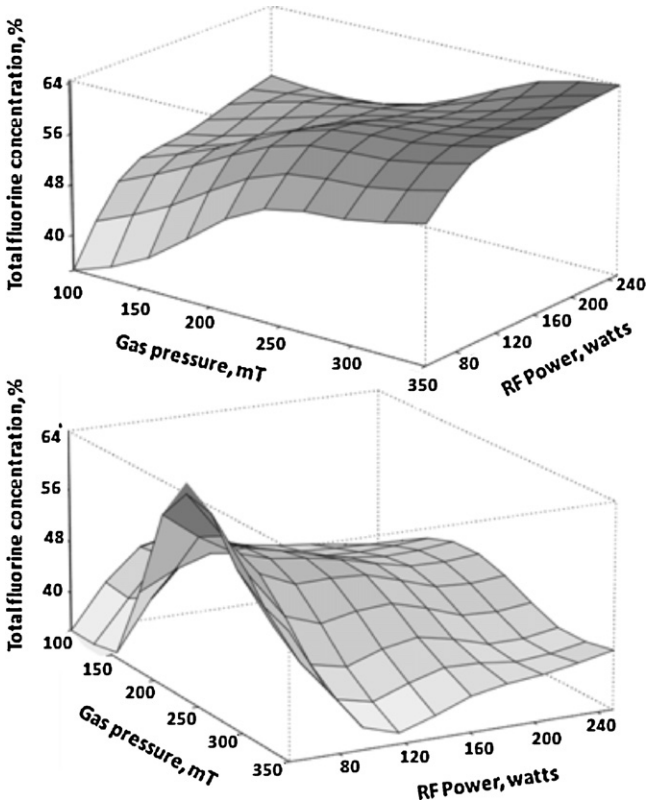


**Fig. 3.** Response surfaces of atomic concentration of fluorine in samples treated with $CF_4$ (above) and $SF_6$ (bottom).

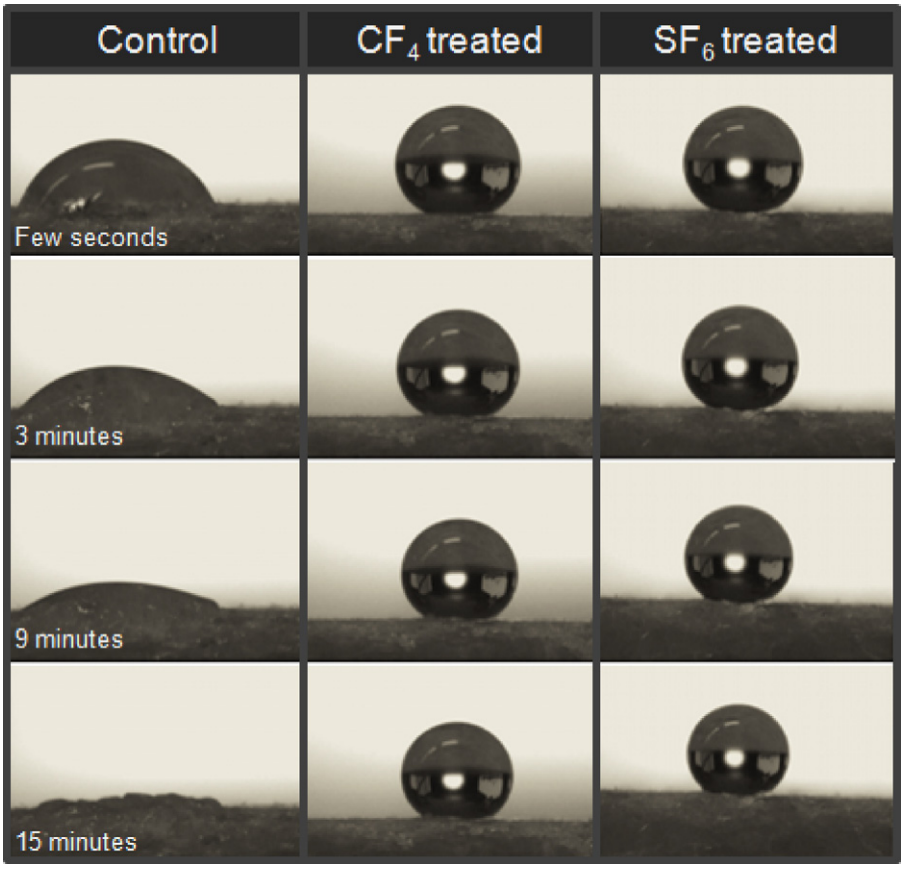


**Fig. 4.** Water droplets on Aspen-starch foam tray samples untreated and treated with $CF_4$ [350 mT–250 W] and $SF_6$ plasma [200 mT–250 W].

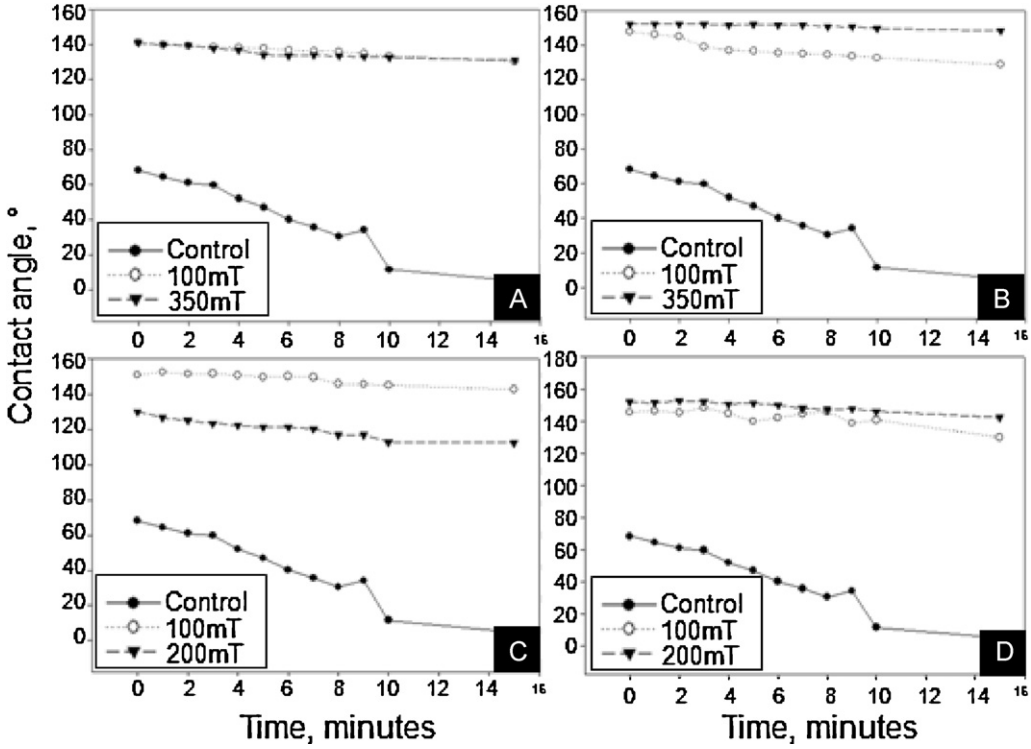


**Fig. 5.** Contact angles of plasma-treated starch-aspen foam tray according to different gas pressure levels [A: $CF_4$ treated at 100 W, B: $CF_4$ treated at 250 W, C: $SF_6$ treated at 100 W, D: $SF_6$ treated at 250 W].

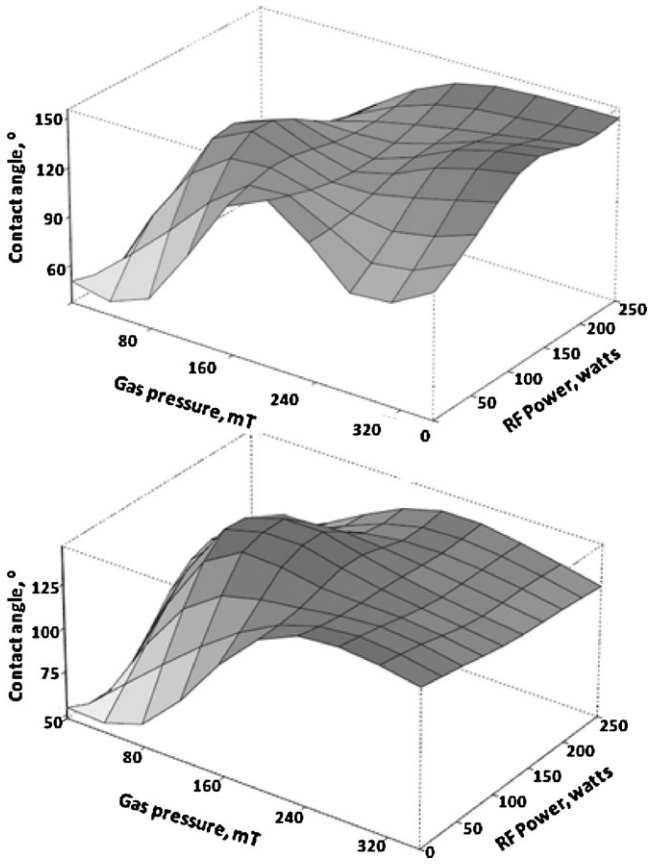


**Fig. 6.** Response surfaces of contact angle in samples treated with $CF_4$ (above) and $SF_6$ (bottom) according to the different treatment conditions.

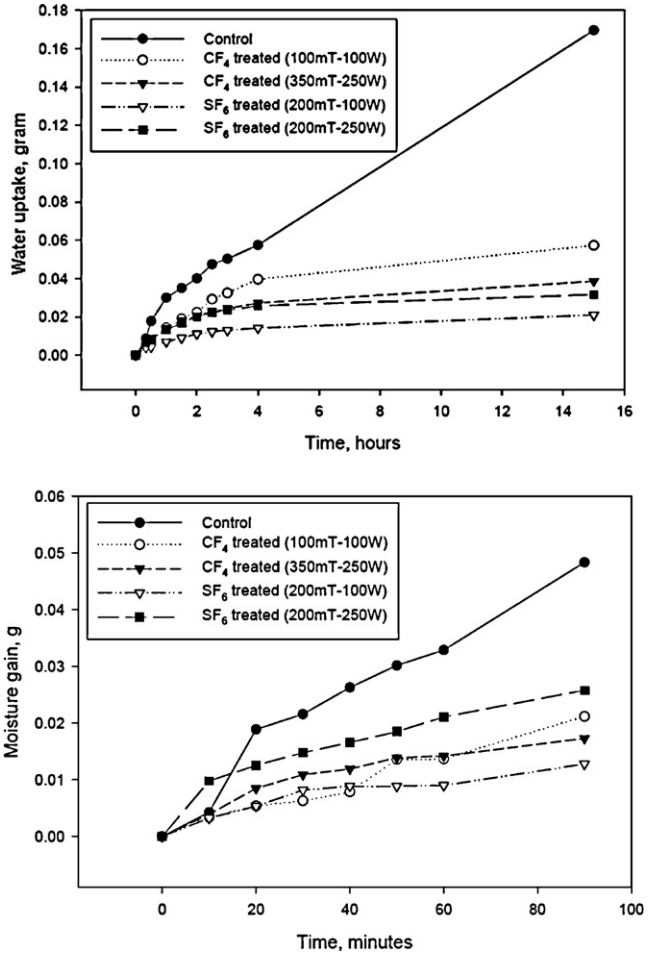


**Fig. 7.** Liquid water and vapor uptake of starch-aspen foam tray samples untreated and treated with $CF_4$ and $SF_6$ plasma.

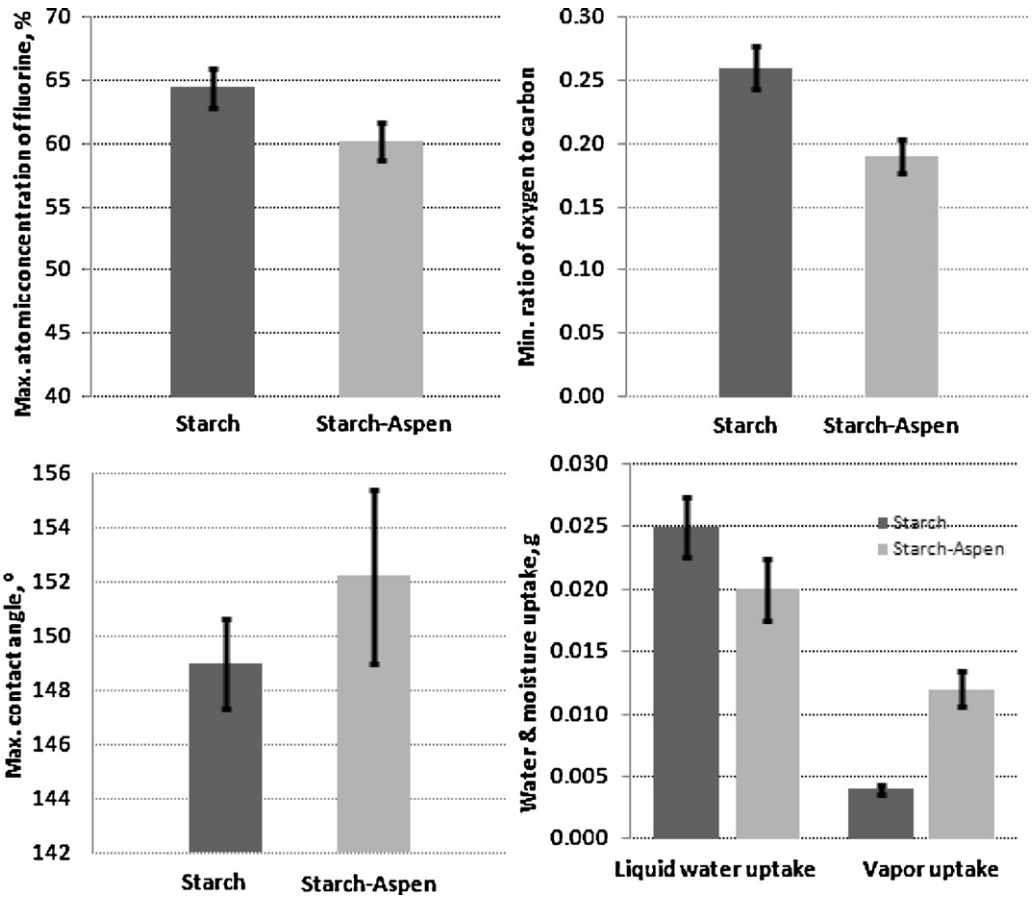


**Fig. 8.** Property comparison between starch foam tray and starch-aspen foam tray treated with $CF_4$ and $SF_6$ plasma.

implying that the chemical structures are complicated with multi fluoro carbons ($CF_x$). The complicated structure formation is a result of different deposition mechanisms in each plasma treatment. It is safe to address that the removal of oxygen from starch-aspen foam tray is clarified by the fact that the ratio of oxygen to carbon decreases in the $SF_6$ plasma treatment because there was no additional carbon source in the system. Conversely, the removal of oxygen cannot be directly proved in the $CF_4$ plasma treatment by the ratio of oxygen to carbon since extra carbons can be continuously attached to the samples from $CF_4$ molecules, the plasma gas. In spite of the lack of direct proof, the fluorine attachment, which was shown at ESCA, must remove some oxygen since the fluorine tends to create strong bonding to carbon with detaching hydroxyls from the cellulose chains.

### 3.2. Treatment parameters

The fluorine concentration and oxygen ratio of samples' surfaces are noticeably affected by treatment parameters, plasma gas pressures and radiofrequency (RF) powers. Fig. 3 shows the response surfaces of atomic concentration of fluorine deposited by different treating parameters. The dependence of gas pressures is more significant on the fluorine concentration in $SF_6$ treated samples, while those of RF power and gas pressure are just comparable to each other in $CF_4$ treatments. In each plasma gas, all chemical modifications of deposition, etching, grafting, and functionalization are expected due to reactive fragments of radicals, ions, and molecules. The dependence of fluorine deposition is susceptive on the treating parameters, and it must be suggestive that the deep deposition of elements can be damaged too by etching effects of the reactive fragments which are rich at more severe conditions with high pressure and RF power. Then, the final deposition can be randomized by the combination of deposition and etching mechanisms. The balancing the mechanisms will be the critical control of the final thickness of the deposition of fluorine. For higher fluorine deposition, moderate gas pressure is recommended in the treatment with $SF_6$, while high RF power and gas pressure are required in the treatment with $CF_4$.

### 3.3. Contact angles

Fluorine-rich surfaces show higher contact angles that indicate hydrophobicity of the treated surfaces [Fig. 4]. The decreasing rate of contact angles is rapid in the untreated sample trays showing that water is absorbed into the samples with the collapse of the surface structures due to the water solubility. In both plasma gases, the different gas pressure produces modifications of angles at particular RF power levels [Fig. 5]. Treated surfaces show strong structures without collapse of the surface skin caused by the water dissolving. The response surfaces of contact angles show significantly different trends according to the different plasma gases [Fig. 6]. Apparently, the increase of contact angle can be predicted by treatment parameters in the treatment with $CF_4$. The absorption tests of liquid water and water vapor attests the hydrophobicity of treated surfaces.

### 3.4. Water uptake tests

The weight gains from liquid water and water vapor were measured and shown in Fig. 7. The treated sample surface prohibits liquid water penetration resulting in retarded rate of water uptake in 16 h duration period. Absorbed water destroys the skin foam structures of the untreated sample so that the water

absorption is accelerated. In the water vapor penetration tests, the hydrophobic surface does not block the absorption as much as in the liquid water absorption test since the sample trays were fabricated for their foamed structures with high porosity resulting in water vapor being easily transported to the inner structures. In spite of the high porosity of the samples, plasma treatments show a positive effect in vapor barrier properties as well as liquid water uptake. The water resistivity of the samples' surfaces enables the application of wet food packaging with plasma-aided surface treatments introduced in this study.

### 3.5. Starch vs. starch-aspen foam trays

It was reported that the addition of aspen wood fiber into a starch foam tray enhanced mechanical properties (Shogren, Lawton, & Tiefenbacher, 2002). In this study, the surface properties modified by the plasma treatments are addressed in Fig. 8. Starch-aspen foam trays show more hydrophobic properties with low permeability of water vapor, which shows another positive aspect of starch-aspen samples for the applications of wet food packaging. Those differences in the surface properties can be explained with the different polysaccharide structures between lignocellulosics (wood fiber) and amylose/amylopectin (starch). Further research concerning the relationship between the structures and modification mechanisms is needed.

## 4. Conclusions

Cold plasma treatments created fluorine-rich layers on the surface of starch-aspen foam tray samples enhancing hydrophobic properties. The treatment parameters have affected on the chemical mechanisms of modifications, which results in different trends of fluorine deposition and the ratio of oxygen to carbon. The treated surface resists liquid water adsorption and permeability of water vapor. The addition of wood fiber to starch foam positively contributed to surface properties and mechanical properties. The hydrophobic barrier on the starch products can expand their uses to wet food packaging applications.

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