Superhydrophilic Anti-Fog Polyester Film by Oxygen Plasma Treatment

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***Abstract* — Superhydorphilic polyester film has been obtained by oxygen plasma treatment to maintain optical clarity under high relative humidity. The original and treated films are simultaneously exposed to the vapor from hot water. The latter keeps its optical clarity because the condensed water formed a thin film on it instead of droplets for the former. Compared with the widely used coating method, plasma treatment to obtain anti-fog polymer film has the potential for mass production, lower cost, better compatibility with thermal extrusion process, and safer for food packaging. It can also be employed to improve the visualization of microfluidic reactors under high relative humidity.**

Keywords — ***Superhydrophilic Polymer, Film Condensation, Anti-Fogging, Plasma Treatment***

I. BACKGROUND

Visualization under high humidity is usually challenging. Temperature fluctuation can easily increase the local relative humidity close to the solid surfaces (e.g., the lenses or transparent walls to see through) and induce significant condensation in form of tiny droplets. As a consequence, the originally transparent solid surfaces will fog and lose their optical clarity. In recently years, the necessity of anti-fog surfaces has been highlighted by micro- and nanofluidic applications such as visualization of two phase flow in the cathode microchannels of proton electrolyte membrane fuel cells [1]. Similar challenges will also be encountered when stagnant multiphase environment in microreactors (e.g., for cell cultivation [2]) needs to be visualized. Anti-fog surface can also found applications in our daily life. When a food item is packaged and displayed in a refrigerated cabinet, the relative humidity inside the package increases due to the decrease of temperature. Consequently, water tends to condense on the inner surface of packages. Polyester is a widely used material in food packaging, in forms of either flexible films or rigid trays. Because polyester is usually hydrophobic, tiny water droplets will be formed on the inner surface of the polyester package and fog the package. The originally transparent food package will thus be turned obscure, so that the displayed items are not properly presented to the consumers. Coating of various surface-treatment agencies has been demonstrated to render glass and plastic surfaces anti-fog property. They have been successfully incorporated into commercial products such as eye glass and swimming goggle. However, the safety of those chemical agencies for food is questionable especially when the packaging is subjected to environments of high temperature and high humidity (e.g., pasteurization process). At the same time, it is difficult for the anti-fog agencies to maintain its efficacy when the film is extruded (process temperature: 200-300 ^{o}C). The cost of the agencies is also a concern.

In this paper, we demonstrate superhydrophilic anti-fog polyester film treated by modifying its surface with plasma. Plasma treatment is known to increase the surface energy of polymer substrate by forming hydrophilic functional groups. This method has been widely used to improve adhesion [3]. Argon plasma followed by oxygen treatment has been reported to change the contact angle of polyester to as low as 33.8° [4]. The hydrophilicity is induced by polar functional groups such as -OH and -COOH. Our experiments show that proper plasma treatment can turn the polyester film to superhydrophilic, which leads to spreading of water on the surface to form a thin film of water instead of droplets. Therefore, the surface can keep its optical clarity even when the relative humidity is high.

II. SURFACE MODIFCATION

The polyester film we choose to test is the poly(ethyleneterephthalate) (PET) transparency from Tri-State Visual Product Inc. A reactive ion etching system (March Jupiter II) is used to treat the polyester film with oxygen plasma under the pressure of 0.130Torr and flow rate at 20 sccm for 5 minutes. The RF power is 50W. The surface contact angles are measured before and after the plasma treatment. Fig. 1. a. shows that the contact angle of untreated polyester film was about 95°. After plasma treatment, the contact angle is decreased dramatically. It is too small to be measured directly by the contact angle

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goniometer because the water spreads on the surface, as Fig. 1. b. shows. The surface after plasma treatment can therefore be considered as superhydrophilic (i.e., practical contact angle is near 0°).

a) Untreated polyester film

b) Superhydrophilic polyester film after plasma treatment

Fig. 1. Contact angle measurement results.

III. Condensation Testing

The two films are simultaneously placed on top of a cup filled with hot water to compare the condensation on them under high relative humidity. As Fig. 2 shows, the untreated polyester film (left side) was covered by water droplets and fogged after several minutes, while the plasma-treated superhydrophilic polyester film (right side) remained clear. It is observed that a thin layer of water was formed on the latter. As a result, the untreated polyester film become obscure and completely blocked the left side of the cup, while the bottom of the cup on the right side can be seen clearly through the superhydrophilic polyester film.

Fig. 2. Condensation and optical clarity of polyester films under high relative humidity. Left side: untreated polyester film is fogged. Right side: plasma-treated superhydrophilic polyester film keeps optical clarity.

IV. XPS Characterization

The surface chemical structures are analyzed by X-ray photoelectron spectroscopy (XPS) with a Kratos Ultra Axis DLD XPS system. The samples are radiated under monochromated Al source at the X-ray power of 120W with energy resolution of about 0.5 eV. Fig. 3 shows the XPS spectra collected from the untreated and treated samples around the C 1s energy region. The peak of the untreated PET is composed of three main components: the peak at 285eV, which corresponds to CH_2 and CH groups, while the peaks at 286.5 eV and 289 eV represent the C-O and COO groups. After oxygen plasma treatment, the intensities of peaks for C-O and COO groups are increased, compared with those in the untreated sample. At the same time, the relative number of CH_2 groups in the treated sample has decreased. The result has indicated that a large amount of CH_2 has been oxidized into the forms of COOH or COH.

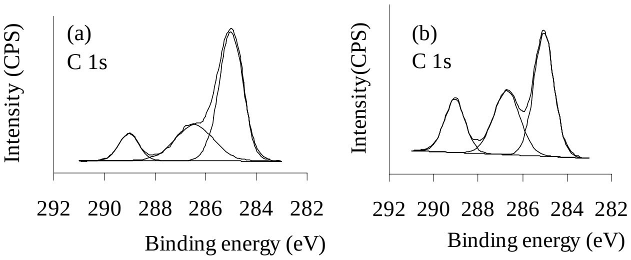

Fig. 3. XPS C1s spectra of (a) untreated and (b) treated PET films

Figure 4 shows the XPS spectra collected from the untreated and treat samples around the O 1s energy region. The two O 1s peaks can both be fitted with two main peaks at energies of 533.5 eV and 532.1 eV. In addition, the O 1s peak from the untreated sample shows a shoulder on the low energy side at 530.9 eV and the O 1s peak from the treated sample shows a shoulder on the high energy side at 535.5 eV. The peak at 532.1 eV corresponds to oxygen atoms doubly attached to carbon in the form of COO groups, while the peak at 533.5eV corresponds to the oxygen atoms singly attached to carbon. The increased intensity ratio between the peak at 533.5 eV and at 532eV shows that COH groups are increased. The peak at 535.5eV implies that small amount of H_2CO_3 molecules are formed, or H_2O molecules are absorbed into the surface due to the high surface energy of the film.

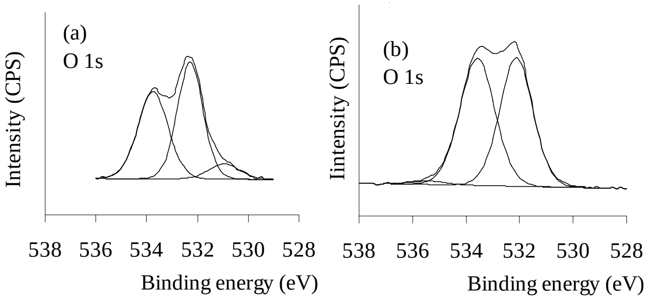

Fig. 4. XPS O1s spectra of (a) untreated and (b) treated PET films

The C1s and O1s spectra both demonstrate that the film is oxidized and many COOH and COH groups are generated. It is confirmed that the more polar groups on the surface are the cause of the superhydrophilicity of the PET surface.

V. STABILITY OF SUPERHYDROPHILICITY

The shelf life of anti-fog membrane is an important aspect when its practical application potential is considered. In order to find the optimum conditions for membrane storage so as to minimize the degradation of superhydrophilicity, the contact angle changes over time in different environments are investigated. The environments used for this testing are 1. room environment with a relative humidity of 15-20%; 2. dry environment in a desiccator; 3. humid environment, the membrane is kept with liquid water in the same container, although the membrane does not contact with liquid water directly; 4. oxygen gas environment; and 5. nitrogen gas environment. All of the films are stored under room temperature (~20^{o}C). Five pieces of polyester film are treated by oxygen plasma following the same procedure described in part II. They are kept in different environments for several days to investigate the effect of environments on the hydrophilicity of the surface. The contact angle are measured by Krüss® contact angle measuring system G10 and recorded each day for all the five pieces of polyester films.

The results of contact angle measurement are shown in Fig. 4. In the room environment, the change in hydrophilicity is very slow. It rises to about 10^o during the first 4 days, after which, no significant change has been observed for the rest of the test duration. Polyester films kept in both dry and humid conditions exhibit faster contact angle increase and thus more severe degradation of hydrophilicity. It is therefore speculated that there is an optimum humidity for the membrane storage in air. In dry environment, the degradation of hydrophilicity of the polyester films can be caused by the conformational change of the functional groups on the polymer surface. After being exposed to dry air for two days, the non polar part of the polymer turns out to contact the air and the polar groups tends to turn inside. Due to this conformational change, the contact angle increases. The degradation of hydrophilicity under high humidity is conjectured to be related to water adsorption to polymer surface, which will affect the surface functional groups. Further investigations are expected to clarify the working mechanism. Currently, no significant difference has been observed by switching the gas environment from air to oxygen or nitrogen. Therefore, we didn’t observe improvement of hydrophilicity stability by storing membrane in oxygen or nitrogen environment. In our experiments, humidity has shown more substantial effect on the stability of film hydrophilicity. However, our observation period is still short and the humidity of oxygen and nitrogen environment is not controlled. Long-term testing with more precise environment control will be performed to further reveal the impact of gas environment. Another factor to be considered is the temperature, which is also expected to affect the degradation of hydrophilicity considerably.

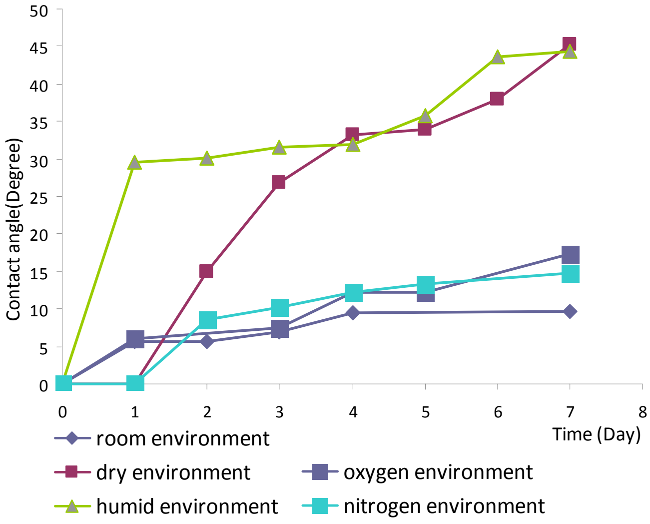

Fig. 3. Degradation of hydrophilicity in different environments

VI. DISCUSSION AND FUTURE WORK

A key advantage of the plasma treatment is its potential to be integrated into the production line for mass production. In this case, the polymer should be treated by atmospheric plasma treatment [5]. Plasma-treated polymer surfaces is considered as biocompatible material [6]. It should be considerably safe for food storage. However, more investigation is needed before it can be employed in the consumer products. The hydrophilicity of plasma-treated surface will degrade over time. However, proper storage condition has been shown to slow down the degradation [4]. The mechanism will be further investigated to obtain superhydrophilic polyester with satisfactory shelf time.

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