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ABSTRACT

In this work, a polyvinyl alcohol (PVA) thin film was modified by exposure to a dielectric barrier discharge argon plasma. The plasma was generated by a sinusoidal power supply with discharge voltage of 4.75 kV (rms), and frequency of 30 kHz at duty cycle 6.13%. The effect of the plasma on the PVA thin film was investigated by analyzing the contact angle, scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, and UV–visible spectroscopy. After the plasma treatment, the contact angle was found to be decrease from 29.6 ± 0.4° to 14.5 ± 0.2°, which implied that the surface property had changed to a hydrophilic state caused by an increase in the surface roughness and introduction of oxygen, including a polar carbonyl group. It was found that the plasma-treated hydrophilic PVA thin film exhibited excellent antifogging and highly transparent characteristics, making it an appropriate material for food packaging and green houses.

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I. INTRODUCTION

Over the few decades, polymers as structural materials have tremendous attention in the industrial1–4 and biomedical field5–9 owing to their excellent material properties such as low density, high flexibility, and high chemical resistance.1 Despite these excellent characteristics, polymers are often unsuitable for certain applications because of their low surface free energy,2,4–7 leading to poor wettability and poor adhesion.8 It has been suggested that the reason polymer films have such low wettability and adhesion is the lack of surface polar groups.9 Various methods such as wet chemical processing, flame spraying, radiation,10 plasma processing,11 and ion implantation12 are available for modifying the surface properties of polymers. However, all the aforementioned techniques may not be sustainable; therefore the ecological requirements demand a search for an eco-friendly method.13,14 In the last two decades, plasma treatment of polymers has been gaining more attention as a surface modification technique because it does not require the use of chemicals.15 Therefore, it can be considered as an environmentally beneficial technology.16 The plasma method is a low-temperature,17 non-toxic, low-cost, easy to handle, flexible, and effective process.18,19 Moreover, it is a versatile technique that changes only the surface properties of a polymer without altering its bulk properties,9,20 which is an immense field of interest.

Dielectric barrier discharge (DBD) offers one of the most effective non-thermal plasma sources at atmospheric pressure owing to its feature of a large volume plasma.17,21 Moreover, owing to the low operational and maintenance costs, simplicity of the equipment, and non-requirement of an expensive vacuum system,21,22 in recent years, it has been attracting considerable interest for surface modification.23,24 The DBD plasma technology is a promising method for surface modifications, and some efforts of applying this approach for the surface treatment of thin films have been reported.11,25-27 The advantages of the DBD plasma have made it possible to treat...
polymer material surfaces rapidly, continuously, and uniformly under atmospheric pressure.\textsuperscript{21} The non-thermal plasma resulting from a DBD generates numerous excited species, free radicals, and energetic ions, which lead to a reaction of a few nanometers on the surface of the thin film and physico-chemical changes on the polymeric surface.\textsuperscript{22,23} The energy level of electrons in a plasma discharge is sufficiently high (0–10 eV)\textsuperscript{24} to generate different reactive species and dissociate most of the chemical bonds in organic compounds. Therefore, the interaction of a polymer surface with a plasma can cause hydrogen removal from the polymeric chains and free radical generation.\textsuperscript{25} The radicals are created by an Ar\textsuperscript{+} or electron impact, which disrupts the C-C and C-H bonds.\textsuperscript{26} The DBD plasma treatment can increase the surface energy,\textsuperscript{27} leading to an increase in the surface hydrophilic properties by the introduction of polar functional groups on the polymer surface. The hydrophilic surface thus created on a thin film attracts water molecules so that they can rapidly spread over the polymer thin film and form a uniform and non-light-scattering water film instead of separate water droplets.

Polyvinyl alcohol (PVA) has attracted considerable research interest and is recognized among the largest volume of synthetic polymers that have been produced worldwide for nearly one century. This is owing to its exceptional properties, which led to its extensive use in various applications, particularly in industrial and biomedical fields. However, the studies revealed that PVA has some limitations that can restrict its use or performances in other fields such as green houses and food packaging. These drawbacks include its properties of a low hydrophilicity. In recent years, different methods have been employed to investigate the antifogging property of polymers.\textsuperscript{31–33}

In this work, PVA, a versatile polymer that is non-toxic, transparent, biocompatible, bio-degradable, and water-soluble and has a good mechanical strength,\textsuperscript{34–37} has been used to make thin films on glass substrates. It is of tremendous importance to investigate the influence of plasma treatment on the PVA thin film characteristics resulting in hydrophilicity, excellent antifogging property, and high transmittance by the introduction of O\textsubscript{2} molecules from the ambient air on the polymer surface. Therefore, a non-thermal atmospheric-pressure DBD argon plasma has been used in ambient air environments throughout this experiment because it has a low operation voltage and is easy to discharge. Our finding will be beneficial to the field of agriculture and food packaging industry. The improved light transmission increases the plant growth rates and provides a high crop yield per plant and an early crop maturity. In addition, the antifogging PVA used in food-packaging films is benefited by their ability to maintain clarity and transparency so that the contents can be clearly seen by the consumer at the point of sale. A highly transparent and antifogging plasma-treated PVA can be used in automobiles and mirrors, which can be others application of our experiment.

II. EXPERIMENTAL SETUP

A schematic of the DBD argon plasma is shown in Fig. 1. Here, a high-voltage electrode is fabricated by a silver paste using the screen-printing method on glass dielectric. The thickness of the electrodes is 5–10 \( \mu \)m, and the inter-electrode gap is 100 \( \mu \)m. These electrodes are covered with a dielectric layer (SiO\textsubscript{2}) of thickness 50 \( \mu \)m. All the electrodes are connected to the same polarity of a high-voltage source, and the ground electrode composed of a copper plate is connected to the opposite polarity of the high-voltage power supply. This grounded electrode is attached below the dielectric acrylic material. Argon gas (1 L/min) was flown for discharge throughout the experiments so that a plasma was generated between the high-voltage electrode and ground. The sample was kept 1mm below the bottom of the glass. The facing DDB argon plasma to be exposed was generated between the bottom of the glass and top of the PVA thin film. The discharge was obtained by applying a sinusoidal inverter voltage in the duty-cycle-controlled mode of 30 kHz frequency at discharge voltage 4.75 kV operated by a direct current (DC) power supply. During the discharge, the plasma on-time was 29.70ms and off-time was 455.10 ms, so that the duty ratio was calculated as 6.13%.

A microscopic glass substrate of 1-mm thickness was cut into small pieces (20mm×20mm) and cleaned ultrasonically for 10 minutes with alcohol and Deionized (DI) water, respectively. Each substrate was placed on a desiccator for 1 one day for drying, and it was further cleaned by blowing air to make it dust free. The solution (600 mM) of polymer was prepared by dissolving PVA (mW 89000–98000, 99% hydrolyzed) powder in DI water and heating at 80° C in a glass bottle. The hot solution was slowly stirred continuously for about 30 minutes until the polymer completely dissolved. Then, the solution was left to cool down at room temperature. The PVA thin films were formed on a glass substrate by the spin coating method.

The Tektronix P6015A, High Voltage (HV) probe is used for measurement of discharge voltage whereas, LeCroy CP030 current probe is used to measure the discharge current. The measured voltage and current waveforms are monitored and displayed by 434 LeCroy wide- band digital oscilloscopes. Optical emission spectra (OES) have been also measured by spectrometer of Ocean Optics, Inc. HR4000+CG-UV-NIR. The contact angle of the samples are measured by Phoenix MT (M) where volume of water drop is 3.86 ± 0.27 \( \mu \)L. Relative humidity during experiment is about 21% and surface morphology of PVA thin film is investigate using scanning electron microscope (SEM) of JEOL JSM-7001F, at the same time, surface roughness is measured by atomic force microscope (AFM).
by FlexAFM, Nanosurf AG and the surface chemical composition is analysis by x-ray photoelectron spectroscopy (XPS) by k-alpha Thermo Scientific Inc., U.K.

III. RESULTS

A. Electrical and optical properties of plasma

Fig. 2(a) shows the typical current–voltage waveform of the argon DBD plasma discharge. The discharge current was calculated by subtracting the displacement current from the total current. The current peaks appear on both the rising part and falling part of the discharge voltage. The current peaks on the rising part correspond to positive polarity, where some of the charges accumulate on the glass, and the current peaks of the falling part correspond to a reversed negative polarity, in which the accumulated charges are changed. The optical emission spectrum of argon DBD plasma is shown in Fig. 2(b). Because the plasma is generated in an ambient air environment, weak emission lines of nitrogen molecules from second positive system (SPS) and first negative system (FNS) appear in the range 315-380 nm and around 400 nm respectively. Additionally, the emission line of OH radicals appears around 309 nm, whereas those at 777.1 nm and 844 nm arise from atomic oxygen (O). Similarly, strong emission lines of argon can be seen in the range from 696.5–912.8 nm.

B. Contact angle measurement

Contact angle is an important tool that determines the surface hydrophilicity by evaluating the tendency of a liquid drop to disperse over a flat surface. Here, the contact angle (θ) measured for glass is found to be 37.7 ± 0.3°, as shown in Fig. 3(a), and that of the PVA thin-film surface is 29.6 ± 0.4°, as shown in Fig. 3(b). Thus, both the samples do not show antifogging property because of the poor hydrophilicity. After 10 minutes of plasma treatment, the water contact angle is significantly decreased to 14.5 ± 0.2°, as depicted in Fig. 3(c), exhibiting that plasma treatment can be used for the improvement of the surface wettability of PVA thin films.

C. Surface morphology

During plasma treatment, high-energy plasma particles bombard and cause etching of a PVA thin film surface, leading to an increase in the surface roughness. Fig. 4 shows the scanning electron microscope (SEM) images of (a) an untreated and (b) a plasma-treated PVA thin film, respectively. The morphology of the untreated sample is smoother than that of the plasma-treated one. The increase in the surface roughness of the PVA thin film could have been caused by the excited reactive species and ionized argon atoms from the discharge plasma in the ambient air. These highly reactive species could have etched and roughened the PVA thin film surface.

To investigate the change in the surface morphology after the facing DBD argon plasma treatment, atomic force microscopy (AFM) measurements were performed. Fig. 5 shows the AFM images of an (a) untreated and (b) a plasma-treated PVA thin film, respectively. The plasma-treated PVA thin film exhibits an uneven surface morphology, as shown in Fig. 5(b), which provides large contact area for the water droplets, and therefore, improved adhesiveness, resulting in a small contact angle. The surface of the untreated sample is shown to be relatively smooth with an average surface roughness of 0.26 ± 0.035 nm in a measured area of 10 × 10 µm². Comparatively, the average surface roughness is increased to 2.5 times, i.e., 0.65 ± 0.038 nm after the 10-min plasma treatment. This increase in the surface roughness can be responsible for the decrease in the contact angle.

FIG. 2. Electrical and optical characteristic of discharge. (a) Current–voltage waveform and (b) optical emission spectroscopy results of facing DBD argon plasma exposure. [Discharge voltage: 4.75 kV, frequency: 30 kHz, duty cycle: 6.13%, argon gas flow rate: 1 L/min].

FIG. 3. Water contact angle of (a) glass, (b) untreated PVA thin film, and (c) plasma-treated PVA thin film.
angle, as shown in Fig. 3(c) which is explained in discussion section.

D. Surface chemical analysis

To study the chemical composition of the untreated and plasma-treated surface of the PVA thin films, X-ray photoelectron spectroscopy (XPS) was performed. XPS is commonly accepted as one of the most powerful techniques to investigate the chemical changes occurring on a polymer surfaces. The investigation of the core electronic structures of the C or O elements provides precise information about the chemical environment of the different atoms in the sample surface. Here, Fig. 6(a) and 6(b) show the results of the curve fittings into the C 1s spectra of the untreated and plasma-treated PVA thin film, respectively, to obtain information about the presence of different functional groups.

The curve-fitted C 1s peaks of the untreated sample, as shown in Fig. 6(a), reveals the existence of carbon in two states, the peak at 284.59 eV corresponds to the C-C and C-H bonds, and the peak at 286.10 eV belongs to C-O and C-OH. During the DBD plasma treatment, the oxygen species having a high reactivity in the plasma can react with the polymer surface resulting in the incorporation of oxygen. After the plasma treatment, a new peak is observed in the high binding energy side of the C 1s at 287.2 eV, corresponding to the C=O, indicating oxygen incorporation, which is also responsible for the improved wettability, as shown in Fig. 3(c) in this experiment.

E. Antifogging property

The antifogging property of a surface is strongly influenced by its hydrophilicity such that very hydrophilic surfaces can maintain a good optical transmission. Therefore, in this experiment, to investigate the antifogging characteristics, the glass and untreated and plasma-treated PVA thin films were exposed to a humid environment (relative humidity (RH): 50%–60%) using a humidifier. The glass, untreated, and plasma-treated samples were exposed to the above humidified environments by placing them inside a chamber for 10 s; subsequently, they were taken out into the air environment with their wetted surface. Here, all the samples are immediately placed simply above a word sheet by 0.3 mm to take photographs for examining the antifogging properties. The letters written on the word sheet placed below the glass are found to be less blurred and unclear compared to those for the untreated PVA thin films, as shown in Fig. 7(a). In comparison, the untreated PVA thin film is more blurred and unclear owing to the strong light scattering caused by very tiny water droplets, as shown in Fig. 7(b). By contrast, a plasma treated...
sample was found to have a thin water layer, exhibiting clear transparent letters, with excellent antifogging behavior, as shown in Fig. 7(c).

**F. Transmittance**

Fig. 8 shows the transmission spectra of the glass and untreated and plasma-treated PVA thin film as measured by UV–Visible spectroscopy in the range between 300–800 nm. The samples were placed in a humid environment (relative humidity (RH): 50%–60%) for 10 second by using a humidifier inside the chamber. Subsequently, the samples were taken out to into the air environment, and the light transmittance was measured. In this method, the transmittance is estimated by comparison of the transmitted signal ($I$) passing through all the three samples with those of incident signal ($I_o$) coming from the light source (Deuterium lamp). This was calculated by using the following relation:

$$T = \frac{I}{I_o} \times 100\%$$  \hspace{1cm} (1)

The experimental results show that the plasma-treated PVA thin film has a high transmittance ~86% compared to that of the untreated sample; it is also slightly lower than that of glass. Our experiment confirms that the plasma-treated PVA thin film is optically clear owing to the increase in the hydrophilicity.

**IV. DISCUSSION**

PVA has attracted substantial research attention due to its exceptional properties which dictated its widespread use in variety of applications, such as in medical and pharmaceutical fields. Nevertheless, researches revealed that PVA has some limitations which confine their use or performances in other field. PVA polymers are also considered as an environmental friendly polymer because of its solubility in water at > 80°C however it was not used in some other field like greenhouse and food packaging because of its properties of low transmittance and less hydrophilicity. To overcome these limitations our results from this experiment could be a milestone in future.

Based on our results, excellent antifogging behavior and high transparency of PVA thin film is seen in Fig. 7 and 8 respectively are attributed due to the increase of surface hydrophilicity. The results of increased in hydrophilicity is combinedly due to the increased in surface roughness as presented in Fig. 5(b) and appearance of
oxygen containing polar functional group (C=O) as illustrate in Fig. 6(b) after the plasma treatment. This polar functional group can absorb the water molecules by hydrogen bonding and dipole-dipole interaction, which prevents the formation of small water droplets on the PVA thin film. Thus, light cannot scatter from the water surface, resulting in high transmittance and excellent antifogging characteristics. This combined effect of surface roughness and oxygen containing polar functional group for hydrophilicity of materials are also illustrated in other reports which are similar to our results.

The enhancements in the light transmission by this PVA thin film can be used in a greenhouse to increase the plant growth and production rate. In addition, the plasma-treated PVA maintains clarity and transparency during food packaging so that a consumer can see the food product more clearly and the product itself appears fresher and more hygienic. Therefore, our results would be of tremendous contribution in the field of agriculture and food packaging. Furthermore, acquired properties of plasma treated PVA could also be useful in vehicles and mirrors by maintaining transparency and antifogging characteristics.

V. CONCLUSION

We have investigated the effect of plasma treatment for improving the antifogging property of PVA thin film. Our finding shows that plasma treated PVA thin film has smaller contact angle as compared to untreated one because of enhance the hydrophilic property. Atomic force microscope and x-ray photoelectron spectroscopy result reveals the increase of surface roughness in nanometer scale and presence of hydrophilic polar functional group (C=O) respectively after the plasma treatment are the possible reasons of observed hydrophilic property to ensure better antifogging behavior and highly transparent nature. The results from our experiment show that the facing DBD argon plasma treatment can be an effective technology to improve the hydrophilicity of a PVA thin film.

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