Research Paper

Hydrophilic Surface Modification of Polytetrafluoroethylene Film with Gliding Arc Plasma

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Abstract

Gliding arc plasma is a non-equilibrium phase and can be generated at atmospheric pressure. Surface treatments are a popular application of this form of plasma because of its relatively low temperature. Polytetrafluoroethylene (PTFE) film is naturally hydrophobic with low surface energy caused by its very stable covalent carbon bonds. In this study, the surface of PTFE film was made hydrophilic by treating it with gliding arc plasma. Tests were conducted with argon, oxygen, air, and nitrogen as discharge gases to test the effects of different species of active radicals formed by the arc. The treated film surfaces were analyzed after surface treatment with different gases and for different times, and the contact angle of the PTFE was 80° before treatment. OH radicals from the ambient air were generated by the gliding arc and these attached to the surface of PTFE. However, the contact angle increased again over time, and when oxygen or nitrogen were used during the plasma treatment, the PTFE surface returned to its original hydrophobic state after about 8 days. The OH radicals attached to the surface likely reacted with ambient air and left the surface over the course of this process.

Keywords: Gliding arc plasma, Polytetrafluoroethylene, Surface modification, Surface treatment, Hydrophilicity, Hydrophilic surface

1. Introduction

Surface treatments using atmospheric plasma are simpler, economical, and more flexible than vacuum-plasma surface treatments [1-5]. Many studies have used gliding arc plasma, dielectric barrier discharge (DBD) [6,7], RF discharge [8,9], corona discharge [10], and microwave plasma [11] for atmospheric-plasma surface treatments. A gliding arc is an oscillating periodic phenomenon that develops between at least two opposite-sign electrodes. When voltage is first applied, an arc spans the narrowest points of the electrodes, and this arc is dragged downstream by the flow of some gas. The discharge grows in length as it travels down the widening gap between the electrodes until it reaches a critical value at which the arc disappears; another arc immediately forms across the shortest path between the two electrodes; thus, the phenomenon is cyclic [12,13]. The arc length and number of repetitions can be controlled easily by adjusting the gas

flow rate or the voltage. The cyclic nature of this process means that the gliding arc plasma simultaneously has a high-temperature plasma region and a low-temperature plasma region. Because only the low-temperature plasma comes in contact with the material being treated, materials with low heat resistance such as polymer film can be treated. Gliding-arc plasma is well-suited for surface treatments, and it is more environmentally friendly than mechanical or wet-chemical processes. Gliding-arc plasma treatments are also not limited by the thickness of the material because the plasma only touches the material like a torch. Therefore, gliding arc plasma is useful in many industrial applications that require coating, painting, printing, or bonding [14]. Figure 1 shows the optical emission spectra of a gliding arc plasma using air as the discharge gas. These observations were taken with a spectrometer (HR2000+, Ocean Optics). Spectral fingerprints of NO (A-X), N₂ (C-B) and OH (A-X) appear in this figure. The intensities of these features increased as the samples were treated with higher flow rates. We know that OH and NO radicals are the most

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Figure 1. Optical emission spectra of the gliding-arc plasma in air.

common highly reactive species generated in atmospheric plasma [15–17]. NO radicals are known to be involved in acid effects [15], and OH radicals are the most important mechanism by which hydrophilicity is increased by treatment with gliding arc plasma. The mechanisms by which atmospheric plasma generates OH radicals can be divided into three types. First, electrons collide with water vapor molecules in the air ($\text{H}_2\text{O} + e \rightarrow \text{H} + \text{OH} + e$), second, metastable atoms dissociate ($\text{H}_2\text{O} + \text{Ar}^m \rightarrow \text{OH} + \text{H} + \text{Ar}$), and third, excited oxygen atoms react with water-vapor molecules ($\text{H}_2\text{O} + \text{O} \rightarrow 2\text{OH}$) [18]. When gliding-arc plasma is used to irradiate a polymer surface, hydroxyl groups like OH radicals adhere to the surface. These hydroxyl groups are hydrophilic, so they change the surface of the polymer from hydrophobic to hydrophilic [19].

PTFE (polytetrafluoroethylene) is a polymer that has strong atomic bonds between carbon and fluorine. This atomic bonding grants PTFE many useful properties like chemical and thermal resistance, low coefficient of friction, and electrical stability. PTFE was discovered in 1938 and has since been applied in a wide variety of products. PTFE is used, for example, as non-stick coating for kitchen utensils, electrical cables, and waterproof fabrics [20]. Owing to the high electronegativity of fluorine-bonded carbon, the surface of PTFE is hydrophobic, which makes it difficult to adhere to other materials, as is needed in forming cabling. Hydrophilicity is also a problem when printing on or dyeing the material, and some biomedical applications need a more hydrophilic surface. We have tested a gliding-arc plasma treatment that attaches OH radicals to the PTFE film surface in order to

Figure 2. (Color online) Schematic of gliding-arc plasma treatment system.

make it useful in applications that require a hydrophilic surface.

II. Experimental methods

Figure 2 shows a schematic of the gliding-arc plasma system we used for testing surface treatments. The system consists of two curved electrodes, an AC power supply, and a gas-flow inlet. The two stainless-steel electrodes are 100 mm long and the gas inlet diameter is 4 mm. The shortest distance between the electrodes is 6 mm, the longest distance between the electrodes is 20 mm, and the electrodes are 3 mm from the treatment target. When a 25 kHz power source is connected to the two electrodes and the discharge gas is injected, a gliding arc plasma is generated. Oxygen, nitrogen, argon, and air were tested as discharge gases. Square PTFE samples were cut to 3 cm on a side, and they were cleaned by ethanol and dried thoroughly before treatment. In all tests, the flow rate of the discharge gas and the treatment time were 15 slpm and 30 min, respectively.

The contact angle is a good indicator of whether a polymer surface is hydrophilic or hydrophobic. Contact-angle measurements were used to confirm the hydrophilicity of the PTFE surface. A contact angle measurement device (Phoenix-150, SEO Company) was used to measure contact angles. When taking these measurements, about 9 μl of deionized water is dropped onto the sample vertically using a syringe. The droplets are imaged the contact angle is analyzed in software (Surfaceware, SEO Company). For each sample, the

Figure 3. (Color online) Pictures of gliding arc plasma in different discharge gases: (a) O₂ (b) N₂ (c) Ar (d) air, and (e) He.

contact angle was measured before treatment, immediately after treatment, and once daily over 8 days. The treated and untreated samples were also imaged with a field emission scanning electron microscope (FE-SEM, MIRA3, TESCAN) and an atomic force microscope (AFM, NX ii, EM4SYS) to observe how the treatment changed the film-surface morphology. X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo scientific) was used to quantitatively analyze the elements on the surface before and after treatment.

III. Results and discussion

The shape of the gliding arc with different discharge gases is shown in Fig. 3. As the flow rate of the discharge gas increases, the arc-cycle duration decreases and the length of the arc increases. At flow rates of about 15 slpm or more, however, the arc length was fixed. Thus, the arc length can only be increased so much by increasing the flow rate, and the arc length also depends on factors like the distance between the electrodes and the voltage. The arc shape was similar when using oxygen, argon, nitrogen, and air as the discharge gas. However, the arc length of the plasma was relatively short when using helium as the discharge gas. The density of helium is lower than that of the ambient air, so the helium flow generates a weak drag force for elongating the generated arc. This short arc did not make good contact with the surface of the PTFE sample. The sample could be crumpled up to make contact with the arc, but then the results were difficult to compare with those from the other samples. Therefore, helium was not used as

Figure 4. FE-SEM images of (a), (b) untreated and (c), (d) treated PTFE film surfaces with oxygen discharge gas.

Figure 5. (Color online) AFM images of (a) untreated and (b) treated PTFE film surface with oxygen discharge gas.

a discharge gas in our tests.

The morphology of the PTFE samples was examined with FE-SEM analysis. Figures 4(a) and 4(b) show the untreated PTFE film surfaces at different locations, and Figure 4(c) and 4(d) show the PTFE film surfaces at different locations after gliding-arc plasma treatment for 30 min in oxygen. These images show that the morphologies of the untreated and treated surfaces are practically the same. The surface of the treated sample was damaged slightly, but this damage did not affect the physical properties of the PTFE film. This result confirms that the low-temperature region of the gliding arc in fact treats the surface. Further, the SEM images suggest that the increased hydrophilicity is not related to a physical change to the surface of the PTFE but instead is explained by a chemical change. The low risk of thermal damage means that the process can be used to treat heat-sensitive materials like polymers.

Figure 5 compares the AFM analysis results of the (a) pristine sample and (b) sample after treatment for 30 min in oxygen. The untreated sample was flat, and the surface was less uniform after treatment. In several studies, the surface of plasma-treated PTFE

Figure 6. Images of water droplets on the PTFE film surface (a) before and (b) after treatment for contact-angle analysis.

Table I. Contact angles of untreated and treated PTFE using different discharge gases.

Discharge gas	O ₂	N ₂	Ar	Air
Untreated	81.46°	77.20°	81.27°	81.04°
Treated	44.98°	51.49°	49.19°	61.04°

Table II. Enthalpies of dissociation and ionization of the discharge-gas components.

	O ₂ (kJ/mol)	O (kJ/mol)	N ₂ (kJ/mol)	N (kJ/mol)	Ar (kJ/mol)
Dissociation (M ² → 2M)	498	-	945	-	-
Ionization (P → P ⁺ + e)	1167	1310	1505	1402	1520

Table III. Contact angles for different treatment times under oxygen gas.

Treatment time	30 s	1 min	5 min	10 min	15 min	30 min
Contact Angle	76.52°	74.48°	61.7°	57.64°	50.24°	44.98°

has been shown to be rougher because of plasma-etching reactions, which tend to increase the contact angle of the surface [21]. In the present work, however, the contact angle decreased. This means that the chemical species attached to the surface have a greater influence than the physical changes made to the surface.

Figure 6 shows the results of using oxygen for the discharge gas. The untreated PTFE sample had a contact angle of 81.46° and the contact angle of the treated sample was 44.98°. Table I lists the results from the PTFE samples treated using nitrogen, argon, and air as the discharge gas. These have contact angles of 51.49°, 49.19° and 61.04°, respectively. As can be seen Table II, the plasma surface treatment using oxygen yields the lowest contact angle presumably because the ionization energy of oxygen is the lowest of those we tested and because dissociated oxygen

Figure 7. (Color online) Contact angles of treated PTFE films over time.

atoms react with the ambient air to form hydroxyl groups. Surface treatment using air yields the highest contact angle because moisture in the air adheres to the sample surface and prevents free radicals from attaching to the sample surface.

The contact angle after treatment is plotted against the treatment time in Table III. These tests used oxygen as the discharge gas because it proved to yield the lowest contact angle. The contact angle decreases as the treatment time increases, presumably because OH radicals have more time to attach to the surface of the PTFE film. The contact angle was greatly different after treatment for 1 min and 5 min. With longer treatment times, the contact angle increases in smaller steps.

Figure 7 plots the changes in the contact angle over time after treatment. The contact angle was the lowest when treated with oxygen plasma, but it increased rapidly with time. Treatments with argon and air plasma yielded the most-durable changes to the surface wettability, and nitrogen yielded the least-durable change. The radicals attached to the surface by the treatment tend to react with the ambient air and disappear over time, returning the PTFE surface to its original hydrophilic state.

C1s spectra from untreated and treated PTFE samples are shown in Fig. 8. The spectrum has peaks at the binding energies of 292 and 284 eV, which correspond to (CF₂) and (C-C) bonds in PTFE, respectively. Figure 9 shows the F1s spectra, with a main peak at 689 eV, which represents the (F-C-F) structure in PTFE [22,23].

The surface compositions of the PTFE samples as

Figure 8. (Color online) XPS C1s spectra from untreated and treated PTFE films.

Figure 9. (Color online) XPS F1s spectra from untreated and treated PTFE films.

Table IV. Atomic composition of untreated and treated PTFE film by XPS analysis.

	Atomic percentage (%)				Elemental ratio
	F	C	O	N	F/C
Untreated	63.07	35.16	1.69	0.08	1.79
O ₂	62.71	33.81	3.17	0.31	1.85
N ₂	61.74	31.19	6.59	0.48	1.97
Ar	52.56	27.63	19.35	1.52	1.90
Air	59.26	31.49	8.62	0.62	1.88

measured by XPS are shown in Table IV. These results show that nitrogen atoms were the least common on all the PTFE surfaces we tested. The PTFE samples treated under oxygen and nitrogen gases have percentages of fluorine and carbon similar to those of the untreated sample. In addition, PTFE samples treated with plasma under oxygen and nitro-

Figure 10. (Color online) XPS O1s spectra from untreated and treated PTFE films.

gen gas became more hydrophilic relatively quickly, as shown in Fig. 7. Conversely, the samples treated in argon and air plasmas were low in fluorine and carbon percentages relative to the samples before treatment, and the contact angle changed slowly over the treatment time. These results mean that a stable hydrophilic surface treatment is only achieved if the chemical structure of the surface is changed, rather than simply attaching chemical species to the surface. This goal can be achieved by removing fluorine atoms from the material at the surface. Figure 10 shows O1s spectra from untreated PTFE and treated PTFE. The high binding energy in the range of 523 eV indicates chemisorbed oxygen on the surface [24]. Chemisorbed oxygen plays an important role in the hydrophilicity of the treated PTFE surface. This peak was also found in weaker form in tests of the untreated PTFE surface. The chemisorbed oxygen peak of the sample treated with argon plasma was more prominent than that of the sample treated with oxygen plasma, but contact angle of the sample treated with oxygen was lower. It is estimated that during the contact angle measurement of the sample treated with oxygen, the chemisorbed oxygen disappears faster than treated with argon. Even after contact angle measurements, the argon-plasma-treated sample likely shows the stronger O1s peak because the chemisorbed oxygen is attached more stably to the surface, because the fluorine to carbon ratio has been reduced by the treatment.

IV. Conclusions

Surface treatments using gliding arc plasma to make

the surface of PTFE film hydrophilic were tested with several discharge gases. The surface can be made hydrophilic by gliding arc plasma treatment while leaving the surface morphology intact. Oxygen proves to be the best discharge gas for efficiently changing the wettability of the surface. During the treatment, reactive species such as OH radicals are attached to the PTFE film surface. Over time, however, these radicals react with ambient air so that the contact angle increases over time until the surface returns to being hydrophobic. Analysis of changes to the PTFE surface show that the surface wettability can be changed easily by a gliding arc plasma under atmospheric pressure.

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