

Surface Modification of Nylon 6 Films Treated with an He/O₂ Atmospheric Pressure Plasma Jet

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ABSTRACT: To investigate the effect of the gas composition of the plasma treatment on the surface modification of an atmospheric pressure plasma jet (APPJ), nylon 6 films were treated with APPJ with pure helium (He), He + 1% oxygen (O₂), and He + 2% O₂, respectively. Atomic force microscopy showed increased surface roughness, whereas X-ray photoelectron spectroscopy revealed increased oxygen contents after the plasma treatments. The plasma-treated samples had lower water contact angles and higher T-peel strengths

than the control. The addition of a small amount of O₂ to the He plasma increased the effectiveness of the plasma treatment in the polymer surface modification in terms of surface roughness, surface oxygen content, etching rate, water contact angle, and bonding strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2201–2206, 2011

Key words: adhesion; atomic force microscopy (AFM); ESCA/XPS; polyamides; surfaces

INTRODUCTION

Nylons are the most widely used semicrystalline engineering thermoplastics and also yield excellent fibers,¹ characterized by their good thermal stability, flexibility, and mechanical properties. Nylon 6 is one of the most important synthetic textile fibers originally used for women's stockings. Many of the applications for nylons besides textile fibers lie in the field of packing, but nylon can also be used for tapes and cable insulation.² Nylon 6 films have been used for the vacuum packing of foodstuffs, particularly cheese slices, because of its low gas permeability. Their high softening point and low odor transmission properties make them suitable for boil-in-the-bag packs and the packing of surgical equipment for steam sterilization. Because of their resistance to grease, they are used for the packaging of machine parts protected with a film of grease.

Although nylon 6 adsorbs more water than other frequently used synthetic polymers,³ it is still classified

as hydrophobic in many applications. Traditional methods of surface treatment are mostly wet chemical processes. However, ecological requirements force the industry to search for alternative environmentally friendly methods.⁴ Plasma technology has been applied effectively to the modification of the surface properties of polymers as an environmentally favorable alternative.^{5–16} It is regarded as an environmentally friendly process because no chemicals are involved and also as an effective way to modify the bondability and wettability of polymer surfaces through the introduction of polar groups or increasing surface roughness without affecting the bulk properties. However, most plasma systems operate under low pressure and, thus, require an expensive and complicated vacuum system.⁶ Atmospheric pressure plasma devices that do not need a vacuum system have been developed to overcome the drawbacks of low-pressure plasma treatments. In recent years, the atmospheric pressure plasma jet (APPJ) was invented to produce homogeneous plasma at low temperatures.

In this study, we used APPJ to modify the nylon 6 film surface and investigated the effects of atmospheric pressure plasma on the chemical and physical changes on the surface of the nylon 6 films. The nylon 6 films were treated by APPJs with pure helium (He), He + 1% O₂, and He + 2% O₂. The surface wetting properties were evaluated by measurement of the water contact angle with the sessile drop method, and the surface physical and chemical changes were examined by atomic force

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microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The weight loss and T-peel strength after plasma treatment were also studied.

EXPERIMENTAL

Material

The sample materials studied here were commercial low-density nylon 6 films with a density of 1.134 g/cm³. The films were cut into 2 × 5 cm² specimens. To remove finishes and surface contamination, the specimens were soaked in acetone for 10 min and then dried in a desiccator for 24 h at room temperature.

Plasma treatment

The specimens were treated on an APPJ apparatus (Atomflo-250, Surfex Technologies Co., Culver City, CA, US) with pure He (99.99% pure), He + 1% O₂, and He + 2% O₂. The plasma-treatment time was 30 s for each lap, which was equivalent to 4 s of stationary time. Therefore, for plasma-treatment times of 30, 60, 90, 120, and 180 s, the stationary treatment times would be 4, 8, 12, 16, and 24 s, respectively. The APPJ employed a capacitively coupled electrode design and produced a stable discharge at atmospheric pressure with a 13.56-MHz radio-frequency power source. More detailed information about the plasma machine was given in refs. 17 and 18. After the plasma treatments, the specimens were immediately placed into clean plastic bags to minimize potential contamination.

Morphological study

The surface morphologies of the nylon 6 films before and after plasma treatment were scanned with an atomic force microscope (Multimode Nanoscope IIIa, Digital Instrument, Plainview, NY, US). Changes in surface roughness of the plasma-treated nylon 6 films were expressed as differences in the root mean square (RMS) roughness. Each surface roughness value was calculated as the mean of at least 10 measurements in different locations on each film.

XPS analysis

The changes in the chemical composition of the nylon 6 film surfaces and chemical binding state were examined with XPS. The X-ray source was Mg K α (1253.6 eV), operating at 300 W. The analysis was carried out under ultra-high-vacuum conditions of 10⁻⁷–10⁻⁸ Pa. Photoemitted electrons were collected at a take-off angle of 45°, and the deconvolution analysis of C1s peaks was carried out with XPS Peak analysis software (XPSPEAK 4.1, Kwok, The Chinese University of Hong Kong, Shatin, Hong Kong).

Water contact angle measurement

The water contact angles were measured within 2 h after plasma treatment to determine the wettability of the nylon 6 film surface with the sessile drop method. A 2- μ L drop of distilled water was put on the film surface with a microliter syringe and was observed through a microscope. At least five readings at different places on each film were taken.

Weight loss

After the plasma treatments, the specimens were immediately weighed to estimate the etching effects on the layers of nylon 6 films. The plasma-etching effect described by the mass loss ratio was calculated with the following equation:¹⁹

$$\text{Mass loss(\%)} = (W_0 - W_1)/W_0 \times 100\%$$

where W_0 and W_1 are the masses of the nylon 6 films before and after plasma treatment, respectively.

T-peel strength

To study the effect of the plasma treatment on adhesion, a standard T-peel test was carried out with a universal testing machine (Model YG065H, Laizhou Electron Instrument Co., Laizhou, China) at a rate of 100 mm/min at room temperature. An adhesive tape with a width of 2 cm was stuck over a length of 4.0 cm on a sample nylon 6 film. To minimize potential air gaps and wrinkles, the specimens were kept under a dead weight of 1.0 kg for 10 min. We carried out the T-peel test by clamping one end of the sample in one jaw and the adhesive tape end with a piece of releasing paper in the other jaw. The T-peel strengths are reported as the force of peeling per centimeter of specimen width. For every treatment, five specimens were tested to obtain a mean value.

RESULTS AND DISCUSSION

Morphological study

The surface morphology of nylon 6 films was studied with AFM analysis, and the results are shown in Figure 1. After the plasma treatments, the surfaces of the nylon 6 films were rougher than that of the control. As shown in Table I, the RMS roughness of the control was 12.1 nm, whereas after treatment with the pure He, He + 1% O₂, and He + 2% O₂ plasmas, the RMS roughness values were 14.0, 16.3, and 22.0 nm, respectively. The values of RMS gradually increased as more oxygen (O₂) was mixed into the plasma gas; this could have been due to the fact that more atomic oxygen was available in the

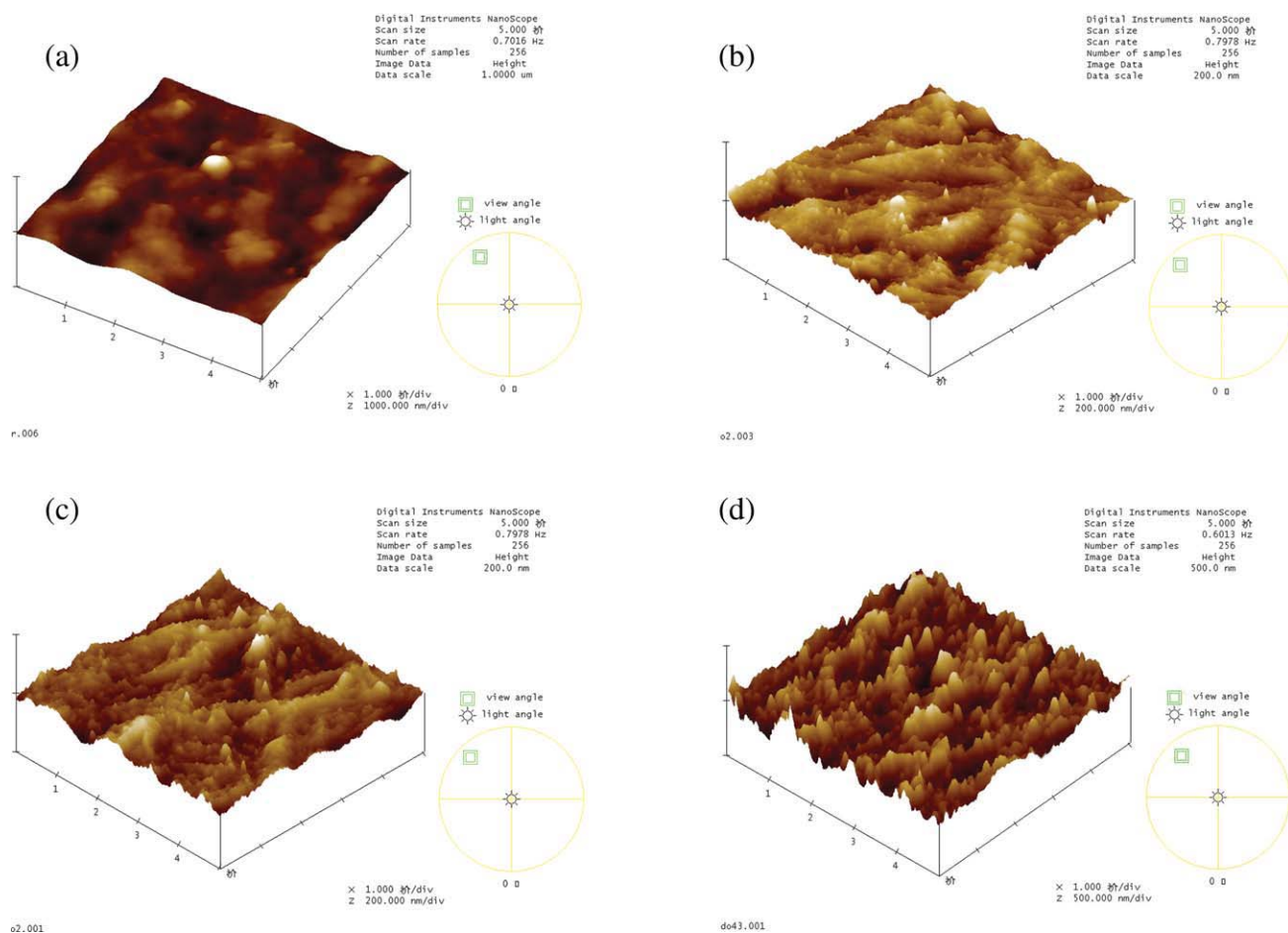


Figure 1 AFM images of nylon 6 films: (a) control, (b) pure He, (c) He+1% O₂, and (d) He+2% O₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plasma gas, which facilitated the etching and oxidation of the film surface.²⁰

XPS analysis

XPS was applied to analyze the surface chemical compositions of the nylon 6 films before and after the plasma treatment. The photoelectron peaks at 532, 400, and 285 eV corresponded to O1s, N1s, and C1s, respectively. Compared with the control, the O1s peak intensities after plasma treatment were

raised at the expense of the C1s peak intensities. The concentrations of these elements are given in Table II. The results of the element compositions of the control samples were in accordance with those described in the literature.^{21,22} For the plasma-treated samples, the oxygen content increased from 14.5 to 26.3, 33.3, and 36.0% for pure He, He + 1% O₂, and He + 2% O₂ groups, respectively. This phenomenon probably resulted from more atomic oxygen generated when O₂ was used as the reactive gas.²³

TABLE I
Surface Roughness of Nylon 6 Film Before and After Plasma Treatment

Sample	RMS (nm)	
	Average	SD
Control	12.1	0.9
Pure He	14.0	0.9
He + 1% O ₂	16.3	1.9
He + 2% O ₂	22.0	2.1

SD = standard deviation.

TABLE II
XPS Elemental Analysis of the Control and Plasma-Treated Nylon 6 Films

Sample	Chemical composition (%)			Atomic ratio (%)	
	C1s	O1s	N1s	O/C	N/C
Control	77.4	14.5	8.1	18.8	10.4
Pure	60.3	26.3	13.4	43.7	22.2
He + 1% O ₂	56.4	33.3	10.4	59.0	18.4
He + 2% O ₂	54.7	36.0	9.3	65.8	17.0

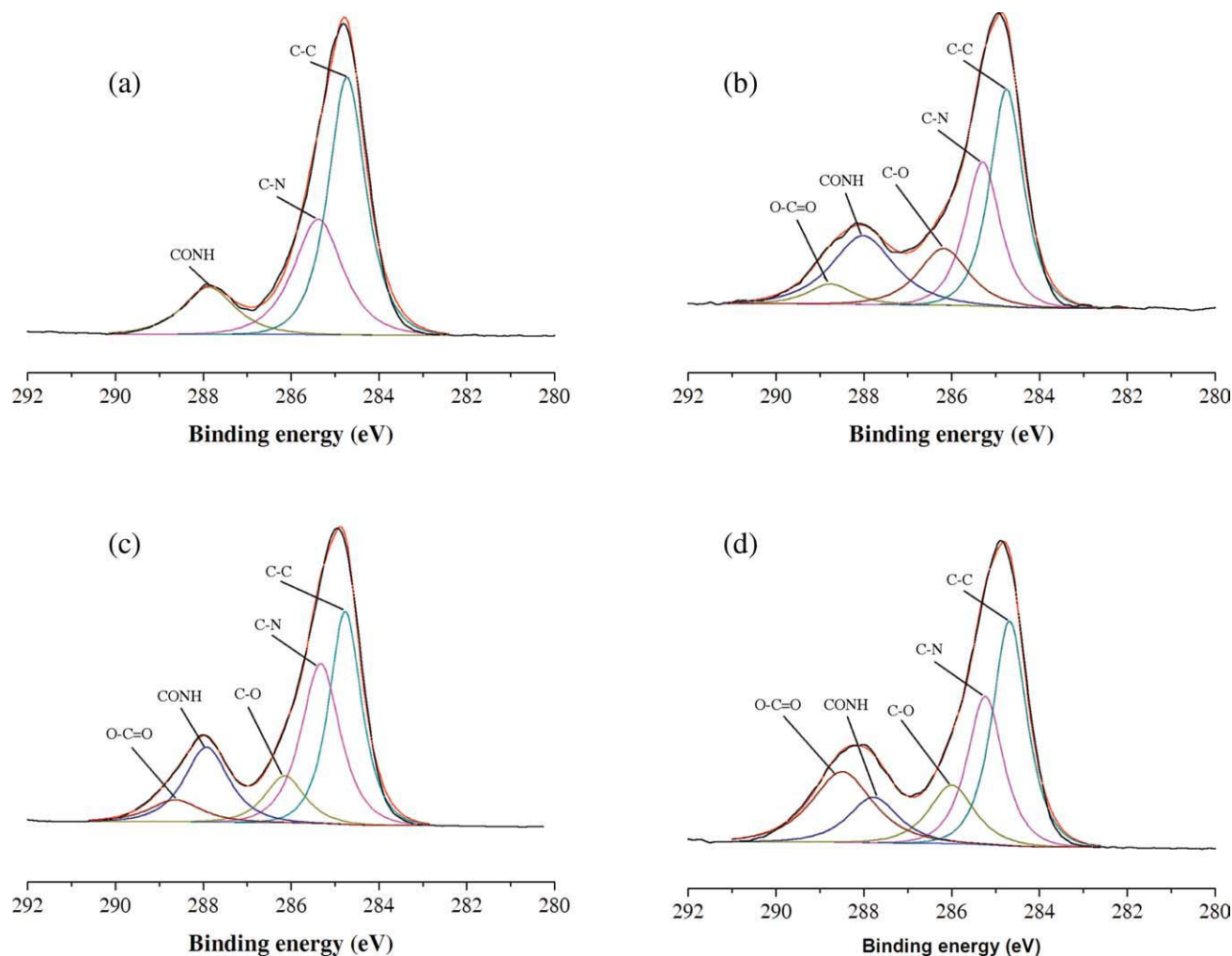


Figure 2 Deconvoluted XPS C1s peaks for nylon 6 film: (a) control, (b) pure He, (c) He+1% O₂, and (d) He+2% O₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To investigate the change in functional groups, deconvolution analysis of the C1s peaks was performed, as shown in Figure 2. After plasma treatment, an increase in oxygen functional groups, such as C—O (286.5 eV) and —COO— (288.5 eV) groups, were observed^{24,25} (Table III). From the results shown in Table III, for the plasma-treated samples, the amount of —COO— bonds increased in an

ascending order of pure He, He + 1% O₂, and He + 2% O₂ and showed that more oxygen in the plasma-gas mixture could lead to a higher degree of oxidation due to more activated oxygen-containing species, such as O, O⁺, H₃O⁺, and O*. Meanwhile, these activated species also greatly facilitated the degradation process of the polymer as the percentage of the amide groups decreased as the concentration of

TABLE III
Results of the Deconvolution Analysis of the C1s Peaks for the Control and Plasma-Treated Nylon 6 Films

Sample	Relative area corresponding to different chemical bonds (%)				
	—C—C— (284.6 eV)	—C—N— (285.4 eV)	—C—O— (286.5 eV)	—CONH— (287.9 eV)	—COO— (288.5 eV)
Control	46.6	40.3	—	13.2	—
Pure He	41.8	21.2	15.1	16.9	4.8
He + 1% O ₂	40.2	20.9	12.6	15.2	11.1
He + 2% O ₂	31.9	27.8	10.6	9.6	20.2

TABLE IV
Water Contact Angle of the Nylon 6 Films Before and After Plasma Treatment

Sample	Contact angle (°)	
	Mean	SD
Control	76	5
Pure He	58	3
He + 1% O ₂	47	2
He + 2% O ₂	29	3

SD = standard deviation.

oxygen increased. This was consistent with the AFM observation, which showed that more oxygen in the gas mixture led to an increased surface roughness.

Water contact angle measurement

Table IV shows that the mean water contact angle for the control was 76°, and it decreased significantly after the plasma treatments. The films treated with He+2% O₂ had lower water contact angles than those treated with pure He and He+1% O₂. This was attributed to more oxygen-containing hydrophilic groups and the greater surface roughness formed after the He+2% O₂ plasma treatment, as shown in the AFM and XPS analysis results.

Weight loss

Plasma etching is due to the physical removal of molecules of fragments or the breaking up of bonds, chain scission, and degradation processes. Figure 3 shows that the weight loss after plasma treatment increased with increasing O₂ concentration in the plasma-gas mixture. This was attributed to the fact

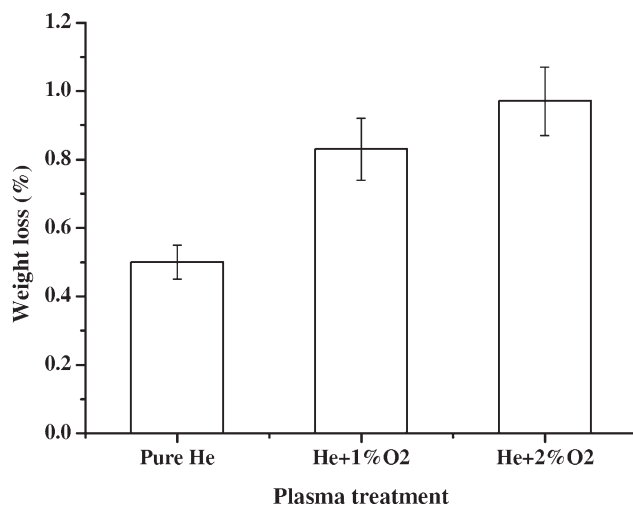


Figure 3 Mass loss with nylon 6 films treated with different plasma gases.

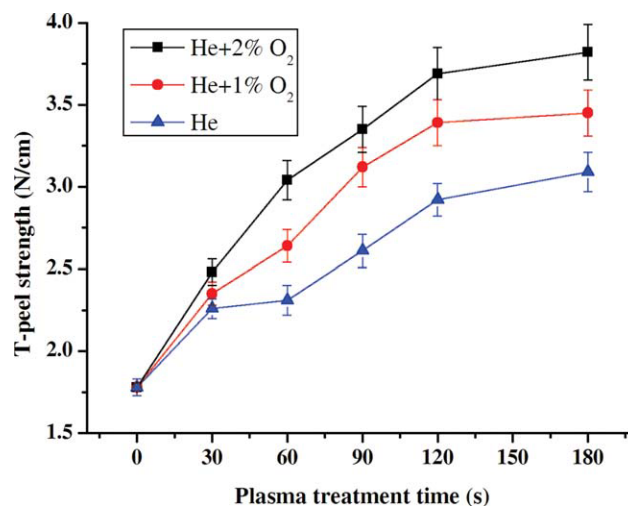


Figure 4 Relationship between the T-peel strength and plasma-treatment time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that more activated oxygen-containing species produced the He+2% O₂ plasma accelerated the etching process via chemical reactions or physical bombardment. This was again confirmed by a drastic reduction in the amide groups and the increased roughness for the He+2% O₂ plasma-treatment group shown in the XPS and AFM results.

T-peel strength

The T-peel strength was measured as a function of the plasma-treatment time to compare the bonding strengths of nylon 6 film surfaces for pure He, He + 1% O₂, and He + 2% O₂ groups (Fig. 4). The peel strength increased steadily up to 180 s of plasma-treatment time, and the T-peel strength for the He + 2% O₂ group was the highest among all of the treatment groups. This was not unexpected because for the He + 2% O₂ group, AFM showed the greatest roughness, which enhanced mechanical keying, and XPS showed the largest percentage of hydrophilic groups, such as —CO— and —COO— bonds, which promoted the surface wettability. The combination of the two factors could lead to greatly improved adhesion strengths.

CONCLUSIONS

The atmospheric-pressure He and He + O₂ plasma-treated nylon 6 films showed increased surface roughnesses, increased surface oxygen contents, and hydrophilic polar groups; this led to lower water contact angles and improved T-peel strength over the control. When the amount of oxygen increased from 1 to 2% in the plasma-gas mixture, all of these favorable effects were further enhanced. The plasma-etching rate was promoted as the amount of

oxygen in the plasma-gas mixture increased. The T-peel bonding strengths of the plasma-treated nylon 6 films increased steadily as the treatment time increased, and among the three types of gas mixture, the He + 2% O₂ plasma had the highest bonding strength for the same duration of plasma treatment.

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