Three different low-temperature plasma-based methods for hydrophilicity improvement of polyethylene films at atmospheric pressure*

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Three different low-temperature plasma-based methods were used to improve the surface hydrophilicity of polyethylene (PE) films, and all the modification processes were carried out by employing an atmospheric pressure plasma jet (APPJ) system. (a) PE films were directly modified by APPJ using a gas mixture of He and O_2. (b) Acrylic acid (AA) was introduced into the system and a polymer acrylic acid (PAA) coating was deposited onto the PE films. (c) AA was grafted onto the PE surface activated by plasma pre-treatment. It was found that the hydrophilicity of the PE films was significantly improved for all the three methods. However, the samples modified by Process (a) showed hydrophobicity recovery after a storage time of 20 days while no significant change was found in samples modified by Process (b) and Process (c). The Fourier transform infrared spectroscopy (FTIR) results indicated that the most intensive C=O peak was detected on the PE surface modified by Process (c). According to the X-ray photoelectron spectroscopy (XPS) analysis, the ratios of oxygen-containing polar groups for samples modified by Process (b) and Process (c) were higher than that modified by Process (a).

Keywords: atmospheric pressure plasma jet, plasma modification, acrylic acid, hydrophilicity improvement

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1. Introduction

Polyethylene (PE) has been widely used in various technological fields because of its several excellent properties such as high transparency, easy workability, chemical resistance, and low manufacturing costs.[1] However, further application of PE has been limited by its poor hydrophilicity induced by the lack of polar and reactive groups (e.g. carboxyl, hydroxyl, and amines) in the molecular structure. Therefore, it is necessary to modify the surface of PE films in order to improve its wettability and adhesive properties. Traditional methods for polymer surface modification include chemical processes,[2] laser radiation,[3] and plasma treatment.[4] Among these, plasma treatment is an effective and promising method for modifying the surface of materials without changing the bulk properties.[5–10]

Over the decades, low-pressure plasma treatments for the modification of surface properties of materials have been well studied.[11,12] However, an expensive vacuum setup is required and the treatment is a time-consuming batch process.[13] To overcome the vacuum limitation of low-pressure plasma, atmospheric pressure plasma systems are gaining popularity due to the advantages of eliminating vacuum equipment, on-line processing capability, and high efficiency.[14–18] Typically, the dielectric barrier discharge (DBD) atmospheric pressure plasma jets (APPJs) systems are developing very quickly because they can produce homogeneous plasmas at room temperature, produce plasmas in ambient air and modify the complex three-dimensions objects.[19,20] In general, there are mainly three strategies for surface modification carried out by APPJs: (1) direct modification of the substrate surface without adding any chemicals, usually with the noble gases acting as the discharge gases;[21–23] (2) depositing a functional film on the substrate surface by plasma polymerization;[24,25] (3) grafting polymer on substrate surface activated by plasma pre-treatment.[26,27] Up to now, few studies have focused on the differences among these three methods in regard to the efficiency of the surface modification. Accordingly, it is necessary to study the working mechanisms generated in these plasma processes, which can help us to choose the most suitable approach to modifying the surface of a given material.

In this paper, we utilized an APPJ system to modify PE films with the three different plasma-based methods mentioned above. The preliminary discharge characterization of the He/O_2 APPJ was investigated. Simultaneously, the

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modified PE films were characterized to reveal the structure changes after the modification processes.

2. Experimental method

The modification processes were carried out by using an APPJ setup as shown in Fig. 1. The apparatus employed a copper tube as the inner electrode and an electrolyte solution of potassium chloride (KCl) as the outer electrode. Both the electrodes were connected to an alternating current (AC) power source with a maximum peak voltage of 30 kV and an adjustable frequency of from 8 kHz to 30 kHz. More detailed information about the experimental APPJ setup has been presented in our previous publications.[28,29] Before plasma treatment, PE films were cut into strips of 2 cm×2 cm, and cleaned with detergent. Then, the samples were ultrasonically washed in distilled water, and dried at room temperature for 4 h. Figure 2 is the schematic diagram of the three different plasma-based methods. For the first method, gas valve 1 (Fig. 1) was turned on and we named this process non-monomer modification (NMM method) because PE films were modified by He/O_2 plasma directly without any chemical monomers. For the second method, we named deposition-polymerization modification (DPM), the gas valve 2 was only turned on. In this case, the vaporized acrylic acid (AA) monomer was transported to the plasma jet by O_2 gas flow. Thus, the AA was ionized and the polymer acrylic acid (PAA) was deposited onto the PE films. The modification time for NMM and DPM methods was set to be 10 min. For the third method, that we called graft-polymerization modification (GPM), the PE films were pre-treated by He/O_2 plasma for 5 min. After then, the pre-treated samples were immersed in an optimum aqueous solution: 40 wt% AA, 0.1 wt% Mohr's salt, and 0.2 M H_2SO_4. Mohr's salt was used as an inhibitor for polymerization and H_2SO_4 as a grafting accelerator.[30] Graft polymerization was achieved in a water bath with a temperature of 65 °C for 1 h and then dried in a vacuum drying oven. Finally, the samples were post-treated by He/O_2 plasma for 5 min to enhance the graft modification. Detailed processing parameters are listed in Table 1.

The plasma gas temperature was measured using an infrared thermometer (Fluke, Fluke62). The measuring method was similar to our previous work.[31] The applied voltage and the discharge current were monitored by a high voltage probe (Tektronix P6015A) and a current probe (Tektronix P6021), respectively, and the signals were recorded with a digital oscilloscope (Tektronix TDS1012B). The optical emission spectroscopy (OES) system consists of a UV-visible optical emission spectrophotometer (Andor, SR-500i-A, USA) with three grating monochromators with a resolution in the range of 0.14–0.4 nm. This system was used to identify various plasma species generated in the APPJ over a wavelength of 200–800 nm. The spectrum was obtained using an optical fiber. To obtain a strong and clear emission signal, a lens was used in this study to focus the light from the APPJ on the tip of the optical fiber.

The surface morphology of the PE films was analyzed by atomic force microscopy (AFM) (XE-100E, Korea). Squares of 5 μm×5 μm were scanned with tapping mode and all AFM images were collected in ambient air conditions. The surface results were analyzed with the XEI-Image Processing Program software. Fourier transform infrared spectroscopy (FTIR, Image-Pro Nicolet 5700, Germany) and X-ray photoelectron spectroscopy (XPS) (Kratos, Manchester, UK) were

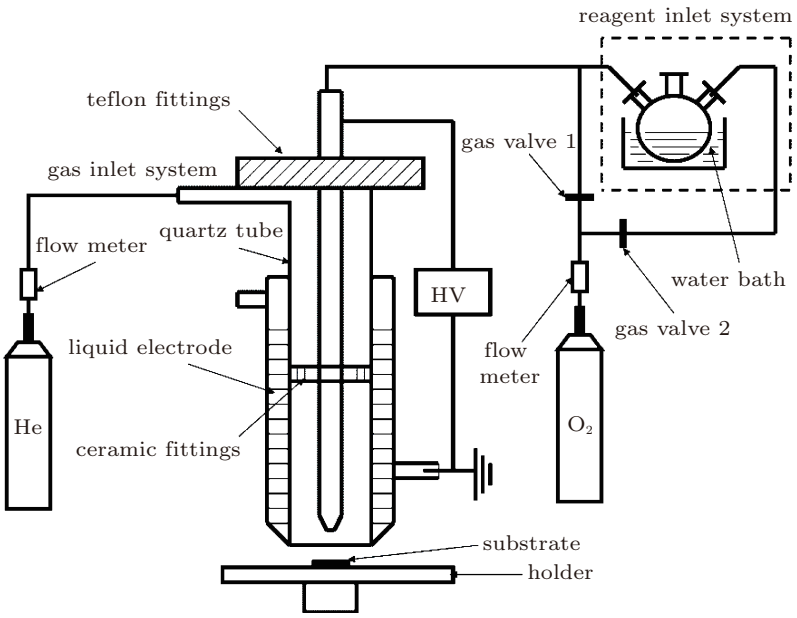


Fig. 1. Schematic diagram of the experimental APPJ setup.

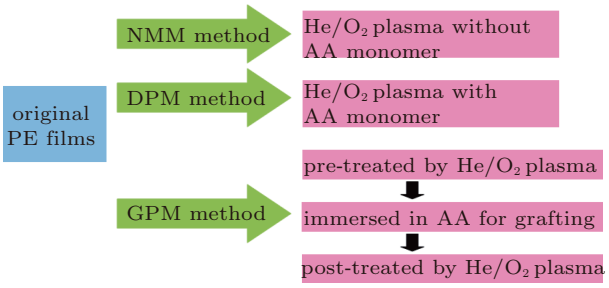


Fig. 2. (color online) Schematic diagram of the processes of the three different plasma-based methods for PE modification.

Table 1. Processing parameters of the APPJ treatments.

Parameter	Values
Input power /W	10, 20, 30
He flow rate /$m^3 \cdot h^{-1}$	0.4
O_2 flow rate /$m^3 \cdot h^{-1}$	0.1
Plasma treatment time/min	10
Jet-substrate distance /cm	1

used to investigate the chemical modifications of the treated surfaces. The FTIR spectrometer was operated in attenuated total reflectance (ATR) mode. The XPS system consists of a conventional hemispherical analyzer positioned at an angle of 45° with respect to the sample surface, and an Al Kα X-ray source (1486.6 eV) operating at 300 W. The surface hydrophilicity of the samples was determined by static water contact angle measurement, which was performed by a Kruss Drop Shape Analysis System (DSA10, Kruss GmbH, Germany). This process was repeated 5 times for each sample to minimize the statistic error.

3. Results and discussion

Plasma gas temperature measurement was carried out in order to ensure that the APPJ can be suitably used for the treatment of heat-sensitive materials. Figure 3 shows the effect of applied power on the He/O_2 plasma gas temperature. It can be found that the plasma gas temperature increased linearly as a function of the applied power. When the power was 30 W, which was the highest power applied in this study, the plasma gas temperature was about 305 K. This temperature was close to room temperature, and the plasma jet can be touched with a bare finger without any painful sensation.[31] This result illustrated that the plasma jet generated by this setup can be used to treat polymer materials (e.g. PE films) without thermal damage.

It is well known that the density of electrons and ions in the plasma plays an important role in the modification processes. It is then necessary to study the relationship between the applied voltage and the discharge current. The measured applied voltage and discharge current curve of the APPJ at atmospheric pressure are shown in Fig. 4. With a sinusoidal excitation (the discharge frequency is 11.5 kHz), the *U*–*I* curve presented that approximately one current pulse registered each half cycle. When the applied voltage was 4.9 kV, as shown in Fig. 4(a) (without AA monomer), the discharge current was about 2 mA. However, under the same applied voltage, a slight decrease of the discharge current can be observed when the AA monomer was carried to the jet (Fig. 4(b)). It is because that some electrons generated in the plasma jet were quenched by the AA monomer.

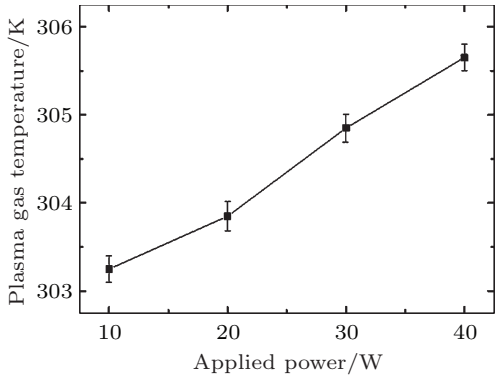


Fig. 3. Effect of applied power on the He/O_2 plasma gas temperature.

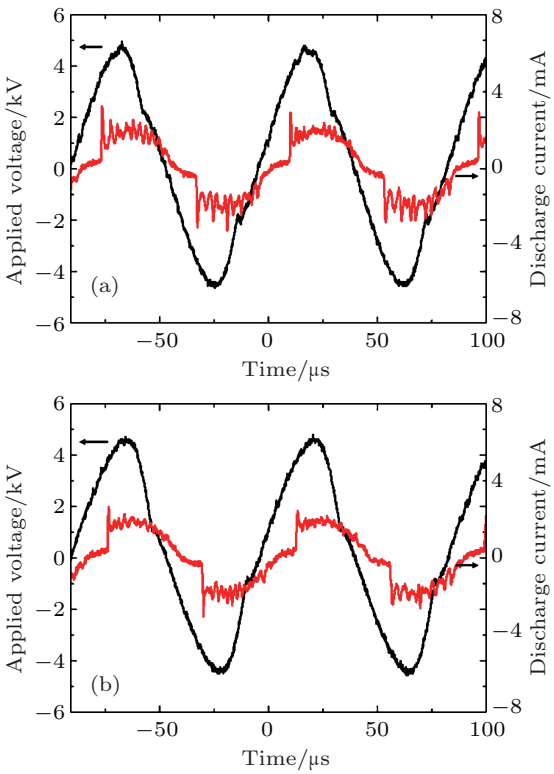


Fig. 4. (color online) Waveforms of the applied voltage and discharge current (a) without and (b) with AA monomer under a discharge frequency of 11.5 kHz.

Figure 5(a) shows the OES result of the He/O_2 APPJ without AA monomer. The emission spectrum reveals the presence of N_2 (second positive system), N_2^+ (first negative system), OH (3064 Å system), O_2^+ (Fox system), H, and O species.[32] The emission of O_2^+ at 427 nm may result from

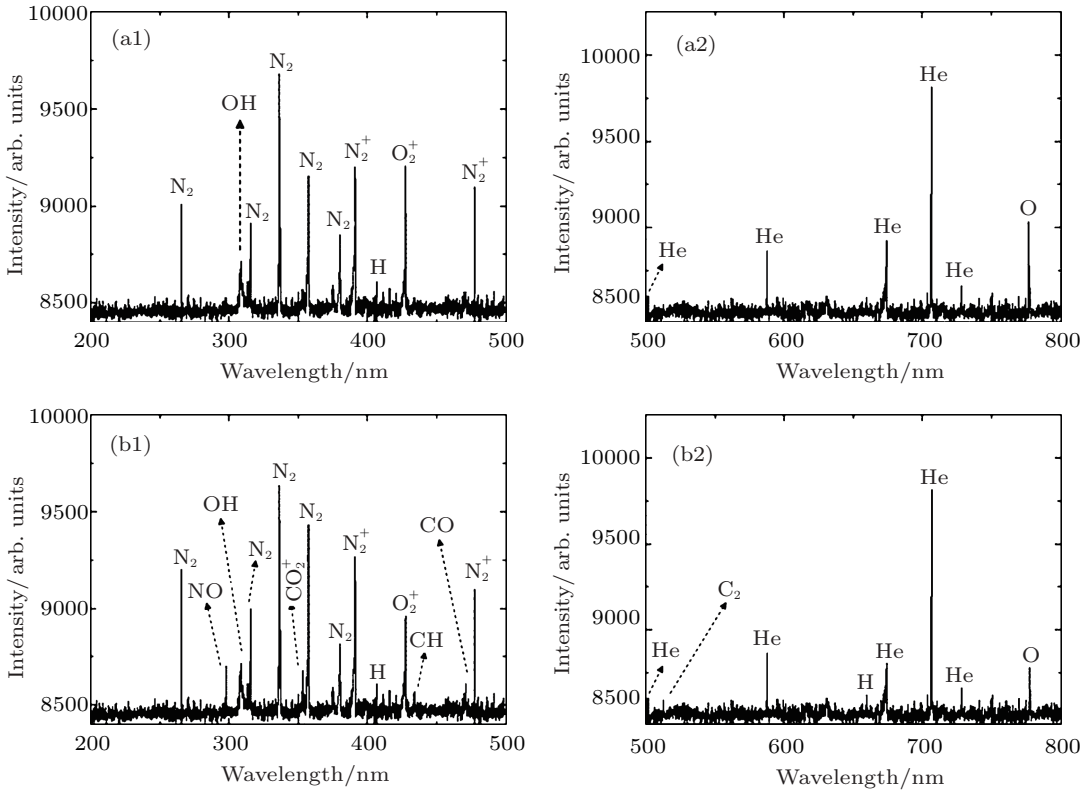


Fig. 5. Optical emission spectra of the He/O_2APPJ (a) without and (b) with AA monomer under an input power of 30 W. (a1) and (b1) are within the wavelength of 200–500 nm, (a2) and (b2) are within the wavelength of 500–800 nm.

the direct electron-impact ionization ($e^- + O_2 \rightarrow 2e^- + O_2^+$) and Penning ionization (He (2^1S) + He (2^3S) + $O_2 \rightarrow$ He + $O_2^+ + e^-$).[32] In addition, OH radicals observed at 309 nm may be formed by the reaction of excited O with water vapour ($H_2O + O^* \rightarrow 2OH$) and by electronic impact dissociation ($H_2O + e^- \rightarrow H + OH + e^-$).[33] The He lines at 501, 587, 667, 706, and 728 nm were also detected. The presence of N_2 (265, 315, 337, 357, and 380 nm) and N_2^+ signals (391 and 470 nm) revealed the air environment. Figure 5(b)[34] shows the OES result of the He/O_2 APPJ when AA monomer was mixed into the jet. Two weak peaks at 430 nm and 512 nm were observed, which were attributed to the C–H bond and C–C bond related to the AA monomer.

Figure 6(a) presents the effect of the applied power on the water contact angle of PE films modified by the three different methods. The untreated PE sample showed a contact angle of 71.1°. The data clearly shows that the contact angles of the PE films decreased with the increase of the applied power. It was found that the contact angles were similar under the same applied power. With an applied power of 30 W, the contact angles dropped to 20.8°, 17.5°, and 12.8°, for samples modified by NMM, DPM, and GPM methods, respectively. The hydrophilicity of the plasma-treated surfaces may change with time, which is potentially caused by surface contamination, orientation of polar groups or blooming of additives.[35] The recovery of hydrophobicity limits the possible usage in many applications. Therefore, it is important to discuss the ageing

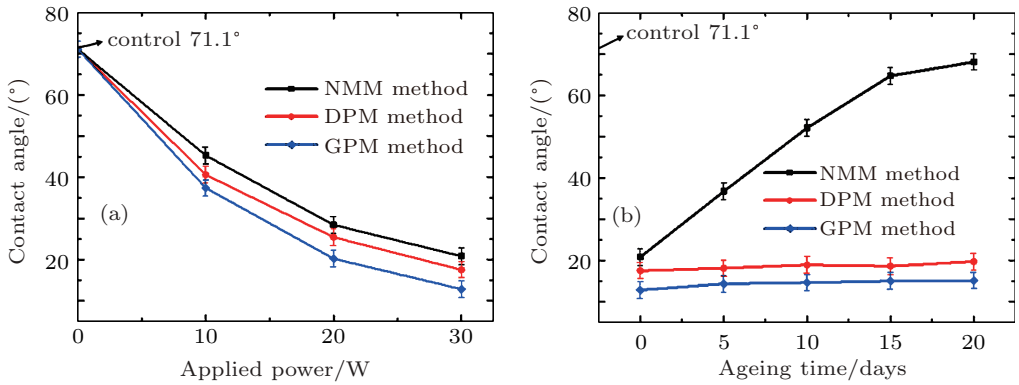


Fig. 6. (color online) (a) Effect of applied power on the water contact angle of PE films modified by different methods. (b) Water contact angle of PE films modified by different methods with an applied power of 30 W, data collected immediately and after 5, 10, 15, and 20 days from the initial treatment.

behavior of the treated samples. In the present work, PE samples treated with an applied power of 30 W were stored at 20 °C under ambient conditions with a relative humidity of 65% for 5, 10, 15, and 20 days. Then, the ageing test was estimated by water contact angle measurements. As can be seen in Fig. 6(b), different ageing behaviors were observed distinctly. For samples treated by DPM and GPM methods, the hydrophilicity showed no significant changes after an ageing time of 20 days (reached values of 19.7° and 15.1°). However, in case of samples treated by NMM method, the contact angle increased from 20.8° to 36.7°, 52.1°, 64.7°, and 68.1° with the extending of storage days, and the water contact angle even came close to the untreated PE films after 20 days.

As the applied power of 30 W gives the most hydrophilic state for each method studied for the modification of PE films, this power was used to treat samples to explore the different effects and efficiencies for these three processes. Normally, the hydrophilicity of organic materials is determined by the morphology and the chemical composition of the outermost surface layer. Therefore, it is important to characterize the surface properties for studying the hydrophilicity change of the samples. Figure 7 shows the AFM images of the PE films. Compared with the untreated one, the surface roughness increased from 19.8 nm to 24.8 nm when the sample was modified by the NMM method. As shown in Fig. 7(b), it was obvious that the plasma treatment created many micro-holes on the PE surface, which may be caused by ion etching (physical etching) and oxidation (chemical etching) induced by atomic O reacting with the carbon in the film.[36] When the sample was modified by DPM method (Fig. 7(c)), the surface showed a tiny recovery with a roughness of 20.1 nm, which may be due to the coated PAA layer. Moreover, the roughness of the sample modified by the GPM method (24.6 nm) was close to that modified by the NMM methods.

The chemical structure changes of PE films resulting from plasma modification were analyzed by FTIR. Figure 8 shows the FTIR spectra of the modified films by different methods. The absorption peaks at 2917, 2848, and 1463 cm^{-1} were attributed to methylene non-symmetry stretch vibration, methylene symmetry stretch vibration, and methylene non-symmetry changing angle vibration, respectively.[37] After plasma modification, new absorption peaks at 1726 cm^{-1} assigned to stretch vibration of C=O were detected. It was found that the most intensive C=O peak was obtained on the surface modified by the GPM method.

The XPS measurements were carried out to detect the chemical composition changes on the PE surface after the plasma processes. Table 2 shows the surface elemental composition and the atomic ratio of O/C for the PE samples. For the untreated sample, the detected oxygen may come from the additives added during the manufacture procedure. After the modification processes, the oxygen content showed a significant increase. Simultaneously, the atomic ratios of O/C increased from original 0.09 to 0.29, 0.28, and 0.31 for PE films modified by NMM, DPM, and GPM methods, respectively. For the NMM method, the presence of oxygen potentially

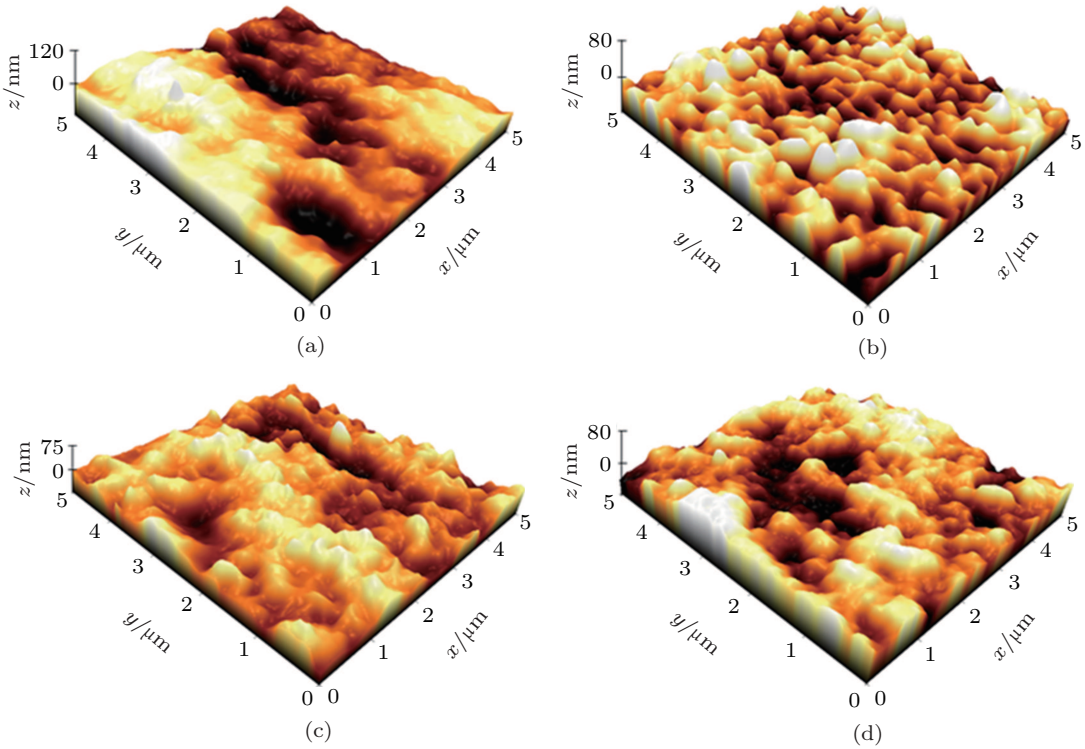


Fig. 7. (color online) Three-dimensional AFM images of the PE films: (a) untreated and modified by (b) NMM, (c) DPM and (d) GPM methods with an applied power of 30 W.

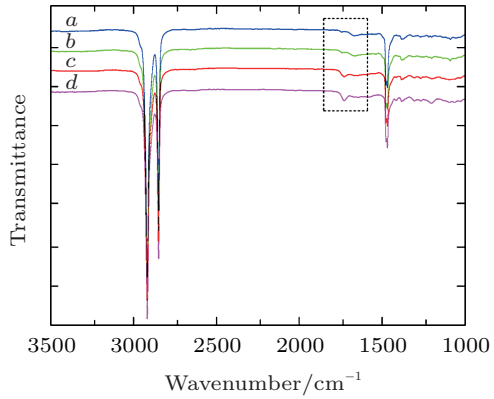


Fig. 8. (color online) FTIR spectra of the PE films: untreated (curve *a*) and modified by NMM(curve *b*), DPM(curve *c*), and GPM (curve *d*) methods with an applied power of 30 W.

Table 2. Relative atomic concentration and ratio of untreated and modified PE films by different methods with an applied power of 30 W.

Condition	Atomic concentration (%)			Atomic ratio
	O	N	C	O/C
Control	8.12	2.17	89.71	0.09
NMM method	22.04	2.55	75.41	0.29
DPM method	21.33	3.01	75.65	0.28
GPM method	23.47	1.12	75.41	0.31

resulted from the reaction between active surface sites and oxygen from ambient air. For the DPM and GPM methods, the incorporation of oxygen was probably due to not only the above reason, but also the presence of the AA monomer.

C1s deconvolution was performed to obtain further insight into the chemical bonds on the plasma-treated PE films. Figure 9 shows the curve fitting results of C1s peaks for PE films before and after plasma modifications. The chemical distribution of deconvoluted C1s peaks was based on the binding energies from the literature:[38–40] C–C (284.7 eV), C–O/C–OH (286.3 eV), C=O (287.9 eV), and O=C–O (288.9 eV). The C–C and C–O/C–OH peaks were detected on the surface of untreated PE film. In the case of PE film modified by NMM method, a new peak at 288.9 eV corresponding to O=C–O appeared, which was a typical result generated in the DBD plasma treatment processes.[41,42] This may be due to the chain scission mechanisms caused by the active species in the plasma, and the broken chain reacted with the oxygen to form the oxygen polar groups on the PE film surface.[43] Table 3 shows the results of the C1s peak deconvolution analysis, revealing a distinctive change of functional groups on the PE film surface after plasma modification. The C–C content decreased from 88.4 % to 86.8 %, 69.6 %, and 62.3 %, and the concentration of newly incorporated oxygen-containing polar group (O=C–O) increased to 4.6 %, 6.3 %, and 8.4 %. Meanwhile, for samples modified by the DPM and GPM methods, the C=O content increased to 4.1 % and 4.7 %, which may be attributed to the AA monomer. These oxygen-containing polar groups were the main contributor to the hydrophilicity improvement of the PE films.

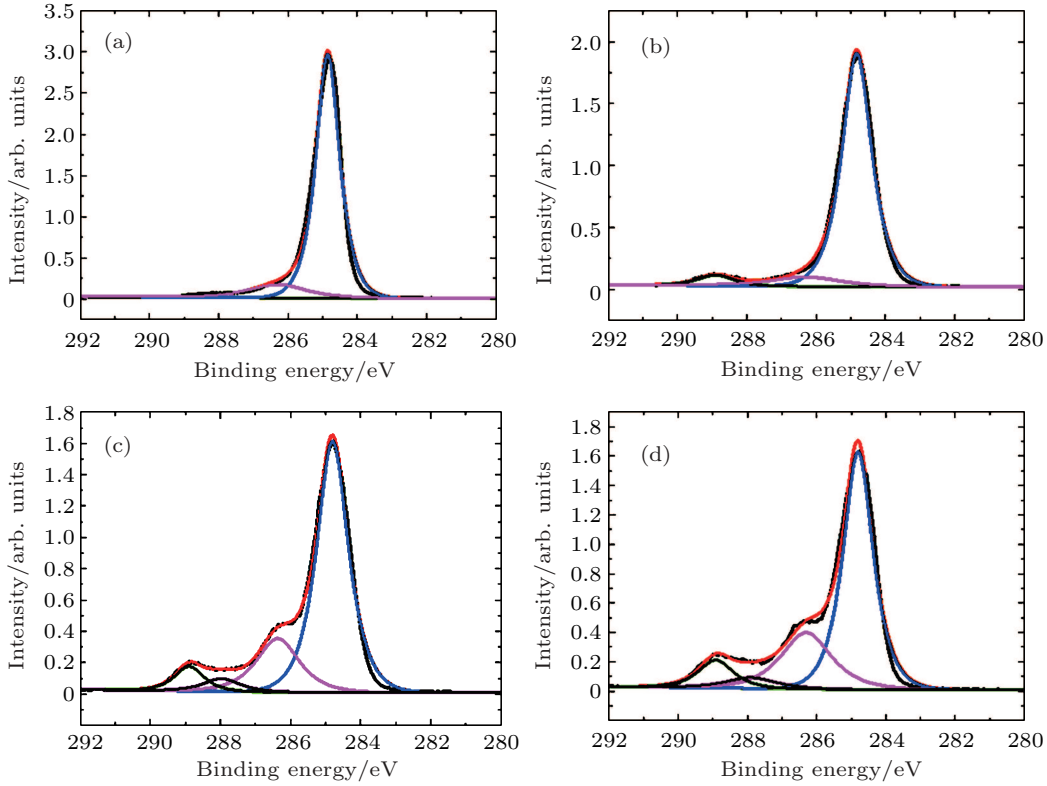


Fig. 9. (color online) The C1s XPS spectra of the PE films: (a) untreated and modified by the (b) NMM, (c) DPM and (d) GPM methods with an applied power of 30 W.

Table 3. Results of deconvolution analyses of C1s peaks of untreated and modified PE films by different methods with an applied power of 30 W.

Condition	Relative area of different chemical bonds /%			
	C–C	C–O/C–OH	C=O	O=C–O
Control	88.4	11.6	0	0
NMM method	86.8	8.6	0	4.6
DPM method	69.6	20.0	4.1	6.3
GPM method	62.3	24.6	4.7	8.4

4. Conclusion

Surface modification of PE films by three different plasma-based methods was explored in this work. It was found that the hydrophilicity of the PE films modified by the three different methods was improved similarly under the same applied power. According to the FTIR and XPS analyses, oxygen-containing polar groups were detected on all the modified PE film surfaces. The NMM method was an environment-friendly process and no chemicals were involved. However, the treated samples may undergo the hydrophobicity recovery, which limited the possible usage in some applications. The DPM and GPM methods can overcome this shortage by employing some chemical monomers in the modification processes. Compared with the GPM method, the DPM method was less complicated, easier to operate, and fewer chemicals were involved. Therefore, the DPM method shows a promising future in surface modification of polymer materials.

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