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Effects of O_2 and H_2O plasma immersion ion implantation on surface chemical composition and surface energy of poly vinyl chloride

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Abstract

Oxygen and water plasma immersion ion implantation (PIII) was used to modify poly vinyl chloride (PVC) to enhance oxygen-containing surface functional groups for more effective grafting. The modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), and contact angle measurements. Our experimental results show that both oxygen and water PIII can greatly improve the O to C ratios on the surface. The optimal plasma processing conditions differ for the two treatments. The hydrophilicity and surface energy of the plasma-implanted PVC are also improved significantly. Our results indicate that O_2 and H_2O PIII increase both the polar and dispersion interactions and consequently the surface energy. It can be explained by the large amount of oxygen introduced to the surface and that many C–C bonds are transformed into more polar oxygen containing functional groups.

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Keywords: Plasma immersion ion implantation (PIII); Poly vinyl chloride (PVC); Surface energy; Hydrophilicity

1. Introduction

Poly vinyl chloride (PVC) has many applications due to its attractive characteristics such as flexibility, softness, transparency, avirulence, and low production cost [1–3]. However, the required surface properties in many applications are frequently different from those of the bulk, for example, biocompatibility, hydrophilicity, antibacterial ability, and adhesive ability [4–9]. Hence, in many applications, the surface properties of PVC must be altered. For instance, PVC is modified to produce functional groups such as –COOH, –OH, $–NH_2$ to bind to biological molecules such as DNA, proteins, and antibacterial reagents [10–13].

A number of techniques have been employed to modify the surface chemistry and other characteristics of PVC [5,14–16]. These techniques typically utilize flame, chemical treatment, grafting, corona discharge, low-pressure plasma, or ultraviolet exposure. However, there are a number of associated drawbacks including pollution, materials damage, inefficiency, and so on. In comparison, plasma surface modification of polymers has a number of advantages. The plasma can be generated using air, oxygen, nitrogen, an inert gas, or a combination of them to produce special functional groups, chain scission, or cross linking on the surface [6,7,17]. In most plasma processes, the polymers are not subjected to a high voltage, and consequently, the modified layer is typically quite thin (on the order of several nanometers), thereby compromising long-term durability and reliability. In plasma immersion ion implantation (PIII), a high voltage is applied to the sample and ions from the overlying plasma are attracted and implanted into the sample conformally at high energy [18,19]. We have shown that PIII can be conducted on insulating samples without electrical arcing and materials damage up to a sample high voltage of −12 kV [20]. However, it is relatively difficult to achieve good control on the

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PIII process to produce the optimal surface properties. The objective of this work is to establish the relationship between the primary plasma parameters (treatment time, RF power, and bias voltage) and surface properties of PVC for O_2 and H_2O PIII which has been shown to improve the surface biological properties of a myriad of materials [21–23]. In addition to measuring the surface properties using X-ray photoelectron spectroscopy (XPS) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), the surface energy of the modified samples is evaluated by contact angle measurements.

2. Experimental details

The PVC samples used in our experiment had dimensions of 50 mm × 50 mm × 1 mm. They were affixed on stainless-steel substrates and laid on the sample platen in the center of the vacuum chamber of the PIII equipment [9,12,18,19]. Oxygen or water vapor was bled into the vacuum chamber at a flow rate of 35 sccm to a working pressure of 5×10^{-5} Torr. A pulsed high voltage with a duration time of 20 μs and frequency of 30 Hz was applied to the sample platen [9,17–20]. The experiments were conducted under various conditions including different treatment time, RF power, and pulsed high voltages in order to determine the optimal conditions.

To investigate the surface chemical composition of the modified PVC, X-ray photoelectron spectroscopy (XPS) was performed on a PHI-5600 equipped with a monochromatic Al Kα source and data acquisition and processing were conducted using the PC Access ESCA version 7.2A program [24–26]. The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were acquired using a Perkin-Elmer16 PC [17,27]. The sampling depth is approximately 1 μm by ATR-FTIR and it is larger than the thickness of the modified layer on the PVC. In order to reduce errors, spectra subtraction was adopted in this work using the following relationship:

$$A_S = A_i - fA_0, \quad (1)$$

where A_S is the degree of absorption on modified layer, A_i and A_0 the degrees of absorption before and after modification, and f is the coefficient related to the wavelength.

Static contact angles using distilled water or glycerin as the medium were performed by the sessile drop method using a Ramé-Hart (USA) instrument at ambient humidity and temperature [9,28]. Each data point represents the average of five measurements conducted on different parts of the specimen for statistical accountability.

3. Results and discussion

XPS was used to evaluate the effects of the three main plasma modification parameters, namely the treatment time, RF power, and bias voltage, on the surface chemical composition of the PVC. The results are shown in Figs. 1 and 2. It can be observed that dechlorination takes place readily during both O_2 and H_2O PIII. In addition, a small quantity of nitrogen can be detected on the surface, and it is believed to be due to nitrogen adsorption onto the active surface upon exposure to air.

In O_2 PIII, while keeping the RF power and bias voltage constant at 1000 W and −4 kV respectively, the amount of oxygen on the PVC surface increases with treatment time (Fig. 2a). The O to C concentration ratio on the surface increases at the largest rate from 0.068 to 0.334 in the initial 30 min and then increases slowly afterwards (only from 0.334 to 0.337). This indicates an optimal treatment time of about 30 min for O_2 PIII from the perspective of the O/C ratio. When the treatment time and bias voltage are kept constant while increasing the RF power, the surface oxygen concentration increases rapidly initially and the increase tapers at around 500 W (Fig. 2b), similar to the trend observed for the treatment time. After more extensive experiments, it is determined that 1000 W is the optimal RF power to obtain the largest O/C ratio. In our third set of experiments, the treatment time and RF power are kept constant at 30 min and 1000 W, respectively while varying the sample voltage. The surface oxygen concentration does not always increase with a higher bias voltage. The oxygen concentration increases up to a voltage of −8 kV but declines when the sample voltage is further increased as shown in Fig. 2c. Furthermore, based on our previous experiments [20], when the sample bias voltage is higher than 12 kV, the bulk properties of the sample will be altered significantly due to heating, electrical arcing, and charging. Based on the O to C ratio and other considerations, the optimal O_2 PIII conditions

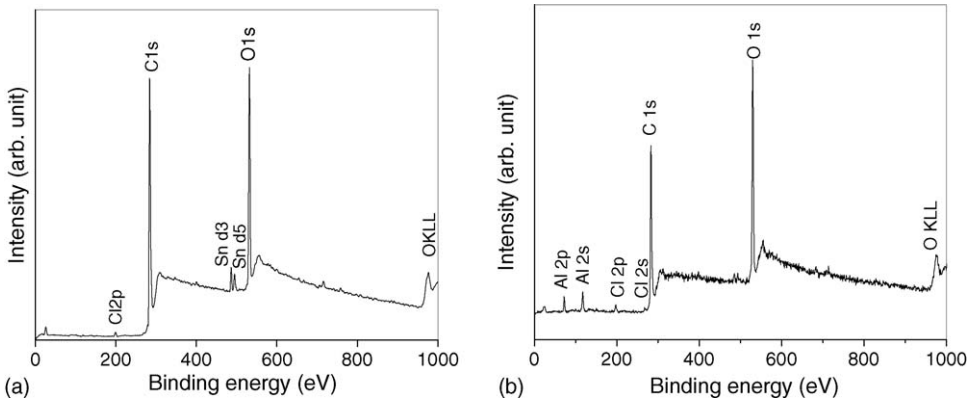

Fig. 1. XPS spectra obtained from the modified PVC: (a) sample 1 and (b) sample 2.

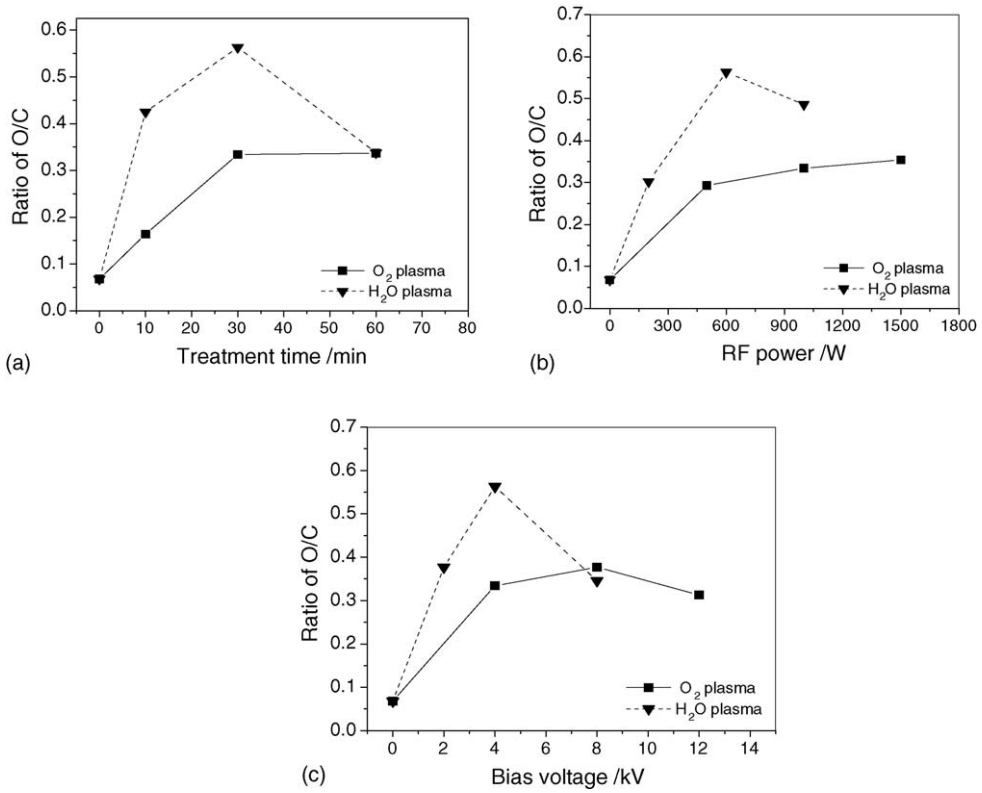

Fig. 2. The ratio of O/C on the modified PVC as the function of each parameter: (a) treatment time, (b) RF power, and (c) bias voltage.

are: treatment time = 30 min; RF power = 1000 W; bias voltage = −4 kV. The sample processed under this set of conditions is designated as sample 1.

When H_2O is used instead of O_2 in our PIII experiments, the surface chemical composition is observed to be quite different. During H_2O PIII (Fig. 2), the surface oxygen concentration initially increases rapidly and then decreases with increasing treatment time for a constant RF power of 600 W and bias voltage of −4 kV. The highest O to C ratio of 0.563 is achieved after a treatment time of about 30 min. By using the same assessment criteria as described in the previous paragraph, the optimal H_2O PIII conditions are: treatment time = 30 min; RF power = 600 W; bias voltage = −4 kV. The sample implanted under this set of conditions is designated as sample 2.

The C 1s high resolution spectra are used to identify the chemical states on the modified PVC. The peak fitting parameters as well as the relative abundances of the fitted carbon are summarized in Tables 1 and 2. Figs. 3 and 4 are the C 1s and O 1s high resolution spectra acquired from samples 1 and 2, respectively. Table 1 and Fig. 3 show that when the treatment time is about 30 min, the amounts of C=O (2.9%) and O–C=O (2.7%) are the highest. Therefore, 30 min is the optimal time for the improvement of C=O and O–C=O groups. In comparison, when the RF power is 1000 W, the amount of C–O is optimized but those of the C=O and O–C=O groups are not. Our results also reveal that the total concentration of the oxygen containing functional groups is the highest when the bias voltage is raised to −12 kV. No further attempt to go to a higher voltage is made here due to materials damage [20]. Table 2 and Fig. 4 show

Table 1
Peak fitting parameters and relative peak areas calculated from the C 1s high-resolution XPS spectrum of sample 1 (O_2 PIII)

Peak/C 1s	Binding energy (eV)	FWHM (eV)	Area (%)											
			RF power = 1000 W, bias voltage = −4 kV				Treatment time = 30 min, bias voltage = −4 kV				Treatment time = 30 min, RF power = 1000 W			
			0 min	10 min	30 min	60 min	0 W	500 W	1000 W	1500 W	0 kV	4 kV	8 kV	12 kV
C–C/*C*–H	282.5	1.2 ± 0.5	86.4	79.0	74.4	62.1	86.4	65.7	74.4	63.2	86.4	74.4	62.8	66.9
C–O	283.6	1.2 ± 0.5	6.5	11.7	9.2	21.6	6.5	23.7	9.2	16.0	6.5	9.2	18.8	16.1
C–Cl	284.3	1.2 ± 0.5	1.9	2.6	5.0	6.6	1.9	3.9	5.0	9.5	1.9	5.0	7.5	6.8
C=O	285.5	1.2 ± 0.5	2.9	1.7	5.1	4.2	2.9	2.8	5.1	5.0	2.9	5.1	3.9	6.2
O–*C*=O	286.7	1.2 ± 0.5	2.3	4.9	6.2	5.6	2.3	3.9	6.2	6.2	2.3	6.2	7.0	3.9

0, 10, 30, 60 min are the varying treatment times; 0, 500, 1000, 1500 W are the varying RF power and 0, 4, 8, 12 kV are the varying bias voltage.

Table 2
Peak fitting parameters and relative peak areas calculated from the C 1s high-resolution XPS spectrum of sample 1 (H_2O PIII)

Peak/C 1s	Binding energy (eV)	FWHM (eV)	Area (%)											
			RF power = 600 W, bias voltage = −4 kV				Treatment time = 30 min, bias voltage = −4 kV				Treatment time = 30 min, RF power = 600 W			
			0 min	10 min	30 min	60 min	0 W	200 W	600 W	1000 W	0 kV	−2 kV	−4 kV	−8 kV
C–C/*C*–H	282.5	1.2 ± 0.5	86.4	66.7	65.4	73.6	86.4	67.0	65.4	78.1	86.4	74.3	65.4	50.0
C–O	283.6	1.2 ± 0.5	6.5	18.4	21.9	15.6	6.5	14.9	21.9	8.9	6.5	16.3	21.9	23.9
C–Cl	284.3	1.2 ± 0.5	1.9	7.0	7.1	7.3	1.9	8.8	7.1	5.8	1.9	4.0	7.1	17.4
C═O	285.5	1.2 ± 0.5	2.9	3.5	2.9	0.6	2.9	4.5	2.9	2.1	2.9	2.0	2.9	4.2
O–*C*═O	286.7	1.2 ± 0.5	2.3	4.4	2.7	2.9	2.3	4.9	2.7	5.1	2.3	3.4	2.7	4.9

0, 10, 30, 60 min are the varying treatment times; 0, 200, 600, 1000 W are the varying RF power and 0, −2, −4, −8 kV are the varying bias voltage.

that the C–O group is most abundant when the oxygen concentration is the highest at a treatment time of about 30 min. In comparison, the C═O and O–C═O groups are more abundant at a treatment time of 60 min. With regard to the RF power, the C–O group is the most abundant at 600 W, but 200 W is better for the C═O and O–C═O groups. Based on a similar investigation, the C–O, C═O and O–C═O groups are most abundant at a bias voltage of −8 kV.

The surface chemistry of the O_2 and H_2O PIII PVC samples are further evaluated using ATR-FTIR. Fig. 5 depicts the spectra obtained from samples 1 and 2. In spite of the small thickness of the modified layer compared to the sampling depth of the ATR-FTIR technique, the peaks at 1717 cm^{-1} designated to C═O stretching vibration and at 1270–1250 cm^{-1} designated to C–OH stretching vibration can be readily observed. The peaks between 2970 and 2840 cm^{-1} are the stretching vibration of the C–H group, and the emergence of the peak at 1410 cm^{-1} designated to –COO– illustrates that both O_2 and H_2O PIII produces the O–C═O functional group. Our ATR-FTIR data indicate unequivocally the appearance of oxygen containing functional groups on the PVC surface after PIII and it further corroborates the XPS results.

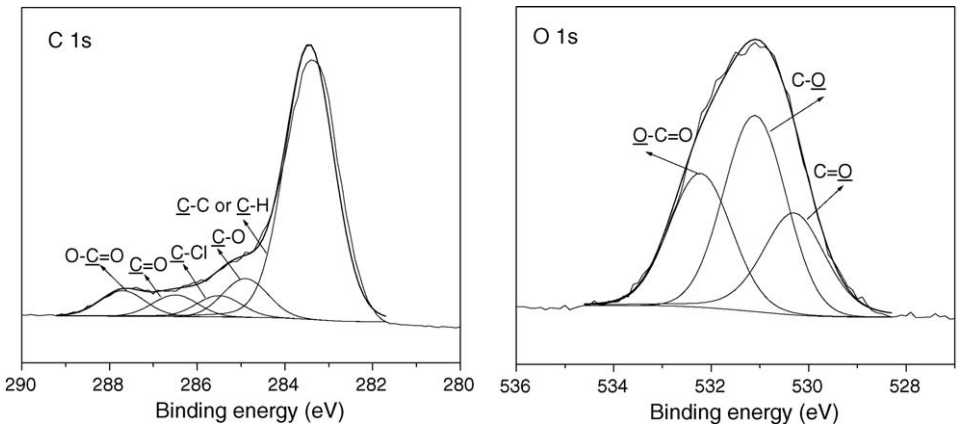

Fig. 3. C 1s and O 1s core level spectra acquired from sample 1.

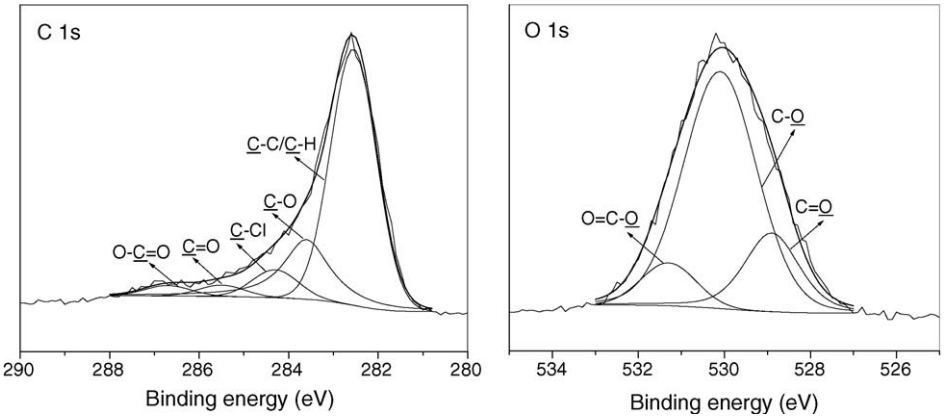

Fig. 4. C 1s and O 1s core level spectra acquired from sample 2.

Table 3
Contact angle and surface energy calculated from the untreated PVC (control) as well as samples 1 and 2

Samples	Contact angle (°)		Dispersion, γ_S^d (nJ/cm^2)	Polar, γ_S^p (nJ/cm^2)	Surface energy, γ_S (nJ/cm^2)
	Distilled water	Glycerin			
Control	97.2	96.9	11.0	2.2	13.2
Sample 1	21.7	48.8	25.3	18.3	43.6
Sample 2	26.9	57.4	17.8	20.3	38.1

The wetting properties of samples 1 and 2 are investigated using contact angle measurements [9,28]. The wetting ability is the ability of a liquid to adhere to a solid and spread over its surface. The classical model by Young suggests that:

$$\gamma_{SV} = \gamma_{LV}\cos\theta + \gamma_{SL}, \tag{2}$$

where θ is the measured contact angle, γ_{SV} the surface tension of the solid in contact with air, γ_{LV} the surface tension of the liquid in contact with air, and γ_{SL} is the surface tension between the solid and the liquid. The work of adhesion W_a between the solid and liquid can be expressed in terms of the Dupre equation as follows:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}. \tag{3}$$

By combining these two equations, the Young–Dupre equation becomes:

$$W_a = \gamma_{LV}(1 + \cos\theta). \tag{4}$$

The solid surface tension can be separated into the intermolecular attraction of polar interaction γ_S^p and dispersion interaction γ_S^d as:

$$\gamma_S = \gamma_S^d + \gamma_S^p. \tag{5}$$

Therefore, the work of adhesion can be expressed as the sum of the different intermolecular forces at the interface.

$$W_a = 2(\gamma_{LV}^d \gamma_S^d)^{1/2} + 2(\gamma_{LV}^p \gamma_S^p)^{1/2}. \tag{6}$$

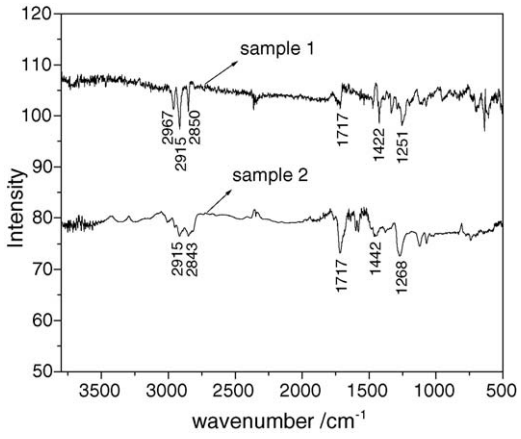

Fig. 5. ATR-FTIR spectra acquired from samples 1 and 2.

Eqs. (3) and (4) can further be simplified to:

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_{LV}^d)^{1/2}(\gamma_S^d)^{1/2} + 2(\gamma_{LV}^p)^{1/2}(\gamma_S^p)^{1/2}. \tag{7}$$

Finally,

$$\frac{\gamma_{LV}(1+\cos\theta)}{2(\gamma_{LV}^d)^{1/2}} = (\gamma_S^d)^{1/2} + (\gamma_S^p)^{1/2}\left(\frac{\gamma_{LV}^p}{\gamma_{LV}^d}\right)^{1/2}. \tag{8}$$

Table 3 shows the decrease of the contact angle and improvement of wetting property can be attributed to the change of physical and chemical properties of the surface after PIII. The surface energy of the solid is determined by the intermolecular attraction of the polar interaction (γ_S^p) and dispersion interaction (γ_S^d). From Table 3, O_2 and H_2O PIII increase both the polar and dispersion interactions. As a result, the surface energy of the modified PVC increases. It can be explained by the large amount of oxygen introduced to the surface and many C–C bonds are changed into more polar oxygen containing functional groups. Our aging experiments, however, indicate that the hydrophilicity of the modified PVC degrades after storage under ambient conditions for half a month. For example, the contact angle of distilled water observed on samples 1 and 2 decreases from 21.7° and 26.9° to 95.4° and 83.0°, respectively. It is believed to stem from the high molecular mobility in PVC and we are conducting more experiments to prolong the effectiveness of our plasma treatment and fathom the degradation mechanism in details.

4. Conclusion

Oxygen and water plasma immersion ion implantation (PIII) was employed to modify the surface of PVC. Both processes can significantly enhance the O to C ratio and oxygen containing functional groups on the surface. However, the optimal conditions for these two processes are different. For O_2 PIII, the optimal modification parameters from the perspective of the O to C ratio are: treatment time = 30 min; RF power = 1000 W; bias voltage = −4 kV. For H_2O PIII, the optimal parameters are: treatment time = 30 min; RF power = 600 W; bias voltage = −4 kV. Both treatment processes increase the surface hydrophilicity and surface energy, although the hydrophilicity of the modified PVC deteriorates with time.

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