

Surface Modification of Medical Poly(vinyl chloride) with O⁻ Water

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ABSTRACT: A novel approach to the surface modification of medical poly(vinyl chloride) (PVC) with atomic oxygen radical anions-dissolved solution (named as O⁻ water) has been investigated. The O⁻ water was generated by bubbling of the O⁻ (atomic oxygen radical anion) flux into the deionized water. The surface hydrophilicities of the PVC films were investigated by contact angle measurements before and after the O⁻ water treatment. Surface chemical compositions of the original and treated PVC films were studied using X-ray photoelectron spectroscopy (XPS). The influence of the O⁻ water on the surface roughness as well as morphological alterations of the PVC films was investigated by atomic force microscopy (AFM) measurements. Results show that the O⁻ water treatment caused an

obvious increase in the surface hydrophilicity and surface energy and also caused an alteration of the surface chemical composition, with an increase in surface roughness because of the etching effect. The modifications are attributed to the formation of oxygen-containing functional groups (C—O, C=O, O—C=O, etc.) and dechlorination, mainly caused by the reactions between the molecules on PVC surfaces and the active oxygen species in the O⁻ water. Present method, potentially, may be applied to the surface modification of polymers and other heat-sensitive materials. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 39–48, 2008

Key words: O⁻ water; surfaces; modification; poly(vinyl chloride); hydrophilic polymers

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important polymers and has been widely used in biological and medical applications for storing of substances (e.g., blood products, drugs, and injectables), for catheters with antithrombogenic activity, or as filtration membranes, etc.^{1–3} Surface properties of PVC such as surface chemical composition, surface energy, and surface topography could be critical for biomaterial biocompatibility and must be considered in their selection for medical application. It has been revealed that the interactions between the biological environment and artificial materials are most likely dominated by the materials' surface properties including wettability, morphology, and surface

charge.³ Generally, it is necessary to use the materials having a polarity of the surface and better wettability, which would be critical for the biocompatibility, anticoagulation, and adhesion.^{1–4} Therefore, the modification of PVC toward a hydrophilic surface has attracted considerable attention in the recent years.^{1,3–5}

One common approach to increasing hydrophilicity of surfaces is through the incorporation of hydrophilic functional groups.^{1,3–11} This chemical structural modification has been successfully realized by plasma treatment,^{3,5} UV treatment,^{7,8} or graft polymerization,^{1,9–11} etc. Among these methods, plasma treatments and UV treatments are attractive for their high efficiency. An interesting feature of plasma modification is that the surface structure of the polymer can be modified selectively, whereas the bulk properties remain unaffected.⁶ On the other hand, surface modification by chemical grafting would be more flexible in surface modification of polymers. It has also been demonstrated that graft copolymerization can be performed under mild conditions when their surfaces are pretreated with high-energy radiation, glow discharge, corona discharge, ozone exposure, or UV irradiation.^{9,12} Chemical grafting technology of surface modification generally needs multistep processes and cannot be directly carried out at mild conditions.^{4,13}

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Active oxygen species, such as hydroxyl radical ($\cdot\text{OH}$), superoxide (O_2^-), and peroxide radical ($\cdot\text{OOH}$), become more and more attractive because of their strong chemical reactivity.¹⁴ For instance, it is reported that active oxygen species produced by the combination of ozone aeration and UV irradiation have been used for improving the hydrophilicity and adhesion properties of polymer surface.^{15,16} Atomic oxygen radical anion (O^-) is also one of the most important active oxygen species and has strong oxidation ability in chemical reactions.¹⁷ O^- is a monovalent anion, and also could be considered as a radical because of the unpaired electron in its outmost orbit. O^- may be one of the most active oxygen species and therefore has various potential applications, such as the chemical synthesis¹⁸ and the thin film oxidation.^{19–21}

The conventional way to generate O^- is the attachment of a free low-energy electron to atomic oxygen or is through negative ion/molecule reactions that can occur in the following processes: plasma process, electron impact process, or laser irradiation on molecules in gas phase. But O^- generated by above methods is generally accompanied by the formation of other ion species. To generate pure and sustainable O^- flux, a new approach has been developed by our research group, where O^- can be emitted from the anionic storage-emission material of $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot 4\text{O}^-$ (C12A7- O^-).^{22–25} Recently, we have also synthesized the various derivatives of C12A7- O^- such as C12A7-OH^{26,27} and C12A7-H^{28,29} and we found that the C12A7- O^- material or the modified ones would be practically used in a one-step synthesis of phenol from benzene,¹⁸ the reduction of NO ,³⁰ the dissociation and oxidation of bio-oil,³¹ and a fast inactivation of microorganisms.³²

Present work aims to investigate a new approach to increase surface wettability of PVC by introducing the oxygenated functional groups with the O^- water treatment, which may provide a flexible and environmental-friendly method for the surface modification of PVC, and may be useful in biological and medical applications. The modification performance and the surface features of the medical PVC treated by the O^- water were studied.

EXPERIMENTAL

Preparation of the O^- water

The O^- water was prepared by bubbling the O^- flux into the deionized water. Pure and sustainable O^- flux was emitted from the anionic storage-emission material of C12A7- O^- , which was synthesized by the solid-state reaction of CaCO_3 and $\gamma\text{-Al}_2\text{O}_3$. First, the powders of CaCO_3 and $\gamma\text{-Al}_2\text{O}_3$ with the average particle diameter of 20–30 μm were mixed at a molar

ratio of $\text{CaCO}_3 : \gamma\text{-Al}_2\text{O}_3 = 12 : 7$. Then, the samples were temperature programmed to 1350°C with the heating rate of 10°C/min and sintered at 1350°C for 10 h under flowing dry oxygen environment. Finally, the sintered samples were cooled to room temperature naturally. The structure of C12A7- O^- is characterized by a positive-charged lattice framework $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}$ including 12 subnanometer-sized cages with a free space of about 0.4 nm in diameter.²⁵ The concentration of O^- stored in the bulk of C12A7- O^- was about $2.0 \times 10^{20} \text{ cm}^{-3}$.²⁵ When heating the sample, the O^- stored in the bulk of C12A7- O^- can be emitted into the gas phase and formed the gaseous O^- flux, and the emission current density (i.e., beam intensity) strongly depends on the surface temperature of the C12A7- O^- .²⁴ Generally, the surface temperature is set up ranging from 600 to 800°C, depending on the beam intensity required.

In this study, the O^- flux was produced from O^- generator (length: 120 mm, width: 120 mm, thickness: 8 mm) made by Oxy Japan (Japan). The O^- generator is made up of three parts: a C12A7- O^- -coated film ($50 \pm 10 \mu\text{m}$) by using a plasmas-spraying process, a ceramic support, and a Fe–Cr alloy filament heater embedded in ceramic layer (110V/220V, 750W). The purity of O^- emitted from the surface of the O^- generator was more than 95%, which was measured by time-of-flight (TOF) mass spectrometer.²⁴ The emission current of O^- from the O^- generator was detected by a picoammeter (Keithley model 6485, USA). Total O^- current in the gas phase was determined by the emission current density of O^- from the C12A7- O^- material and also the effective emission area in the O^- generator. Typically, the emission current density from the C12A7- O^- material was about 0.75 $\mu\text{A}/\text{cm}^2$ at 750°C.²² To increase total emission area (i.e., to increase the emission amount of O^-), two O^- generators were used simultaneously in this work, giving an O^- current of $220 \pm 18 \mu\text{A}$ when the O^- generator run at an output power of 750 W.

The O^- water was prepared by bubbling of the O^- flux into the deionized water. A self-designed reactor was shown in Figure 1. The system includes three parts: two O^- generators installed in the emission chamber, a carrier gas feeding/controlling section, and the collection system of O^- water. By heating the sample, the O^- flux was emitted from the O^- generators and then bubbled into the deionized water for a given duration. To decrease the loss of O^- flux (e.g., quenched by the tube), the O^- flux was carried by a fast-flowing inert gas (argon) and pumped by a minitype air pump (APN-110kv-1; Iwaki, Japan). The O^- concentration in the O^- water mainly depends on the O^- current emitted from the O^- generator, the volume of the deionized water as well as preparation duration. In this work, the O^-

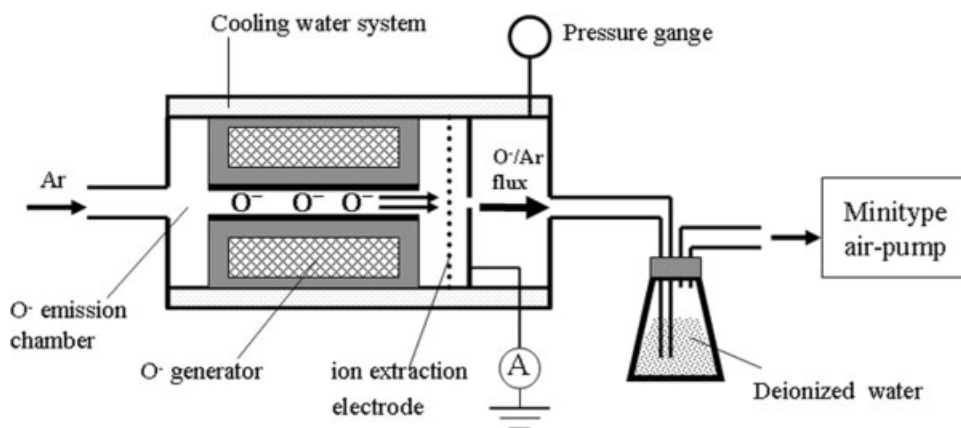


Figure 1 Schematic structure of O^- water generating system.

generators worked at 750°C and the output power was 750 W (total O^- current of two O^- generators: $220 \pm 18 \mu\text{A}$). The flow rate of inert gas was 5 L/min. The O^- flux was bubbling into deionized water (50 mL) for 2 h. It is also possible to use one generator if we change the preparation conditions such as the O^- current, the solution volume, and/or preparation duration.

The O^- concentration in the O^- water was measured by electron paramagnetic resonance (EPR) spectroscopy. Besides, a little amount of H_2O_2 was also generated in the O^- water, which was measured by an UV spectrometer. In this work, the O^- water, containing O^- of $0.03 \pm 0.01 \text{ mM}$ and H_2O_2 of $0.2 \pm 0.1 \text{ mM}$, was used for the surface modification of all PVC films.

Preparation of PVC film

Medical PVC film (50 μm thickness, made by CaoYang Medical Device Company, Shanghai) was cut into pieces of dimensions 10 mm \times 10 mm. Before the experiment, the film was washed thrice with deionized water in an ultrasonic bath and dried naturally at room temperature.⁵

O^- water treatment

The cleaned PVC films were placed in a quartz tube with stopper (200 mm in length, 25 mm in inside diameter) containing 50-mL new-made O^- water (typically, O^- concentration: $0.03 \pm 0.01 \text{ mM}$; H_2O_2 concentration: $0.2 \pm 0.1 \text{ mM}$) for a given duration at $25.0 \pm 1.0^\circ\text{C}$. After the treatment, the PVC films were rinsed with deionized water immediately.

Surface characterization methods

Contact angle measurement

The surface hydrophilicity of the PVC film was quantified by measuring the water and formamide

contact angles on PVC surface at room temperature with a contact angle meter (JY-82, Chengde, China) by sessile-drop method. Two test liquids, deionized water and formamide, of known polar and dispersion components of surface energies were used for contact angle measurement.³³ To lessen the effect of gravity, the volume of each drop was regulated to about 0.03 mL by a microsyringe. The droplets (the deionized water or the formamide) were dropped at five different sites on each sample, and the values of the contact angles were averaged.

In addition, to clarify the effect of H_2O_2 in the resultant O^- water on PVC hydrophilic modification, the treatment with the diluted H_2O_2 (0.3 mM) was used as a comparison, which was in the same concentration with that in O^- water.

Surface energy measurement

The surface energies of PVC films were estimated by the Young's equation as follows:³³

$$(1 + \cos \theta)\gamma_L = 2\sqrt{\gamma_S^D \gamma_L^D} + 2\sqrt{\gamma_S^P \gamma_L^P} \quad (1)$$

where θ is the measured contact angle of standard liquid on the polymer surface, subscript L represents standard liquids used, S represents solid to be measured, and superscripts D and P represent dispersion and polar component, respectively. According to Young's equation, the surface energy (γ_L) of liquid can be divided into two components: dispersion component (γ_L^D) and polar component (γ_L^P). The known surface energies (γ_L) of deionized water and formamide with their dispersion component (γ_L^D) and polar component (γ_L^P) are shown in Table I.³⁰ The unknown γ_S^D and γ_S^P of PVC film could be estimated by solving the two equations set up for the measured contact angles of deionized water and formamide following eq. (1), and the total surface

TABLE I
Dispersion and Polar Components of Surface Energy of Reference Liquids at 25°C (mN/m)

Liquid	γ_L^P	γ_L^D	γ_L
Deionized water	50.2	22.0	72.2
Formamide	18.6	39.6	58.2

energy γ_S of polymer can be obtained by adding γ_S^P and γ_S^D as given in eq. (2).

$$\gamma_S = \gamma_S^P + \gamma_S^D \quad (2)$$

X-ray photoelectron spectroscopy

The surface elements of PVC films treated with O^- water were analyzed by the X-ray photoelectron spectroscopy (XPS) with the instrument ESCALAB-250, made by Thermoelectron, USA, using a Mg K α as a excitation source. The base pressure in the analytical chamber was 1.0×10^{-9} Torr. The size of the X-ray spot was 1 mm diameter, and the take-off angle of photoelectrons was 90° with respect to the sample surface. All the C_{1s} and O_{1s} curve-fitted components were calibrated and referenced to 284.6 eV for C_xH_y type of carbon. Atomic concentration data were determined using evaluation of relative peak areas. For statistical analysis, these relative peak areas were calculated from five XPS spectra obtained from different locations of each sample.

Atomic force microscope

To examine the surface roughness alteration, the PVC films were detected with an atomic force microscope (AFM, Nanoscope IIIa, Digital Instruments). The AFM images were obtained in a tapping mode, and the root-mean-square (RMS) R_q of the samples was calculated from the data collected on an area of $10 \times 10 \mu\text{m}^2$.³⁴ For statistical analysis, roughness data were calculated as averages of five measurements obtained from each sample.

RESULTS AND DISCUSSION

Effects of O^- water on hydrophilicity and surface energy of PVC

In this work, the O^- water was prepared by bubbling of the O^- flux into the deionized water. To increase the emission amount of O^- , the O^- flux was produced from two O^- generators (total emission area: 288 cm²) that were coated with the O^- storage-emission material of C12A7- O^- .²⁴ Based on the EPR measurements, the O^- concentration in the O^- water was about 0.03 ± 0.01 mM when the O^- water was prepared by bubbling of the O^- flux (the

output power of O^- generator: 750 W, the emission current of O^- : $220 \pm 18 \mu\text{A}$) into the deionized water (50 mL) for 2 h. In addition, it was also found that a small amount of H₂O₂ had been formed, which was analyzed via UV-absorption spectroscopy and calibrated with a standard solution of 0.3 mM H₂O₂. Absolute concentration of H₂O₂ was determined by the absorbance at 206 nm, which was compared with that of the standard diluted H₂O₂. The H₂O₂ concentration in the O^- water was about 0.2 ± 0.1 mM when the O^- water was prepared by bubbling of the O^- flux (the output power of the O^- generator: 750 W, the emission current of O^- : $220 \pm 18 \mu\text{A}$) into the deionized water (50 mL) for 2 h. According to the earlier investigation, the active oxygen species of O^- and H₂O₂ existed in the O^- water. The O^- water, containing O^- of 0.03 ± 0.01 mM and H₂O₂ of 0.2 ± 0.1 mM, was used for the surface modification of all samples in this work. The 0.3 mM H₂O₂ solution was also used as a comparison solution to clarify the effect of H₂O₂ in the resultant O^- water on PVC hydrophilic modification.

Surface hydrophilicity of the PVC films was investigated by the contact angle measurements before

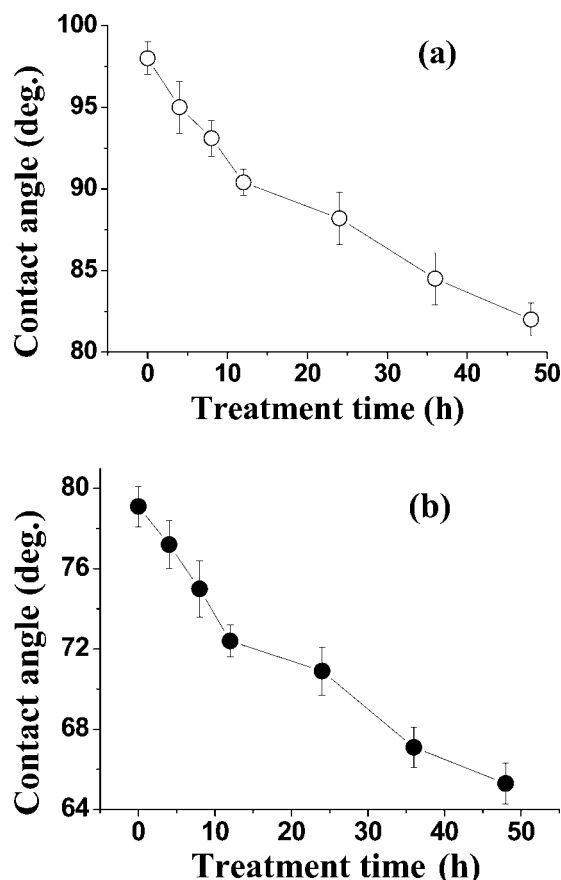


Figure 2 (a) Water contact angles and (b) formamide contact angles of the PVC films treated by the O^- water measured as a function of treatment time.

TABLE II
Contact Angles and Surface Energies of the Original PVC Film, the PVC Film Treated by the O⁻ Water and H₂O₂ Solution for Different Time, Respectively

PVC samples	Time (h)	Contact angle (°)		Surface tension (mN/m)			γ_S^P/γ_S (%)
		Water	Formamide	γ_S^P	γ_S^D	γ_S	
Original		98.0	79.1	1.8	20.8	22.6	8.0
O ⁻ -water treated	4	95.0	77.2	2.8	20.3	23.1	12.1
	8	93.1	75.0	3.1	21.3	24.4	12.7
	12	90.4	72.4	3.9	21.9	25.8	15.1
	24	88.2	70.9	4.8	21.5	26.3	18.3
	36	84.5	67.1	6.0	22.6	28.6	21.0
	48	82.0	65.3	7.2	22.3	29.5	24.4
H ₂ O ₂ treated	48	97.3	78.5	2.0	20.9	22.9	8.7

and after the O⁻ water treatment. The contact angles of PVC were determined by the sessile-drop technique using deionized water and formamide solution. The water contact angles [Fig. 2(a)] and formamide contact angles [Fig. 2(b)] and the surface energies (Table II) of the treated PVC samples were measured as a function of treatment time. For the PVC samples treated via the O⁻ water, the contact angle of the PVC surface monotonously decreased with increasing of the treatment time in present investigated ranges. Both the water contact angle and the formamide contact angle of PVC obviously decreased by 16.0° (from 98.0° to 82.0°) and 13.8° (from 79.1° to 65.3°) for 48-h treatments, respectively, indicating an obvious increase in the hydrophilicity of PVC surface after treatment. Furthermore, it was also found that the contact angle of O⁻-water-treated PVC remained relatively unchanged during the 10-day period of aging (not shown), which indicated that there were no appreciable changes in the modified surface properties of the samples during storage. As treated by the 0.3 mM H₂O₂ solution, no significant variation in the water contact angle and formamide contact angle of the PVC surface was observed for 48-h treatments (Table II), which means that the composition of H₂O₂ in the O⁻ water had neglectable effect on the contact angle alteration of PVC films.

The surface energy (γ_S) and its components [the dispersion force (γ_S^D) and the polar force (γ_S^P)] of PVC were calculated from the contact angles of water and formamide based on eq. (1). Table II sum-

marizes the data of γ_S , γ_S^D , and γ_S^P for the original PVC films and the treated ones via the O⁻ water and 0.3 mM H₂O₂ solution, respectively. As shown in Table II, both the surface energies and polar forces of the medical PVC film remarkably increased after the modification by the O⁻ water treatment. Compared with the untreated sample, the surface energy (γ_S) rose from 22.6 to 29.5 mN/m for the 48 h treatments. It was also noticed that the ratio of γ_S^P/γ_S increased from 8.0% to about 24.4%, which means the improvement of the surface wettability would be mainly caused by the increase of the polar component.^{5,35} To further clarify the O⁻ water effects on the increase of hydrophilicity, we investigated the alterations of surface composition, surface chemical bonds, and surface roughness by the XPS and AFM measurements.

Influences of O⁻ water on surface composition and functional groups of PVC

The varieties in contact angle and surface energy could be due to the formation of hydrophilic functional groups on the PVC surface via the O⁻ water treatment. Therefore, we investigated the surface elements and functional groups of the original and treated PVC films by the XPS measurements.

The quantitative analysis of the variation of the chemical composition was determined by the wide-scan XPS spectra before and after the treatment. Table III shows the relative content (atomic %) of main atomic composition and the ratio of O/C and Cl/C

TABLE III
Atomic Contents (Atomic %) of O, C, and Cl and Atomic Ratio of O/C and Cl/C of the Original PVC Film, the PVC Film Treated by the O⁻ Water for 24 and 48 h, Respectively

Treatment time (h)	C (%)	O (%)	Cl (%)	O/C	Cl/C
0	82.6 ± 0.5	3.1 ± 0.3	11.6 ± 0.4	0.04	0.14
24	80.6 ± 0.7	7.3 ± 0.8	8.0 ± 0.6	0.09	0.10
48	78.7 ± 0.4	10.4 ± 0.7	5.5 ± 0.5	0.13	0.07

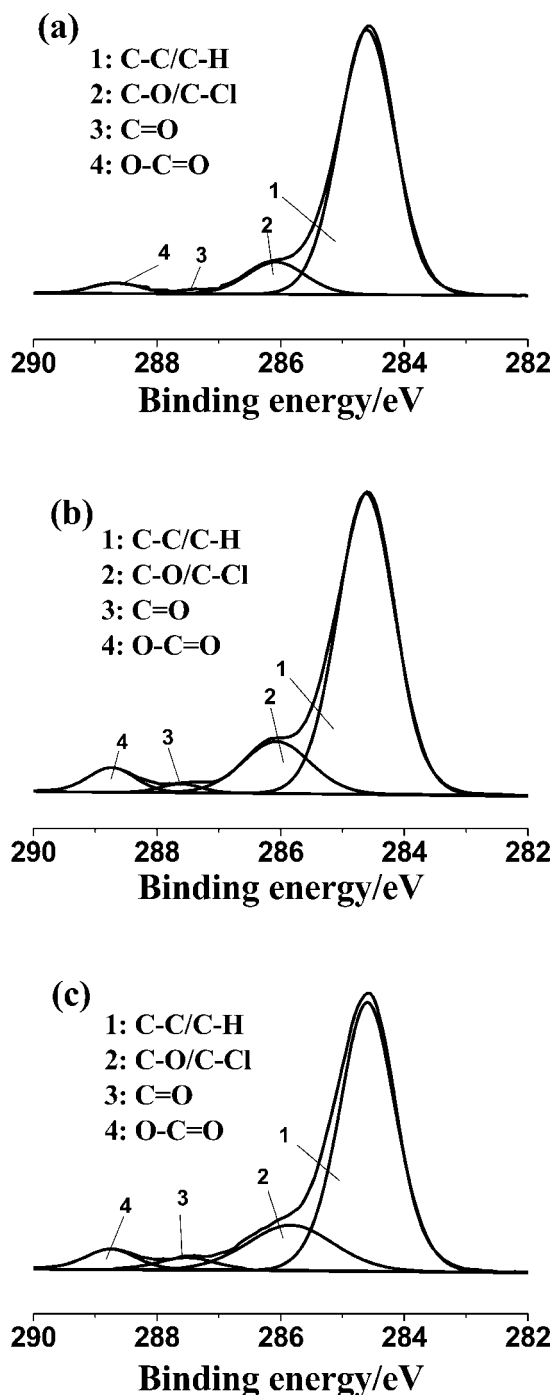


Figure 3 Representative C_{1s} spectra for the PVC surface (a) original, (b) O^- water treated for 24 h, and (c) O^- water treated for 48 h, respectively.

for the PVC films treated with O^- water for different time. The relative content of O atoms measured on the untreated PVC surfaces was 3.1% and changed to 7.3% and 10.4% for 24- and 48-h treatment, respectively. The relative content of Cl atoms, however, dropped from 11.6% to 5.5% for the untreated and 48-h treated surface. For more analysis, the Cl/C ratios were about 0.14, 0.10, and 0.07 for the original, and the 24- and 48-h treated PVC samples, respectively. The O/C ratios, on the other hand, increased from 0.04 to 0.13 after 48-h treatment. It was noticed that a decrease of chlorine content was observed, whereas oxygen content got a remarkable increase for treated PVC surface. It was obvious that the O^- water initiated the dechlorination of the PVC film and introduced the oxygen-containing functional groups. The small amount of oxygen observed on the original PVC surfaces may be due to plasticizers in medical PVC^{5,35} and deposited through atmospheric oxidative degradation during the sample preparation or storage in the oxygen-containing environment.³⁶

Figure 3(a–c) shows the representative C_{1s} XPS spectra (282–290 eV) of the original PVC surfaces, the PVC treated by the O^- water for 24 and 48 h, respectively. As can be seen from Figure 3(a), the C_{1s} peak for the original PVC films was decomposed into four components: C–C/C–H at ~ 284.6 eV, C–O/C–Cl at ~ 286.1 eV, a small C=O bond at ~ 287.6 eV and O–C=O groups at ~ 288.8 eV, respectively.^{5,6,35} Figure 3(b,c) displays the C_{1s} core-level spectra for the O^- -water-treated PVC films, which were different from those of the original ones. A longer trail from 286 to 290 eV was added into the strong band of 284.6 eV, indicating an obvious increase of the C–O, O–C=O and C=O intensity with increasing the treatment duration. Table IV summarized the relative content (given as area percentages) of various functional groups before and after treatment, which were the average results of five XPS spectra obtained from different locations of each sample. For the C_{1s} components, the data in Table IV stands for the ratio of a given functional group to all functional groups containing in the C_{1s} peak. The relative contents of the C–O bond, C=O bond, and O–C=O bond on the O^- -water-treated PVC films increased with the increase of treatment time. Additionally, the content of the C–H bond decreased af-

TABLE IV
Relative Intensity (Area Percentages) of Various Functional Groups (Chemical Bonds) of the Original PVC Film, the PVC Film Treated by the O^- water for 24 and 48 h, respectively

Treatment time (h)	C_{1s} components (%)				O_{1s} components (%)		
	C–C/C–H	C–O/C–Cl	C=O	O–C=O	C=O	C–O	O=C–O
0	84.8 \pm 0.6	12.6 \pm 0.4	0.5 \pm 0.1	2.1 \pm 0.4	10.8 \pm 0.5	53.7 \pm 0.4	35.5 \pm 0.6
24	77.3 \pm 0.7	15.9 \pm 0.8	2.2 \pm 0.4	4.6 \pm 0.5	17.9 \pm 0.6	43.1 \pm 0.8	39.0 \pm 0.5
48	73.9 \pm 0.7	16.6 \pm 0.9	3.7 \pm 0.3	5.8 \pm 0.8	20.1 \pm 0.7	42.4 \pm 0.7	37.5 \pm 0.9

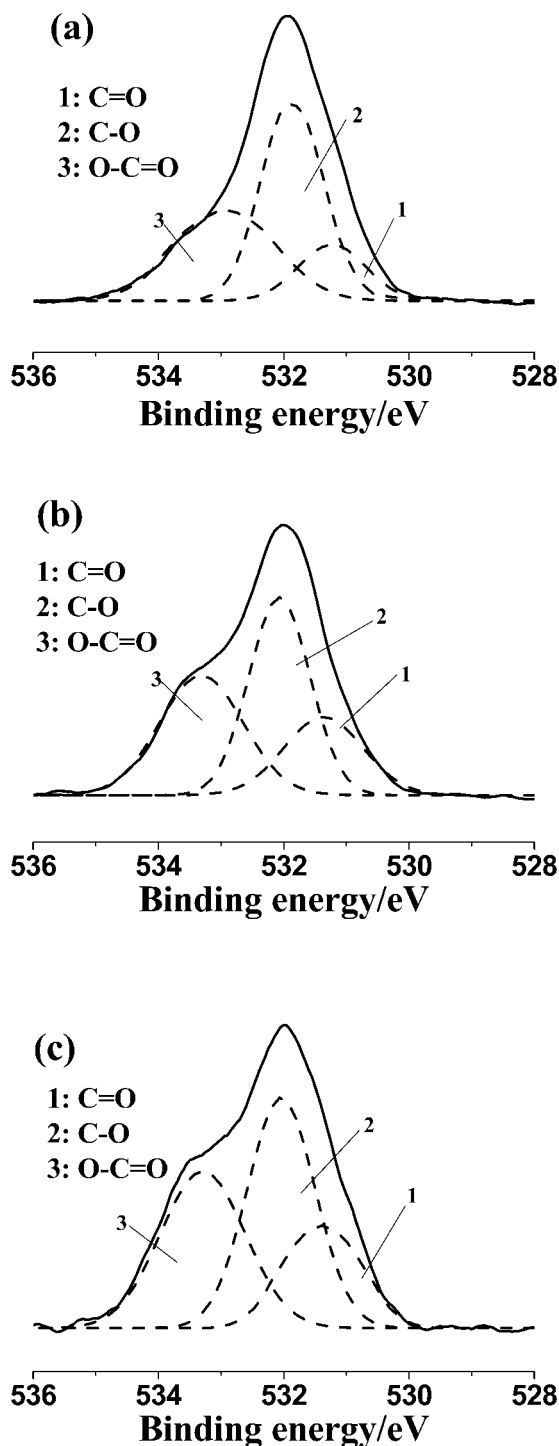


Figure 4 Representative O_{1s} spectra for the PVC surface (a) original, (b) O⁻ water treated for 24 h, and (c) O⁻ water treated for 48 h, respectively.

ter the O⁻ water treatment. The above results clearly showed that the functional groups such as the C—O, C=O, and O—C=O were introduced onto the PVC film surfaces via the O⁻ water treatment.

Figure 4(a–c) displays the representative O_{1s} XPS spectra (528–536 eV) of the original PVC films and the PVC films treated via the O⁻ water for 24 and

48 h, respectively. All O_{1s} XPS spectra can be deconvoluted into three components: C=O at ~ 531.5 eV, C—O at ~ 532.1 eV, and O—C=O at ~ 533.2 eV.^{6,37} The relative contents (area percentages) of O_{1s} components are, also shown in Table IV, represented by the ratio of a given functional group to all functional groups containing in the O_{1s} peak. The O_{1s} results further confirmed that the oxygen-containing functional groups (C=O and O—C=O, etc.) were introduced onto the PVC film surfaces after the O⁻ water treatment, which is corresponding with the C_{1s} analysis mentioned earlier.

Influences of O⁻ water on surface roughness and morphological alterations of PVC

The influence of the O⁻ water on the surface roughness of the PVC films as well as morphological alterations was investigated by the AFM measurements. The measured area was 10 × 10 μm² for all AFM images. Figure 5(a–d) presents typical AFM images from the original PVC surface and the treated ones by the O⁻ water for 12, 24, and 48 h, respectively. The original PVC surface shows relative smoothness [Fig. 5(a)], whereas the surfaces of the O⁻-water-treated PVC films became relative roughness [(Fig. 5(b–d)]. Table V shows the root-mean-square (RMS) R_q in each case, which was calculated from the corresponding AFM profile data.³⁴ The R_q of the original PVC surface was about 158.8 nm. However, after treated with the O⁻ water for 48 h, the R_q value increased to 286.9 nm. Besides, the surface roughness, R_q , appeared approximately linear increase with increasing the treatment time within our investigated range. The AFM results indicated that the PVC surfaces became rougher after the O⁻ water treatment. The morphological alterations of the treated PVC surfaces might arise from reactions between the active oxygen species and the PVC constitutes followed by the surface etching of polymer during the O⁻ water treatment.

Present results showed that the O⁻ water treatment caused an obvious decrease of contact angle and an increase of surface energy of the PVC film, indicating an increase of the surface hydrophilicity after the treatment. The reasons for the alteration of contact angle and surface energy via the O⁻ water treatments may be very complex including the formation of hydrophilic functional groups and change of surface roughness. Based on the AFM observations, the surface roughness increased for the treated PVC surfaces, acting toward the increase of contact angle as well as reducing surface wettability.³⁸ On the other hand, it was found that the hydrophilic groups (e.g., C=O, O—C=O) were introduced onto the treated surfaces. These hydrophilic groups would enhance the hydrophilicity of PVC. The appa-

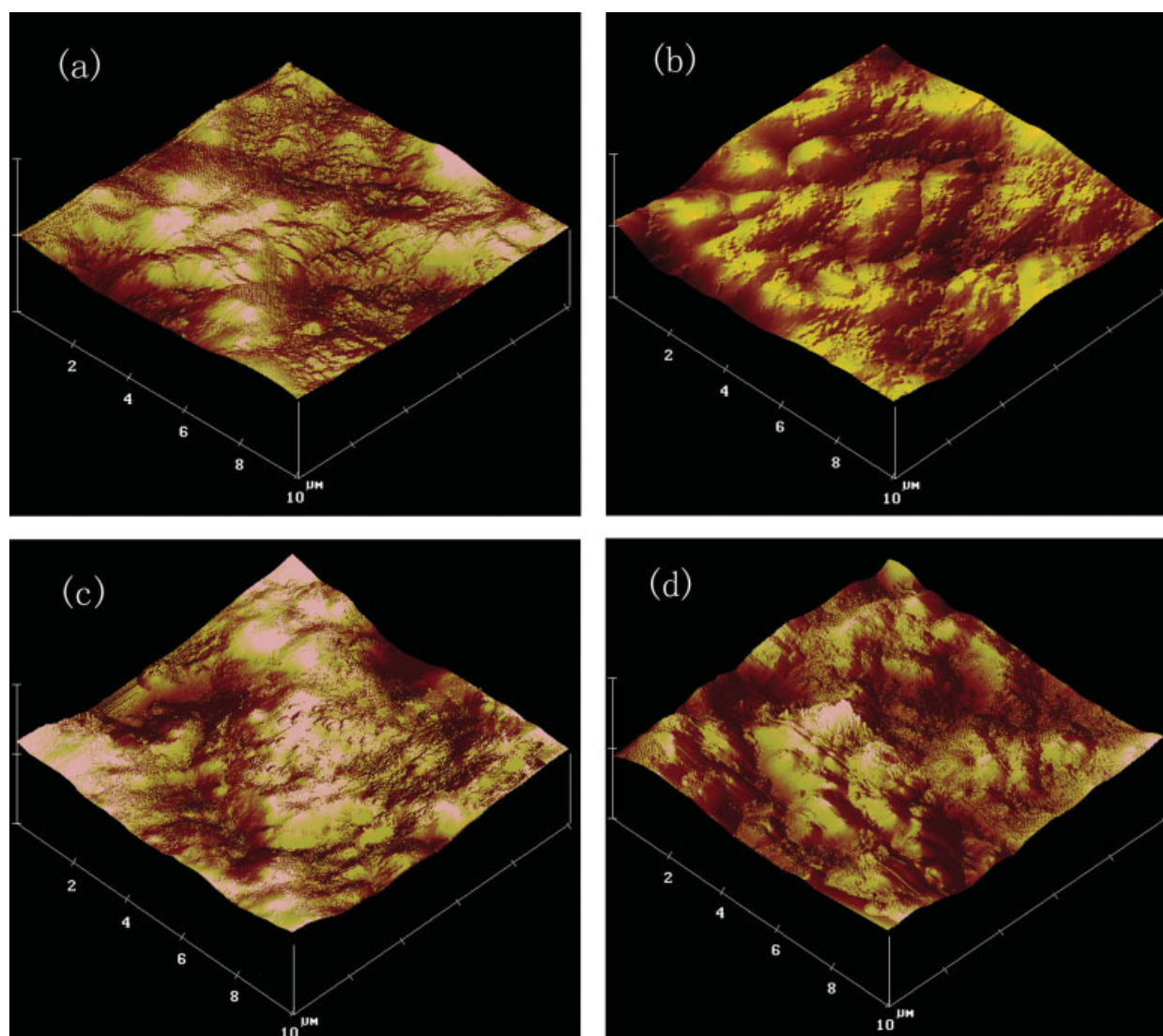


Figure 5 Representative AFM images of the PVC films (a) original, (b) O^- water treated for 12 h, (c) O^- water treated for 24 h, and (d) O^- water treated for 48 h, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rent change of the hydrophilicity after the O^- water treatment may be mainly caused by two factors mentioned earlier. The introduction of hydrophilic groups, most likely, is the dominating factor to account for the reduction of the contact angle and the increase of the hydrophilicity observed.

It is well known that O^- is high reactive radical in the anion chemistry.¹⁷ O^- has strong oxidation power, particularly in low-temperature oxidation of

hydrocarbons.^{17,18} O^- can dissolve in the deionized water by aerating the O^- flux, as observed by the EPR measurements. Part of the O^- anions dissolved in water may react with H_2O and O_2 , producing other active oxygen species such as $\cdot OH$ and $\cdot OH_2$.^{32,39,40} In our previous study, it was found that O^- could decompose and oxidize hydrocarbons via the hydrogen abstraction reaction on the C12A7- O^- surface.¹⁸ The PVC contains hydrogen atoms and

TABLE V
Variations of Surface Roughness (R_q) of the Original PVC Film, the PVC Film Treated by the O^- Water for 12, 24, and 48 h, Respectively

	Original	O^- -water treated (h)		
		12	24	48
R_q (nm)	158.8 ± 20.3	197.1 ± 27.5	232.2 ± 31.4	286.9 ± 35.2

chlorine atoms, consisting of numerous repeated linked units of $[-CH_2-CHCl-]_n$. Present investigation shows that the hydrophilic (C—O, C=O, etc.) groups can be introduced onto the PVC surfaces, whereas some of the Cl atoms are removed. The generation of the oxygen-containing groups may be due to postreactions of carbon radicals with active oxygen species in O^- water. Carbon radicals are formed by means of bond scission of C—C and C—Cl bonds and the abstraction reaction of Cl atoms and H atoms from the PVC surfaces by the reactions of the active species in the O^- water (e.g., O^-).⁵

In general, the active oxygen species (e.g., O^-) might react with the molecules on the PVC surfaces and/or decompose constitutes to produce hydrophilic compounds. Accordingly, the hydrophilic groups formed by the reactions between the active oxygen species and PVC surfaces were added to the polymer surfaces. Thus, introduction of hydrophilic (C—O, C=O, O—C=O) groups by the O^- water treatments is most likely to account for the reduction of the contact angle and the increase of hydrophilicity of PVC surface.

CONCLUSION

This work presents a novel approach to increase surface wettability of medical PVC film via the O^- water treatment, which may be useful in biological and medical applications. The O^- water treatment caused an obvious decrease of contact angles and increase of surface energies, leading to a rise in the hydrophilicity. The water and formamide contact angles on treated PVC surface gradually decreased by 16.0° and 13.8° for 48-h treatment, and the surface energy increased from 22.6 to 29.5 mN/m for 48-h treatment, respectively. The surface roughness increased from 158.8 to 286.9 nm for 48-h treatment via the AFM investigation. The O^- water treatment also resulted in a remarkable increase of the oxygen content on the treated PVC surface from 3.1 to 10.4% for 48 h. Simultaneously, the O^- water treatment also initiated the dechlorination of the surfaces, introducing oxygen-containing functional groups of C—O, C=O, and O—C=O, which were most likely to account for the increase of surface hydrophilicity. The active oxygen species in O^- water would play an important role in the modification processes.

In addition, the O^- water would be considered as a "clean solution" without adding any toxic chemicals or infectants. It is environmental friendly and easy to be handled at room temperature. Present approach, potentially, may be applied to the surface modification of polymers and other heat-sensitive materials. Comparing with some known modification methods (e.g., plasma and UV treatments), however, the modification efficiency for PVC (evaluated

by the alteration of contact angle per minute) by present O^- water was still low, which would be attributed to lower concentration of active species in the O^- water. It needs to further increase the concentration of active species by modifying the O^- generator as well as the preparation procedure of the O^- water in future.

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