

IMPROVEMENT IN LEATHER SURFACE HYDROPHOBICITY THROUGH LOW-PRESSURE COLD PLASMA POLYMERIZATION

by

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ABSTRACT

Vinyltriethoxysilane (VTES) was polymerized and deposited on the surface of upholstery crust leather by using low-pressure cold plasma technology. After plasma treatment (50 W, 300 s), the initial water contact angle of the leather surface increased from 120° to 140°, showing a significantly improved hydrophobicity of leather surface. The increased hydrophobicity of leather surface could remain even the leathers were stored for 240 d. The surface morphologies of leather were characterized by Scanning Probe Microscope (SPM) and Scanning Electron Microscope (SEM). Unlike the fiber-like texture of untreated leather, a coating of VTES polymer on the plasma treated leather surface was observed by SPM. SEM and SPM images indicated that this coating film was on the surface of collagen fibers rather than the whole surface of leather, which would not reduce permeability of air and water vapor of the leather. Energy Dispersive X-ray Spectroscopy (EDS) was performed to determine the chemical composition of leather surface. The contents of Si and O increased remarkably as leather surface was covered with polymerized VTES. The X-ray Photoelectron Spectroscopy (XPS) showed that the peaks attributed to C=C bonds of VTES and C=O bonds of collagen disappeared after plasma polymerization. All these results demonstrated that VTES was polymerized and deposited on the surface of collagen fibers after plasma treatment, which resulted in a hydrophobic surface of leather.

INTRODUCTION

Manufacture of water resistant leather has attracted dramatically attention in recent years as the increasing demand for waterproof upper, upholstery and garment leathers. Until now, there are two ways to achieve water resistance of leather. One is to perform retanning or fatliquoring with waterproof agents, so that the collagen fibers of leather are wrapped up with the water repellent agents.¹⁻⁵ The other one is the use of waterproof finishing agents, so that a hydrophobic coating is formed on leather surface.⁶⁻¹² In general, the water resistant leather was prepared by using the low surface free energy chemicals that cover the surface.^{13, 14} These chemicals are commonly polymers containing silicon, fluorine or long chain hydrocarbon.^{1,4,5,15} However, the permeability of air and water vapor of the waterproof leather prepared by traditional approaches was greatly reduced.^{15, 16} Therefore, the development of new methods for the production of waterproof leather with reserved natural characteristics is still a challenge.

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Plasma polymerization is an advanced technology in modification of surface characteristics of materials by depositing a thin polymer coating. Based on this technology, some special performances, such as hydrophobicity or hydrophilicity of surfaces, were obtained.¹⁷⁻²⁰ Generally, the monomers are vaporized and introduced directly into the reactor chamber to perform plasma polymerization. Then polymers are deposited on the surface.^{21, 22} This surface modification using plasma is regarded as an environmental friendly (without any solvents or other agents except monomer) and effective (completing reaction in seconds) method that doesn't produce considerable change of whole properties of material. Therefore, the plasma surface treatment technology are widely used for the surface improvement of natural and synthetic fibers,²³⁻²⁵ textiles and substrates.^{26, 27} In this study, plasma technology was conducted on the surface of leather for the purpose of improving its hydrophobicity. Vinyltriethoxysilane (VTES) was used as the monomer due to its good reactivity and film forming property of its polymer.^{21, 28, 29} The hydrophobicity of the plasma treated leather was evaluated by measuring water contact angle of leather surface. The changes of surface morphology before and after plasma treatment were observed by Scanning Probe Microscope (SPM) and Scanning Electron Microscope (SEM). Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) were used for analyzing the elemental composition and states of leather surface.

EXPERIMENTAL

Materials

Upholstery crust leather was supplied by Ruixing Leather Co., Ltd. (Haining, China). It was cut into 5 cm×5 cm pieces, and dried at 45~50 °C for 2h to remove free water. Vinyltriethoxysilane (VTES, Figure 1), the monomer used for plasma polymerization, was purchased from Chengdu Kelon Chemical Co., Ltd.

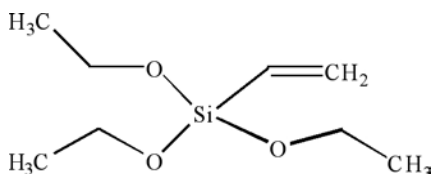


Figure 1. Vinyltriethoxysilane (VTES).

Low-pressure Cold Plasma Treatment

The low-pressure cold plasma treatment of leather samples was carried out in a low-pressure cold plasma reactor (DT-02S, Suzhou OPS Plasma Technology Co., Ltd., China). The schematic diagram is shown in Figure 2. Leather samples were put in the plasma chamber, and the vapor of VTES was directly introduced into the plasma chamber from the monomer vaporizing chamber under 30 Pa and 25 °C. The plasma chamber was first flushed with VTES vapor for 25 min to exhaust the air and fill with the monomer. Then plasma

was generated by discharge of quadrate alloy electrodes (25 cm × 25 cm), and polymerization of VTES was performed. The frequency of the generator was 13.56 MHz RF with the power range from 0 to 300 W. The effects of power and duration of treatment on the water contact angle of leather samples were investigated. The power included 50, 100, 150 and 250 W. The duration of plasma polymerization included 30, 60, 120 and 300 s. Furthermore, the effect of leather aging (1~240 d) on the initial water contact angle (water contact angle at 3 s) of the samples was investigated. It should be noted that the untreated and VTES sprayed (spraying VTES on the surface directly) leather samples were prepared for comparison.

Measurement of Contact Angle and Calculation of Surface Free Energy

In order to evaluate the hydrophobicity of the leather samples, water contact angle of sample surface was measured at room temperature by sessile drop method using a Contact Angle System (OCA20/6, Dataphysics, Germany). A droplet of deionized water (6 μl) was dripped onto the surface of the leather sample by using a syringe. The water contact angles were measured for 120 s with an interval of 3 s. The values of five different places on the sample were recorded to calculate the average contact angle.

Based on the measurements of contact angles of water and formyl amide, surface free energy of the samples was calculated by using the Young's equation shown as below:³⁰

$$(1 + \cos\theta_1)\gamma_{L1} = 2\sqrt{\gamma_{L1}^d \gamma^d} \sqrt{\gamma_{L1}^p \gamma^p} \quad (1)$$

$$(1 + \cos\theta_2)\gamma_{L2} = 2\sqrt{\gamma_{L2}^d \gamma^d} \sqrt{\gamma_{L2}^p \gamma^p} \quad (2)$$

$$\gamma = \gamma^d + \gamma^p \quad (3)$$

where γ is surface free energy of the sample; γ^d is surface free energy of dispersive component; γ^p is surface free energy of polar component; θ_1 is the contact angle of water at 2 s; θ_2 is the contact angle of formyl amide at 2 s; For water, $\gamma_{L1} = 72.8$ mJ/m², $\gamma_{L1}^d = 22.1$ mJ/m², $\gamma_{L1}^p = 50.7$ mJ/m²; For formyl amide, $\gamma_{L2} = 58.0$ mJ/m², $\gamma_{L2}^d = 39.0$ mJ/m², $\gamma_{L2}^p = 19.0$ mJ/m².³¹

Characterization of Leather Surface

The surface morphologies of the untreated, VTES sprayed and plasma treated (50 W, 300 s) leather samples were observed by Scanning Probe Microscope (SPM, SPM-9600, Shimadzu, Japan) in tapping mode and Scanning Electron Microscope (SEM, JSM-7500F, JEOL, Japan). The surface elemental analysis was performed by Energy Dispersive X-ray Spectroscopy (EDS, INCA X-MAX 50, Oxford Instruments, UK). The changes of chemical states of C1s on the sample surface before and after plasma polymerization were characterized by X-ray Photoelectron Spectroscopy (XPS, XSAM-800, Kratos, U.K.).

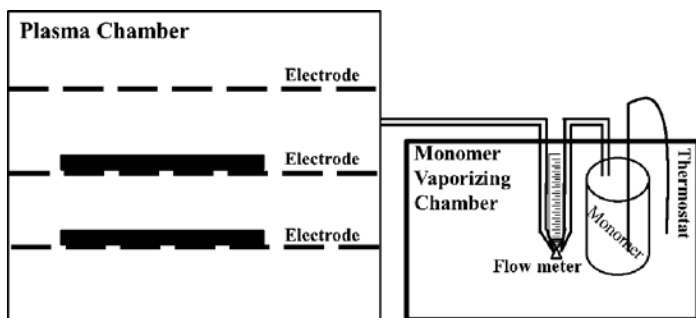


Figure 2. Low-pressure cold plasma reactor.

RESULT AND DISCUSSION

Water Contact Angle and Surface Free Energy

To evaluate the hydrophobicity of the leather surface treated by low-pressure cold plasma, the water contact angle of leather surface was measured and recorded for 120 s, and the surface free energy was also calculated. Figure 3 shows the effects of treatment time and power on water contact angle. The states of the water droplet on the leather surface are also shown in Figure 4. We can see from Figure 3 that the contact angles of plasma treated samples are higher than those of untreated and VTES sprayed samples in the duration of observation. The

wetting of the leather surface was observed at 120 s for the untreated and VTES sprayed samples (Figure 4 (a) and 4 (b)), where the contact angles were decreased to 50° ~ 60° (Figure 3). After plasma treatment, however, the contact angles at 120 s were all higher than those of untreated and VTES sprayed samples, some of which remained over 120° (Figure 3). The state of the droplet even remained unchanged for 120 s under the treatment condition of 50 W and 300 s (Figure 4 (c)). Moreover, its surface free energy is only 6.76 mJ/m² through calculation, which is much lower than that of untreated one (51.78 mJ/m²). These results indicated that the surface hydrophobicity of leather was remarkably enhanced by plasma treatment. This should be due to the formation of a film of silicon-containing polymer with low surface free energy by plasma polymerization. Table I shows the effect of aging of the leather samples on the initial water contact angles. It was found that the initial water contact angles of the treated samples were not influenced by aging, suggesting that the plasma treated leather could keep its hydrophobicity even after aging for 240 d.

In addition, the conditions of plasma treatment were optimized with respect to treatment duration and power. Figure 3 and Table I show that the initial contact angle of water on leather sample treated under 50 W for 300 s was the highest (more

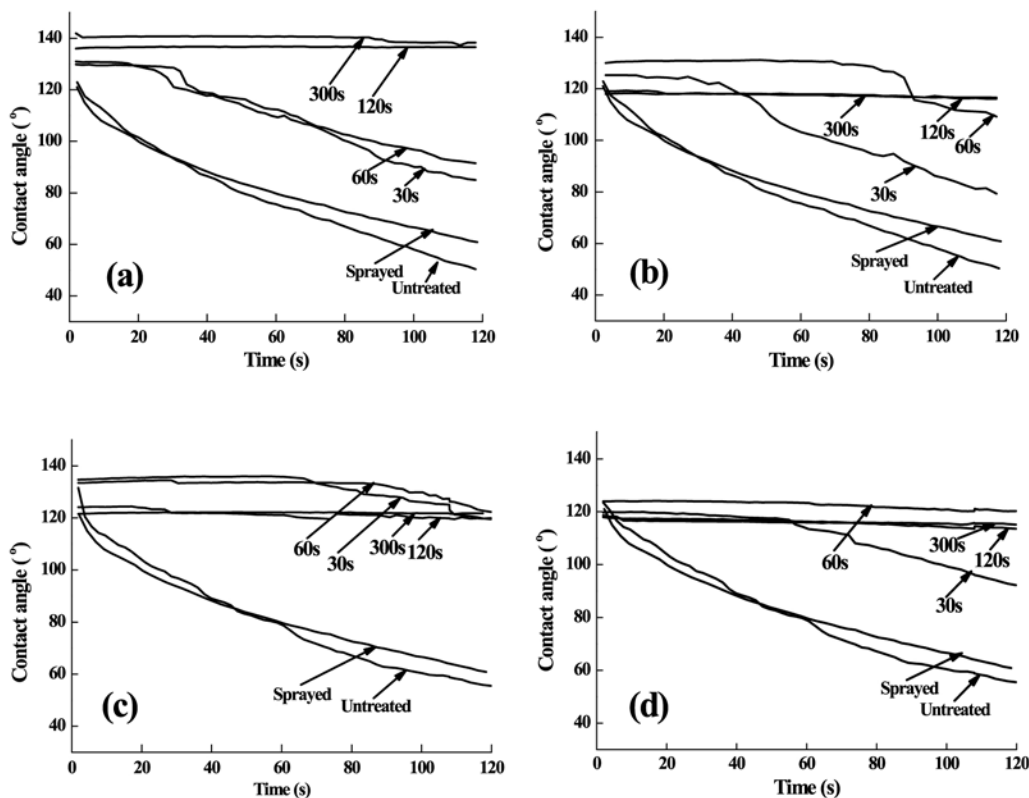


Figure 3. Effects of treatment duration and power on water contact angle: (a) 50 W; (b) 100 W; (c) 150 W; (d) 250 W.

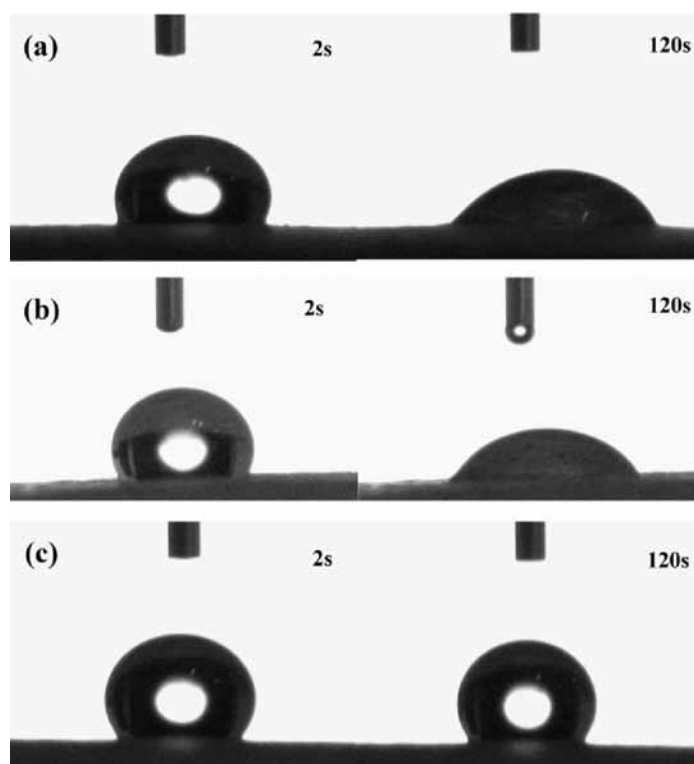


Figure 4. States of a water droplet on the leather surface: (a) untreated sample; (b) VTES sprayed sample; (c) sample treated under 50 W for 300s.

than 140°), and it kept constant even the treated leather sample was aged for 240 d. As power and plasma treatment time increased, the surface hydrophobicity did not increase in terms of contact angle. This result suggests that polymerization of VTES under moderate conditions (50 W, 300 s) may form a suitable film so as to achieve optimal hydrophobicity.

Characterization of Leather Surface

SPM Analysis

The surface morphologies of untreated, VTES sprayed and plasma treated leather samples were analyzed by SPM. Collagen fibers were observed from the untreated sample, as well as the VTES sprayed one (Figure 5 (a) and 5 (b)). These facts suggest that the VTES may penetrate into the leather, or adhere to the surface of collagen fibers, but would not form a coating at the surface of leather. However, after plasma treatment, a coating was formed on the leather surface, and the collagen fibers were fully covered. This phenomenon demonstrates that VTES had been polymerized under low-pressure cold plasma, and the polymer was then deposited on the surface of collagen fiber as a coating, which resulted in the increase of hydrophobicity of leather surface. It should be noted that the coating film was discontinuous, as shown in Figure 5 (c), which implies the leather surface was not completely covered by polymers. This fact suggests that the air and water vapor permeabilities may be greatly reserved

TABLE I
Effect of leather aging on initial water contact angle on leather surface.

Sample	Initial water contact angle (°)			
	Aging for 1 d	Aging for 30 d	Aging for 60 d	Aging for 240 d
Untreated	122.9±3.9	123.5±1.2	124.4±2.3	123.7±1.5
VTES sprayed	121.1±0.9	120.8±1.7	120.2±2.5	122.3±2.2
Plasma treated (50 W, 30 s)	131.0±2.8	133.9±1.6	134.9±1.2	136.7±1.5
Plasma treated (50 W, 60 s)	129.8±1.5	128.1±0.5	127.4±0.7	129.7±0.6
Plasma treated (50 W, 120 s)	136.0±0.1	134.0±0.7	135.3±0.6	135.7±0.5
Plasma treated (50 W, 300 s)	141.9±0.7	138.5±1.3	137.9±0.8	139.4±0.3
Plasma treated (100 W, 30 s)	125.3±2.0	125.2±1.8	125.4±1.0	128.6±2.7
Plasma treated (100 W, 60 s)	130.1±0	131.3±1.9	130.7±2.8	132.3±1.7
Plasma treated (100 W, 120 s)	119.0±0.3	120.3±1.0	118.3±1.0	119.7±3.4
Plasma treated (100 W, 300 s)	118.0±1.3	119.3±0.9	119.4±1.5	121.5±1.0

compared with traditional leather finishing. The mechanism of the polymerization reaction should be that the carbon-carbon double bonds of VTES are broken into free radicals under plasma, and then the free radicals might initiate polymerization reaction. On the other hand, the carbon-oxygen free radicals might generate due to the cleavage of collagen carbonyl (C=O), which leads to the graft polymerization of VTES onto the leather surface.

SEM Analysis

Figure 6 shows the SEM images of the untreated, VTES sprayed and plasma treated leather samples. The surface morphologies of untreated leather and plasma treated leather present few difference at magnification of $\times 500$ and $\times 1000$ (Figure 6 (a) and 6 (c)). The pores are clearly visible on the surface, suggesting that the coating formed by plasma polymerization is very thin and would retain good air and water vapor permeabilities. By contrast, the VTES sprayed leather surface is flat without any pores (Figure 6 (b)), probably because VTES monomer adheres to the leather surface and block the pores.

EDS Analysis

The chemical composition of leather surface was analyzed by EDS. The result is shown in Table II. As expected, the main elements of the untreated leather were C, O and N. After spraying VTES and plasma treatment, additional amounts of Si and O were detected due to the introduction of VTES. As leather surface was covered by VTES monomer or polymer, the percentage of N reduced significantly.

XPS Analysis

The chemical states of C1s on the leather surface were identified by XPS analysis. In Figure 7 (a), the C1s spectrum of untreated leather is resolved into three peaks. The peaks at 284.8 eV, 285.8 eV and 288.4 eV represent C-C/C-H, C-N/C-O and C=O bonds corresponding to the peptide links and functional groups of collagen.^{18,32} As for VTES sprayed sample (Figure 7(b)), a new peak at 284.6 eV attributed to C=C bonds is found, which indicates the existence of VTES monomer on leather surface. The VTES monomer is unlikely to form film on collagen fiber, as shown in Figure 5 (b), so the three peaks attributed to collagen are still remarkably resolved. After plasma treatment (Figure 7 (c)), the peaks at 284.8 eV and

TABLE II
Surface elements of (a) untreated, (b) VTES sprayed and (c) plasma treated leather samples.

Sample	Weight percentage (%)			
	C	O	N	Si
Untreated	60.31	28.6	11.02	0.07
VTES sprayed	59.83	33.74	6.23	0.20
Plasma treated	59.87	33.38	6.48	0.27

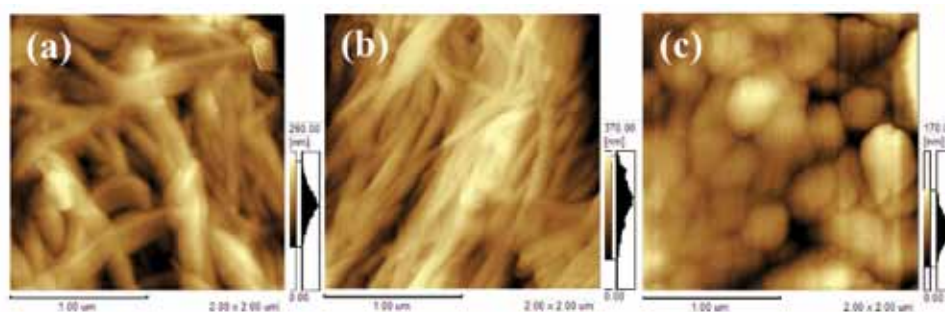


Figure 5. SPM images of the surfaces of (a) untreated, (b) VTES sprayed and (c) plasma treated leather samples.

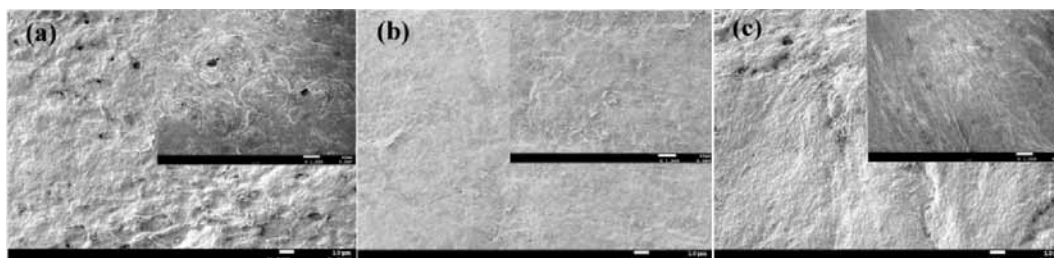


Figure 6. SEM images of the surfaces of (a) untreated, (b) VTES sprayed and (c) plasma treated leather samples.

285.8 eV may be generated by collagen and/or VTES polymer deposited on leather surface since they both contain C-C/C-H and C-O bonds. But the peak at 288.4 eV (C=O) was disappeared, which implies that the carbonyl (C=O) in collagen might be cleaved and participate in grafting polymerization. It should be noted that the peak of C=C bonds of VTES cannot be detected. This fact means that VTES has been polymerized under induction of plasma. However, through XPS analysis, it is still not sure that VTES polymer has been grafted onto collagen. Therefore, much work about the mechanism of polymerization and deposition induced by plasma should be undertaken in the future.

CONCLUSIONS

The leather with enhanced hydrophobic surface was prepared by employing low-pressure cold plasma polymerization using vinyltriethoxysilane (VTES) as monomer. In this technology, a thin polymer coating film was formed on the surface of collagen fibers, which resulted in a higher water contact angle and lower surface free energy than the untreated leather. Unlike the coating in conventional finishing, this coating film was located at the surface of collagen fibers rather than the whole surface of leather. Therefore, the air and water vapor permeabilities and comfort ability of real leather would be greatly reserved. In summary, low-pressure cold plasma polymerization on leather surface is an environmentally friendly and easy-operation technology compared with traditional surface finishing process. This method might be quite useful in making waterproof leather.

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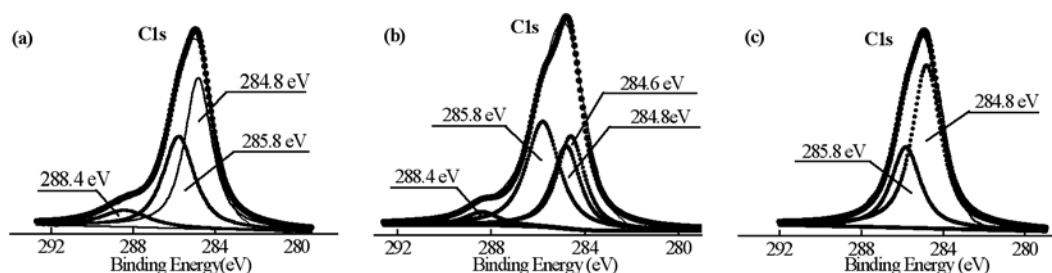


Figure 7. C1s spectra of (a) untreated, (b) VTES sprayed and (c) plasma treated leather samples.

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