

The Mechanism of Air/Oxygen/Helium Atmospheric Plasma Action on PVA

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ABSTRACT: The effect of the air/oxygen/helium atmospheric plasma treatment on desizing polyvinyl alcohol (PVA) on cotton fabric was discussed as compared with the conventional H₂O₂ desizing. The possible change mechanism of PVA during atmospheric plasma exposure was induced through a combination of weight loss of PVA after

plasma, PVA dissolving rate in water at room temperature, X-ray photoelectron spectroscopy, and Fourier Transform infrared spectroscopy. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2233–2237, 2006

Key words: plasma; surfaces; XPS; PVA; desizing

INTRODUCTION

Plasma, a partially ionized gas composed of ions, electrons, and neutral gas molecules, can be produced thermally at very high temperatures or by the action of strong electric or magnetic fields. The applications of plasma treatment in textiles have been widely investigated, with a focus on improving several properties such as wettability, water repellency, soiling, soil release, printing, dyeing, and finishing processes.^{1–6}

Plasma treatments in textiles were generally carried out under low pressure (high vacuum). However, low-pressure plasma treatment for textiles is likely to be a batch process, which is time and energy consuming and therefore may not be economically feasible for many applications. Therefore, atmospheric plasma treatment has been introduced to overcome these drawbacks of low-pressure plasma treatment. It can treat materials continuously with higher activated particle density at temperatures lower than 40°C without a vacuum system.

In our previous studies, we have successfully applied atmospheric pressure plasmas to desizing polyvinyl alcohol (PVA) on cotton and rayon fabrics.^{7–9} However, detailed information about removing of sizes by plasma, especially atmospheric plasma treat-

ment is not available. PVA is a synthetic polymer and was first commercialized in 1939. It was first used as a textile warp size in the mid-60s and a large fraction of PVA production has been consumed by the textile industry in warp sizing since then.¹⁰ One reason for the widespread acceptance of PVA as warp sizing is its impressive tensile strength compared with other sizing materials. The high tensile strength of PVA results in a strong film being added to the yarn to ensure good weaving performance.¹¹ However, a major negative aspect of PVA in size formulations is the difficulty of removing the PVA during desizing. Moreover, chemical differences, such as degree of hydrolysis and molecular weight, among various grades of PVA result in performance differences in warp sizing applications and removal of PVA sizes.¹⁰ PVA is unaffected by enzyme systems that are used to degrade and solubilize other sizing agent such as starch. The general procedure for PVA size removal is to wash the fabric in hot water with detergent. PVA-sized fabrics must be subjected to washing with water at temperatures around 88–93°C to effectively remove the size. Even at higher temperatures, it is very difficult to completely remove PVA size without affecting subsequent wet processes such as bleaching and dyeing or printing because PVA gels.

Recently, the applications of atmospheric pressure plasmas in desizing PVA on cotton and rayon fabrics have been investigated.^{7–9} We found that plasma treatments were able to remove some of the PVA on the fabric and increase PVA solubility in cold water resulting in a higher weight loss in cold washing.

This study is designed to investigate the mechanism of atmospheric pressure plasma on PVA size. It was

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conducted through sizing PVA onto the fabric, plasma treatment, and then washing. The effect of the plasma treatments on percent desizing ration (PDR) was investigated. The fiber surface morphology was examined by scanning electron microscope (SEM). PVA dissolving rate was observed as compared with control sample. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) for PVA film were analyzed.

EXPERIMENTAL

Materials

The fabric used was a 100% cotton (bleached for print cloth) supplied by Test Fabrics Inc., Middlesex, New Jersey. The width of the fabric was 114.3 cm with fabric counts of 33/30 (warp/weft)/cm. The PVA used was 98–99% hydrolyzed, ($M_w = 85,000$ – $146,000$) supplied by Aldrich Chemical Company, Milwaukee, Wisconsin. Dispersing agent NB-S was of industry grade, supplied by BASF Company.

Methods and procedures

Cotton sizing

The cotton fabric was two-dipped-two-nipped in a sizing bath containing 9% PVA with a pickup of (100 ± 5)%. The padded sample was dried at 100 – 105°C , then cut into 21.6×27.9 cm². The percent sizing ratio of the sized fabric used throughout the experiment was 8.9%.

Preparation of PVA film

PVA (0.5 g) was put into an aluminum dish (diameter of 6 cm), and 10 mL deionied water was added. The dish was heated to 100°C in a water bath until the PVA was dissolved completely. The dish was then placed in an oven at 75°C for 4 h. A PVA film in the dish was peeled off from the bottom of the dish. The PVA films were later treated with air/oxygen/helium atmospheric plasma He/O₂ gas mixtures for 5 min.

Plasma treatment

The specimens (cotton fabric or PVA film) were conditioned, weighed, and inserted into the plasma chamber once the plasma was stabilized. This device and the conditions of the treatment were described in our previous publication.¹² This capacitively coupled device operates at low frequencies (audible) between 1 and 12 kHz. The voltage across the plates can be up to 7.8 kV rms, and the electrode gap spacing is adjustable. In this study, the frequency was set at 5.0 kHz and the pressure of air/oxygen/helium gas was maintained at 3430 Pa. In the process, the specimen was laid on a frame and then inserted into the plasma

chamber, once the plasma was stabilized. The temperature of the electrons in the plasma was 3.56 eV (1 eV = 11,604 K), and the density of the electrons was $8.03 \times 10^{13} \text{ m}^{-3}$ for all treatments. The treated samples were then conditioned, weighed, and cold washed, and hot washed as described earlier.

Washing

After plasma treatment (or desizing by H₂O₂) and conditioned in desiccator, the cotton samples were subjected to a cold wash and a hot wash. In the cold wash, the fabric was immersed in deionized water at room temperature at 20 : 1 liquor: fabric ratio and stirred for 15 min. The water was decanted and the fabric was rinsed twice with deionized water at 5 : 1 liquor: fabric ratio at room temperature. The hot wash was performed in the same way except that the temperature of water was 75°C .¹³

Percent desizing ratio

PDR of the fabric was calculated as the weight reduction of the desized fabric divided by the total original weight of the size on the fabric. Here, the original weight of the size on the fabric was 8.9% of the fabric weight.

PVA dissolving rate

Here, the PVA dissolving rate was calculated as the dissolved quantity of PVA (on the plasma-treated fabric) in cold water divided by the total original weight of the size on the fabric. Here, the original weight of the size on the fabric was 8.9% of the fabric weight.

XPS analysis

XPS for PVA film from each treatment was carried out on a Perkin–Elmer PHI 5400 XPS spectrophotometer. The X-ray source was Mg. The takeoff angle was 45° . The holding pressure of the XPS chamber was between 10^{-9} and 10^{-10} Torr. Each specimen was scanned five times at pass energy of 35.75 eV, work function of 4.4 eV, and EV/Step of 1 eV. The data acquisition was carried out with a RBD Enterprises Model 147 Controlling System.

FTIR analysis

FTIR of PVA films was measured using Nicolet NEXUS 470 FTIR system.

Microscopy examination

The surface morphology of the cotton fibers in all treatment groups was observed with a HITACHI S-3200N SEM. The specimens were gold sputter-

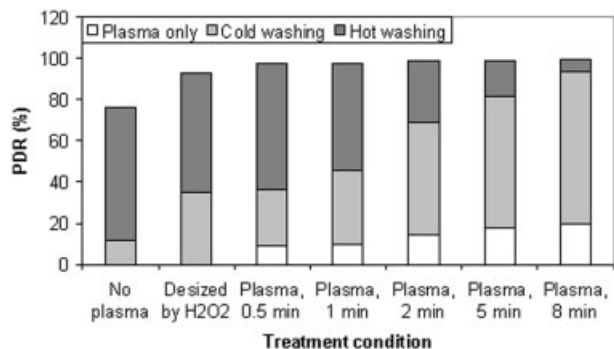


Figure 1 Percent desizing ratio (PDR) vs. treatment (Plasma gas: air/helium).

coated for 150 s with a thickness of ~ 250 Å. Pictures were taken with beam energy of 5.0 keV at 700 \times magnification.

RESULTS AND DISCUSSION

Effect of atmospheric plasma treatment on desizing of PVA

Regardless of the duration of the air/oxygen/helium plasma treatment, the PDR shows a significant increase (Fig. 1). Meanwhile, the PDR after one cold wash was greatly increased compared with both control and H₂O₂ desized samples. After 5 min plasma treatment following only one cold wash, the desizing efficacy nearly equaled that by the traditional H₂O₂ desizing (2 cycles of cold and hot wash), whereas the PDR of the sample treated with 8 min plasma and one cold wash was greater than that by the traditional H₂O₂. SEM observations of specimens treated with various conditions are shown in Figure 2. The 5 min plasma-treated specimen followed by a cold wash was almost as clean as the control (scoured and bleached). Remaining PVA size is evident on the surface of cotton fibers only subjected to cold and hot wash. In addition, small amount of PVA size remained on the specimen desized by H₂O₂. To inspect the effect of atmospheric plasma treatment on the physical properties, the tensile strength and the strain of both the cotton fabric and the yarn before and after plasma treatment were tested. The results exhibited that the atmospheric plasma treatment did not bring negative effect on tensile properties of the fabric.^{8,9}

Atmospheric plasma converting PVA macromolecules to small molecules

From aforementioned discussion, it could be seen that compared with conventional desizing processes, plasma-aided desizing was very effective in desizing PVA on cotton. To inspect the reason of plasma effect on desizing PVA, the relationship between weight loss of PVA film and the plasma exposure time was dis-

cussed. Figure 3 shows 0.939%, 1.36%, and 1.8% of PVA weight loss corresponding to 1, 5, and 10 min plasma exposure time, respectively. This phenomena means atmospheric plasma treatment converted PVA

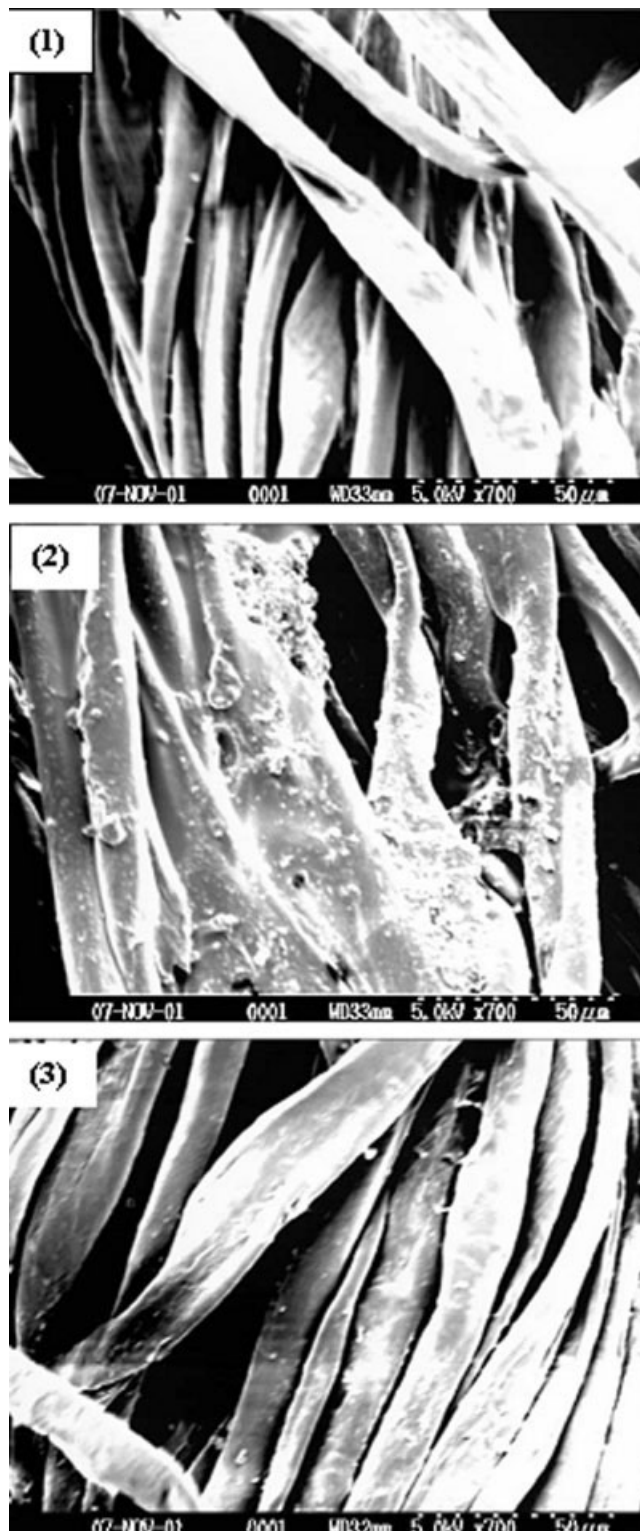


Figure 2 SEM photographs of cotton fibers. (a) control, (b) sized with PVA, (c) cold and hot washing, (d) desized by H₂O₂, cold and hot washing, and (e) 5 min of plasma treatment and cold washing.

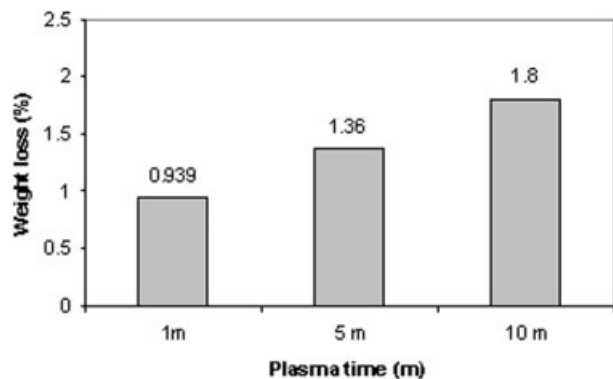


Figure 3 The relationship between weight loss of PVA film and the plasma exposure time.

to some gas, such as H₂O and CO₂, which is left off in the air. Figure 4 indicates the relationship between dissolving rate (at room temperature for 15 min) of PVA on cotton and plasma exposure time. The PVA dissolving degree increased greatly with plasma exposure time extended before 2 min. It still shows significant increase with plasma treatment enhancing during 2–10 min. This means washing could remove PVA size that was not converted into gas products but small molecules during the plasma exposure, and the removing rate enhanced with plasma time increasing.

Functional groups exchanging by atmospheric plasma treatment

The reason why the plasmas are very effective for desizing PVA size and enhancing PVA dissolving properties in water can be attributed to the chemical and physical changes of the PVA-sized fabrics. The changes of chemical composition (elemental analysis) of the PVA-sized fabric surface after plasma treatments can be revealed by XPS analysis of the chemical state (bonding and oxidation) of atom types on the PVA thin films. Table I shows the relative intensities of

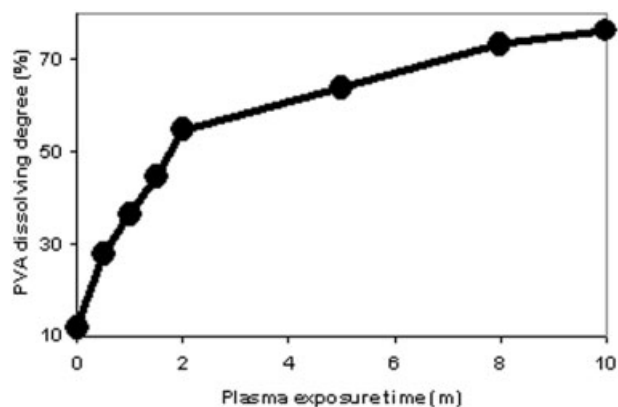


Figure 4 The relationship between dissolving rate (at room temperature for 15 min) of PVA on cotton and plasma exposure time.

TABLE I
Relative Intensities of Chemical Composition of PVA Film Oxygen/Helium Atmospheric Plasma Treatment

Plasma exposure time (min)	Element	
	C _{1s}	O _{1s}
0	87.4	11.9
1	79.6	18.8
10	80.9	17.2

C_{1s} and O_{1s} in XPS measurements of PVA film by plasma exposure time 1 min and 10 min as compared with the control. Regardless of the time used, plasma exposure led to lower C_{1s} and higher O_{1s} intensities. From curve fittings of the C_{1s} spectra for PVA films with or without plasma treatment, relative peak areas of the components by wave separation of the C_{1s} spectra are summarized in Table II. The C_{1s} spectrum of PVA film is divided into several subcomponents, of which the peak at 285 eV corresponding to C—H, C—C, the peak at 286.1 eV corresponding to C—O—, the peak at 287.5 eV corresponding to C=O, and the peak at 289 eV corresponding to O=C—O—. The relative peak areas determined by the curve separation of the C_{1s} spectra are also listed in Table II. The C—H and C—C intensities decreased 24.2% by air/oxygen/helium atmospheric plasma treatment of 1 min, while they decreased 40.4% by plasma exposure of 10 min. The C—O— intensity increased 45.2% and 53.8% with plasma treatment of 1 min and 10 min, respectively. The C=O bond enhanced 60.6% for 1 min plasma and was 98.6% for 10 min plasma treatment. The O=C—O— increased 260 and 440% corresponding 1 min and 10 min plasma treatment, respectively. These results imply that the PVA molecular chains were cut into shorter lengths and oxidized by the plasma treatments, resulting in an decrease of C—H and C—C bonds, and increases of C—O—, C=O, and O=C—O— bonds.

To further confirm the change of PVA molecules during plasma treatment, the PVA films was measured using FTIR. Figure 5 shows the FTIR curves of

TABLE II
C_{1s} Spectra of PVA Film with Oxygen/Helium Atmospheric Plasma Treatment

XPS-data element	Binding energy (eV)	Relative peak area of chemical component (%)		
		Plasma exposure time (min)		
		0	1	10
C—C, C—H	285.0	59.6	45.2	35.5
C—OH	286.1	20.8	30.2	32
C=O	287.5	7.1	11.4	14.1
C—OOR, C—OOH	289	0.5	1.8	2.7

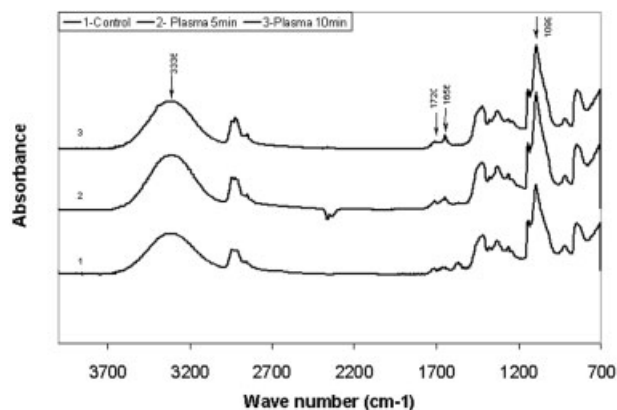


Figure 5 FTIR curve of PVA film after air/He plasma treatment.

PVA films before and after plasma treatment of 5 and 10 min. The main characteristic peaks of PVA in FTIR are listed in Table III. It is very clear that alcohol O—H stretch (3336 cm^{-1}), aldehyde C=O stretch (1720 cm^{-1}), carboxylic acid COOH stretch (1635 cm^{-1}), and aldehyde/ketone C—O (1099 cm^{-1}) peaks of PVA films are all enhanced more or less after either 5 or 10 min plasma treatment, proving that atmospheric plasma led to increase of C—O—, C=O, and O=C—O— bonds.

Mechanism of PVA changing during atmospheric plasma treatment

From the above discussion, the plasma treatments could directly lead to weight loss and thus enhance cold washing rate of PVA on cotton. The plasma treatments also greatly increased PVA film dissolving degree. XPS and FTIR analyses showed that plasma treatments resulted in decrease of C—C and C—H bonds, and increase of C—O—, C=O, and O—C—O— bonds. A possible reaction mechanism is postulated in Figure 6. Although this may be simply an outline that may not give a complete picture of the complexity of the reactions involved, it may represent the main reaction of PVA during the atmospheric plasma treatment.



Figure 6 The possible action pathway of atmospheric plasma on PVA.

References

- Hsieh, Y.; Timm, D. A.; Wu, M. *J Appl Polym Sci* 1989, 38, 1719.
- Jahagirdar, C. J.; Venkatarkrishnan, S. *J Appl Polym Sci* 1990, 41, 117.
- Lawton, E. L. *J Appl Polym Sci* 1974, 18, 1557.
- Oktem, T.; Ayhan, H.; Seventekin, N.; Piskin, E. *J Soc Dyers Colorists* 1999, 115.
- Okuno, T.; Yasuda, T.; Yasuda, H. *Text Res J* 1992, 62, 474.
- Sarmadi, A. M.; Kwon, Y. A. *Text Chem Col* 1993, 25, 33.
- Cai, Z.; Qiu, Y.; Wang, Y.; Zhang, C.; McCord, M. *J Ind Text* 2003, 32, 223.
- Cai, Z.; Qiu, Y.; Zhang, C.; Wang, Y.; McCord, M. *Text Res J* 2003, 73, 670.
- Cai, Z.; Wang, Y.; Park, Y.; Zhang, C.; McCord, M.; Qiu, Y. *AATCC Rev* 2002, 12, 18.
- Geary, M. A. *American Dyestuff Reporter* 85, 74, 28.
- Moreland, J. E. *Text Chem Col* 1980, 12, 71.
- Qiu, Y.; Zhang, C.; Hwang, Y. J.; Bures, B. J.; McCord, M. *J Adhes Sci Tech* 2002, 16, 449.
- Paul, X. P.; Hassan, A.; Friedrich, F. B.; Cate, A. L.; Fecrante, G.; Lee, W. K.; Light, L. L.; Minoff, C.; Roth, P. B. 1973, 5, 239.
- Garton, A. *Infrared Spectroscopy of Polymer Blends, Composites and Surfaces*; Carl Hanser verlag: Munich, 1992.
- Noel, P. G. R. *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*; John Wiley & Sons: England, 1994.

TABLE III

The Characteristic Peak of PVA in IR Spectrum^a

Wave number (cm^{-1})	Functional group
3336	Alcohol O—H stretch (broas)
1720	Aldehyde C—O stretch
1656	Carboxylic acid COOH stretch
1099	Aldehyde/ketone C—O stretch

^a From refs. 14 and 15.