## Application of Corona Discharge on Desizing of Polyvinyl Alcohol on Cotton Fabrics

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**ABSTRACT:** In this study, corona discharge was applied to optimize the desizing of polyvinyl alcohol (PVA) on cotton fabric. The weight of sized fabric decreased slightly when the PVA sized fabric was treated by corona discharge. Percent desizing rate (PDR) of PVA sized fabric increased evidently after the fabric was subjected to corona discharge treatment, PDR increased with the enhancement of corona discharge treatment by increase of applied voltage and treating time. Water dissolution time and water-contact angle decreased at the same time. SEM and AFM photos show the surface of PVA film was modified into uneven morphology with many ridges

pores and cracks. ATR-FTIR analysis shows that the content of C=O, —COOH, and C—O bonds was increased after the PVA film was treated by corona discharge. Corona discharge can be applied to optimize the desizing of PVA on fabric by saving treating time and water or decrease the usage of the detergent of hydrogen peroxide; it provides a green process and energy saving method for textile finishing. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2887–2892, 2009

**Key words:** corona discharge; desizing; polyvinyl alcohol; surface morphology analysis; ATR-FTIR

### **INTRODUCTION**

Corona discharge treatment has been widely applied to modify the surface of polymers. The treatment is simple and practical since the samples can be quickly treated in atmospheric condition.<sup>1</sup> New active groups can be produced and grafted onto the as treated polymers during corona discharge treatment.<sup>2</sup> The amount of high reactive free radical oxygen of hydrophilic polymers was increased after corona discharge treatment, which led to the improvement of the surface affinity and sticking strength of the polymers.<sup>3-5</sup> In textile industry, corona discharge has been applied to modify the surface of wool fiber, the printing, dyeing, and shrink resistant properties<sup>6–10</sup> of which were greatly improved after the treatment. Corona discharge was also used to treat polyester,<sup>11,12</sup> and the hydrophilic and dyeing properties were improved evidently.

Polyvinyl alcohol (PVA) is mainly used as slashing agent for synthetic yarns, it is also widely used as the sizing agent for high count cotton yarns due to its high tensile strength and excellent membrane forming properties.<sup>13–15</sup> Even though PVA size is environmental unfriendly and it is difficult to be

removed of desizing, it is still irreplaceable in most textile mills due to its advantages such as fast processing, less yarn breakage, and shedding on the slashing machine and loom.<sup>16–19</sup> However, remove of the PVA size during the process of desizing is of great challenge,<sup>20–22</sup> PVA sized fabric must be washed in hot water (normally 88–93°C) to effectively remove the size, and complete removal of PVA size without affecting subsequent wet process is very difficult.<sup>23</sup>

Cai et al. studied the influence of low-pressure plasma and atmospheric plasma treatment on desizing of PVA on several different fabrics such as cotton and viscose.<sup>15,21,23,24</sup> However, low-pressure plasma treatment for fabrics is a batch process and enquires a high-cost vacuum environment,<sup>25</sup> which is time and energy consuming. Atmospheric plasma treatment provides continuous treatment, but the atmospheric plasma equipments are complicated which makes the working cost expensive, therefore, the treatment may not be economical or time saving.<sup>26</sup>

Against this background, corona discharge treatment was introduced to overcome this weakness of plasma treatment. It is well known that corona discharge is the obvious alternative to plasma treatment. However, corona discharge apparatus is usually simple and can treat fabrics continuously and economically in the air under room

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temperature. The present study investigated the influence of corona discharge treatment on desizing of PVA on cotton fabric.

### **EXPERIMENTAL**

### Materials

Cotton fabrics (bleached for print cloth) were provided from New Siwu Textile (Hubei, China). The weight of the fabric was 57.25 g/m<sup>2</sup>; with thickness 0.07 mm. Samples for treatment were prepared in the size of  $30 \times 30$  cm. All the samples were washed in deionized water and dried at 100–105°C after predried and conditioned at conventional conditions (temperature 20°C and relative humidity 60%).

PVA1799 (M = 85,000-146,000 and 98–99% hydrolyzed) was provided by Tianshi Chemical Company (Tianjin, China).

Dispersing agent KS-1 was bought from chemical market, analytical grade.

### Treatments and procedures

The prepared cotton fabric was two-dipped-twonipped in a sizing bath containing 9% PVA with a pick-up of 100%  $\pm$  5%. The padded sample was dried at 105°C. The percentage of sizing on the sized fabric used throughout the experiment was 10.5%.

Corona discharge treatment was conducted on a corona discharge machine (SDCD16-3-10, 3000W, Dalian Number 9 Electronic, Dalian, China) with different treating voltages (6, 8, and 10 kV) and different treated speeds (5, 10, 15, and 20 s/3 cm).

After corona discharge treatment and conditioned at room temperature, fabric samples were subjected to a hydrogen peroxide ( $H_2O_2$ ) wash desizing immediately. In the wash, the fabric specimen was immersed in  $H_2O_2$  solution of 6 and 3 wt % with 20 : 1 liquid to fabric ratio, and stirred for 30 and 15 min, respectively. After the treatment, the fabric was rinsed twice with deionized water at 20°C with 5 : 1 liquor to fabric ratio.

At the same time, PVA film was prepared by casting the PVA sizing solution (concentration of the size was 9%) onto a PVC plate using a glass rod. The plate with PVA film was then placed in an oven at 75°C for 4 h. The PVA film, with thickness 0.03 mm, was then peeled from the plate and treated by corona discharge (with applied voltage 10 kV and treating speed 10 s/3 cm).

### Measurements and characterizations

The weight loss of samples subjected to the treatments was calculated by the following equations:

$$P = (W_0 - W_t)/W_0 \times 100\%$$

Where P% is the weight loss of the specimen;  $W_0$  is the weight of the sized fabric;  $W_t$  is the weight of the sample after treatment.

The percent desizing rate (PDR) of the treated fabric was calculated as the weight of size removed from the fabric divided by the total weight of the size on the fabric.

The dissolution time of PVA film treated by corona discharge under different conditions was tested as follows: samples of PVA film were prepared in the size of  $10 \times 1$  cm, then the sample was half immersed ( $5 \times 1$  cm) into hot water ( $80^{\circ}$ C) vertically. The dissolution time of PVA film was recorded when the PVA film was broken. Each sample was tested for 10 times and results were averaged.

Water-contact angle was measured by a JC2000Y stable contact angle analyzer (Powereach Digital Equipment, Shanghai, China) at room temperature with distilled water. Distilled water drops of 20  $\mu$ m were placed on each PVA film from a micrometer pipette with a distance of 5 mm, and the contact angles were observed. Each sample was tested 10 times and the results were averaged.

Scanning electron microscopy analysis was carried out on a field emission SEM (Quanta 200, Manufactured by FEI, Holland), the samples were coated with gold before testing.

Atomic force microscope (AFM) analysis was visualized in non-contact mode by using a Scanning Probe Microscope Controller (DI Nanoscope TC, Manufactured by Veeco, America). Average roughness ( $R_a$ ) and root mean square roughness ( $R_{rms}$ ) of 1  $\mu$ m<sup>2</sup> area were calculated.

The structure of PVA film was analyzed by Fourier transform attenuated total reflection infrared spectroscopy (ATR-FTIR) on a TENSOR 27 spectrometer (BRUKER Optics, Billerica, MA). The transmittance of ATR spectra of the samples between 600 and 4,000 cm<sup>-1</sup> was collected by 32 scans for each spectrum, and the resolution of the ATR spectra was  $4 \text{ cm}^{-1}$ .

### **RESULTS AND DISCUSSION**

# Weight loss of sized fabrics after corona discharge treatment

The weight loss of PVA sized fabric after corona discharge treatment was calculated and the results are shown in Figure 1. Less than 3% weight loss can be observed from Figure 1 after corona discharge treatment. Since corona discharge modifies the surface of polymer, the weight loss here can be ascribed to the loss of sized PVA. It can be explained during the



**Figure 1** The weight loss rate of cotton fabrics with PVA treated by corona discharge. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

process of the treatment, the PVA macromolecules degraded into small molecules (such as  $CO_2$  and  $H_2O$ ) and diffused into the air.<sup>23,27–29</sup>

As shown in Figure 1, the weight loss increases evidently with the increase of treating time and applied voltage, this is due to the increased treating effect on the surface of PVA sizing. However, the weight loss changes little when the applied voltage is extremely high, such as 10 kV, or the treating time is long enough, such as 20 s. Obviously, the sized PVA was modified and partially degraded into small molecules<sup>21</sup> which contributes to the weight loss of the whole sized fabrics.

### **PDR** tests

For conventional desizing method, hydrogen peroxide is widely used to remove the PVA on the surface of fabrics. As Figure 2 shows, the PDR increases evidently from 63.6% (wt 3%, 30 min) to 87.5% (wt 6%, 30 min) with the increase of  $H_2O_2$  concentration. However, if the sized fabric was subject to corona discharge treatment before the  $H_2O_2$  desizing treatment, PDR would be enhanced greatly, as shown in Figure 2. It is probably that the swelling, dissolving, and dispersing of PVA increases after corona discharge treatment.

From Figure 2, the PDR increases evidently with the increase of applied voltage and treating time, this is due to the enhancement of the treating effect. Conventional desizing of PVA is generally conducted by a chemical treatment followed by using  $H_2O_2$  high concentration directly. It is obvious from Figure 2 that the application of corona discharge on the desizing can either decrease the usage of hydrogen peroxide or save the desizing time. This indicates that energy and water consumption can be saved and less chemical has to be used in the desezing process, which is meaningful for green processing in textile mills.

### PVA film dissolution time test

From the results discussed earlier, it is obvious that corona discharge can optimize the desizing of PVA. To study the reason for this, PVA films were prepared and treated by corona discharge under different parameter, the water dissolution time of these



**Figure 2** The PDR of cotton fabric treated by corona discharge. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

	The Dissolution Time of PVA Films (s)					The Water-Contact Angles on PVA Films (°)				
Treating		Treating time (s)				Treating time (s)				
voltages	5	10	15	20	voltages	5	10	15	20	
Control	166 ± 11			Control	32					
6 kV	$97\pm8$	$94 \pm 10$	$90 \pm 9$	$88 \pm 3$	6 kV	21	18	13	10	
8 kV	$74\pm 6$	$70 \pm 5$	$65 \pm 5$	$61 \pm 4$	8 kV	11	8	5	0	
10 kV	$61\pm 6$	$58\pm4$	$53 \pm 4$	$51\pm 6$	10 kV	0	0	0	0	

TABLE I

**TABLE II** 

films were tested and the results are shown in Table I. It is evident that water dissolution time decreases from 166 s to less than 97 s after corona discharge treatment, this suggests that corona discharge treated PVA film can be dissolved into water more swiftly.

Meanwhile, the water dissolution time decreases evidently with the increase of applied voltage and treating time which is due to the strengthening of the corona discharge treatment. Several reasons can be applied to explain this: First, the pores and cracks were formed in the PVA film surface when it was treated by corona discharge,<sup>27</sup> and these tiny pores

and surface became more evident when the treating time and voltage increased. In addition, the modification of corona discharge on PVA film was more thoroughly, and more macromolecules was cut off and was oxidized into CO2 and H2O, and was volatiled.<sup>24</sup> At last, some other macromolecules were oxidized, and form the substances contained watersoluble groups such as C=O, -COOH.<sup>23</sup> As a result, the dissolution time of PVA film was decreased.

The water-contact angles change after corona discharge treatment of PVA films was shown in Table II, evidently the water-contact angle decreased after corona discharge. Much lower water-contact



Figure 3 SEM photos of PVA film before (a) and (b), and after (c) and (d) corona discharge treatment (with applied voltage 10 kV and treating time 10 s).



**Figure 4** AFM 3-D profiles of PVA film before (a) and after (b) corona discharge treatment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

angle was observed when applied voltage increased or treating time increased, this is due to the increase of the treating effects under these situations. it was concluded that the corona discharge treatment can etch the PVA surface seriously.

### Surface morphology analysis

Figure 3 Shows the SEM photos of PVA film with different magnifications before and after corona discharge treatment. It is obvious that the surface morphology of PVA film is plane and smooth, but the PVA film treated by corona discharge shows etched surface with obvious ridge, uneven morphology, and many pores and cracks. This was as a result of the electrical field produced, and minority ions and free electrons in the air were accelerated in the field to obtain high energy.<sup>28</sup> Parts of molecular and free electrons were ionized to new free ions, electrons, and free radicals and others when the molecular and free electrons hit other members in movement. It is evident that corona discharge has strong surface modification on PVA films, thus, the water dissolution time decreased and the PDR increased evidently.

The AFM pictures of PVA film of untreated and treated are shown in Figure 4 and the surface roughness results are shown in Table III. Similar to SEM results, AFM photos show the surface of the PVA film became rough and uneven after treatment. Table III shows the roughness of the treated sample was much greater than that of the control. Therefore,

 TABLE III

 The Roughness of PVA Films Measured by AFM (Nm)

	Roughness (nm)		
Treatment	$R_a$	R <sub>rms</sub>	
Control Treated	18.1 61.3	23.9 82.7	

#### FT-IR analysis

ATR-FTIR analysis was used to test the changes of chemical composition of PVA film before and after corona discharge treatment, as shown in Figure 5. A sharper peak is observed at 1230.6 cm<sup>-1</sup> of the treated PVA film, and other sharper peaks were distributed at 1099.4 cm<sup>-1</sup>, 1329.0 cm<sup>-1</sup>, 1554.6 cm<sup>-1</sup>, which were ascribed to the oxygen-containing groups, such as s aldehyde C=O stretch, Carboxylic acid —COOH stretch, and aldehyde/ketone C—O peaks of PVA. At the same time, the peak at 3296.4 cm<sup>-1</sup> was weaken, which proved that the content of alcohol —OH bonds maybe reduced after corona discharge treatment. Thus, the dissolution of the PVA in water increased greatly.



**Figure 5** The FT-IR of PVA film treated by corona discharge and untreated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.]

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### CONCLUSIONS

Corona discharge treatment can be successfully applied to optimize the desizing of PVA on cotton fabric. Less than 3% weight loss was observed when the PVA sized fabric was treated by corona discharge. Percent Desizing Rate (PDR) of PVA sized fabric increased evidently after it was subjected to corona discharge treatment, which provides a green process by either decrease the desizing time or lessen the hydrogen peroxide concentration. The water dissolution time and water-contact angle of the PVA film decreased evidently after the treatment. SEM and AFM photos show the surface of PVA film was severely etched into uneven morphology with many ridges pores and cracks. ATR-FT-IR analysis shows that the content of C=O, -COOH, and C-O bonds was increased after the PVA film was treated by corona discharge..

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