

# In Situ Polymerization of Aniline on Acrylamide Grafted Cotton

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**ABSTRACT:** In this article, polyaniline (PANI)/cotton composite were prepared by *in situ* polymerization on the grafted cotton. First, acrylamide was grafted onto cotton cellulose using a radical graft polymerization process and some influencing factors were studied. Then polyaniline/cotton conductive composite fabrics were prepared by chemical *in situ* polymerization on the grafted cotton. The influences of the concentration of ammonium persulfate, aniline, hydrochloric acid, and the reaction time to the conductivity and K/S of composite fabric were studied. By contrasting, graft

brought on an improvement of about one order of magnitude to the conductivity of composite fabric. The strength, TG, FTIR-ATR, and SEM of prepared fabric were measured. The thermal stability and tear strength of composite fabric reduced, whereas PANI exhibited a rough but uniform, coherent PANI coating on surface of cotton fiber. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1126–1132, 2011

**Key words:** *in situ* polymerization; PANI; acrylamide grafted cotton

## INTRODUCTION

With the development of the industrial textiles, the demand of electrically conductive textiles has strongly increased as filters, electromagnetic interference shielding materials, antimicrobial, and flame retardancy materials.<sup>1</sup> Intrinsic conducting polymers, especially  $\pi$ -electron conjugate polymers,<sup>2</sup> such as polythiophene, polyaniline, and polypyrrole, have been extensively studied because of its conducting properties.<sup>3</sup> Among those organic conducting polymers, polyaniline (PANI) is regarded as the most commercial promising conducting polymer because of inexpensive monomers, easy to produce, high yield, and thermal, chemical stabilities.<sup>4</sup>

Electrically conductive textiles can be produced by coating of intrinsic conducting polymers on textiles or by *in situ* oxidative polymerization of various monomers. Many quite valuable reports have been published about the electrically conductive textiles made by PANI. PET,<sup>4</sup> nylon,<sup>5</sup> and cotton<sup>6</sup> have been studied as substrates. Owing to insolubility of PANI in water, coating process is hardly acceptable for producing conductive composite fabrics. Thus, *in situ* oxidative polymerization is an acceptable method. The preparation of PANI composite fabrics was more or less the

same: the textiles were immersed in an aniline monomer solution of HCl or other acid, and then, polymerization was initiated by the addition of an oxidant at a low temperature, such as 5°C, for 1 h or even longer. After that, the composite fabrics were carried out, rinsed by HCl solution or water, and dried. This method has some shortcomings. First, the polymerization were took place in strong acid solution. Some kinds of fibers, especially cellulose fibers, are acid nonresistant. Second, PANI deposited in the solution and not on the fabric.<sup>7</sup>

Our objective in this article is to develop a new way (dip-nip process) to prepare PANI conductive fabrics by *in situ* polymerization with acrylamide grafted cotton as substrate. FTIR-ATR, TG, SEM, conductivity, and strength of PANI composite cotton were studied.

## EXPERIMENTAL

### Materials

We used a scoured, bleached, and mercerized, fluorescent whitening agents free, 100% cotton weaving fabric with a density of 96 threads/inch in the warp and 48 threads/inch in the weft direction throughout this study.

Aniline, acrylamide (AAM), hydrochloric acid, ammonium persulfate (APS), and potassium persulfate (PPS) are A. R. grade (analytical reagent) and provided by Shanghai Handa Chemicals Ltd.

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### Acrylamide grafted cotton

Chemical finishing baths were prepared by dissolving all chemicals (AAM/ PPS) in distilled water according to different formulations. Fabrics were under "two-dip two-nip" process with 70% pickup. Dip-nip process means fabrics were dipped in the chemical baths at a certain temperature (for example 20°C) and padded at a required expression. This "dip-nip" process was repeated twice, which is called "two-dip two-nip" process. After the fabric was padded, an amount of solution was picked up by the fabric, which is called pickup in the dyeing and finishing industry. The pickup is calculated as follows:

$$\text{Pickup (\%)} = (A_2 - A_1) / A_1 \times 100 \quad (1)$$

where  $A_1$  is the weight of the dry fabric before immersion, and  $A_2$  is the weight of the fabric after immersion and padded.

The padded fabrics were dried at 60°C for 10 min, cured at an elevated temperature (100–135°C) for a certain period of time, and then washed in a large amount of water. Afterward, the fabrics were dried and stored in a conditioning room (21°C, 65% relative humidity) for over 72 h to reach constant weights. Percentage graft was calculated from the following equation<sup>8</sup>:

$$G (\%) = (w_2 - w_1) / w_1 \times 100 \quad (2)$$

where  $w_1$  and  $w_2$  are the weights of the original and grafted fabrics, respectively.

### Polymerization of the aniline monomer onto the pretreated cotton

The polymerization of aniline onto the grafted cotton was carried out by chemical oxidative polymerization. There were two kinds of chemical reacting bath. One is a solution of APS (Bath 1), the other is aniline in HCl solution (Bath 2). After immersion in Bath 1 for 5 min, the grafted cotton substrate was taken out, padded by the squeeze rolls of the laboratory padder with take-up 70% and then immersion in Bath 2 for some time to push the aniline monomer into the interstice and the inner part of the fabric. The grafted cotton substrate was padded again with the same take-up 70% and finally dried at 60°C for 10 min in a laboratory oven Mathis DHE. The composite fabric was doped with 1M of HCl as a secondary dopant for 30 min, rinsed, and dried.<sup>7</sup>

### Surface conductivity measurement of the treated fabric

The surface conductivity of the PANI/cotton conducting composite fabric was measured with a mul-

timeter. Ten readings at different locations were taken randomly and carefully and the average was recorded. The conductivity ( $\sigma$ ) was calculated according to the following equation:

$$\sigma = 1 / (L \times R) \quad (3)$$

where  $L$  is the length of the fabric sample and  $R$  is the resistance of the fabric sample according to the multimeter.

### K/S measurement

The color properties of the composite fabrics were measured by a GretagMacbeth Color-Eye 7000A spectrophotometer with Optiview software under illuminant D65 using 10° standard observer. The composite fabrics were folded into four layers and placed in the large sample port. To obtain the average of its reflectance, three measurements in different surface positions were carried out for each sample. The reflectance data were recorded every 10 nm from 360 to 750 nm.  $K/S$  values were reported at the maximum of each sample.  $K/S$  value represents color yield.<sup>9</sup>

### FTIR-ATR analysis

FTIR-ATR spectra were taken on a Thermo Nicolet 5700 spectrometer (Thermo Electron Corporation). The data were recorded from 600 to 4000 nm.

### TG analysis

The TGA measurement was performed on a NETZSCH-TG 209 F1 instrument at a heating rate of 10°C /min.

### Measurement of the strength of the fabric

Tear strength of the fabrics was measured with China National Standard GB/T 3917.2-1997<sup>10</sup> by Elmendorf tearing tester (Thwing-Albert Co. Ltd., USA).

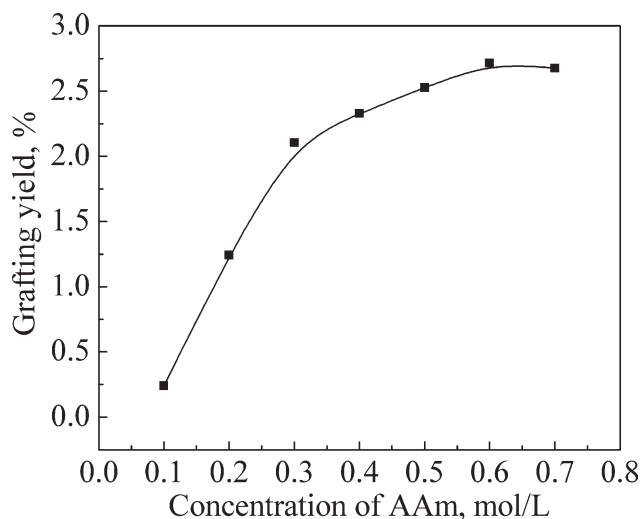
### SEM analysis

Information about surface morphology was obtained by using a JSM-5600LV scanning electron microscope.

## RESULTS AND DISCUSSION

### Influence of initiator and monomer on grafting yield

Vinyl amide monomer (AAM) was grafted onto cellulose by using a free-radical polymerization process. Both initiator and monomers were padded onto the fabric in an aqueous solution; the samples were dried at 60°C for 10 min and then heated to an elevated



**Figure 1** Effect of concentration of AAm on grafting yield. PPS 0.35 mol/L solution, dried at 60°C for 10 min and cured at 120°C for 5 min.

temperature (higher than 100°C) to initiate the radical grafting reaction. This process is very similar to a regular wet fabric finishing operation, and the removal of water before the polymerization prevents side reactions between initiators and water.<sup>8</sup> PPS was selected as a radical initiator in this approach because it is soluble in water and inexpensive.

Figure 1 indicates grafting yield of AAm in varied concentrations of 0.1–0.7 mol. As the monomer concentration increased, the diffusion of the monomer molecules into the fiber structure and the formation of radicals also increased, which led to a higher grafting yield. The decrease in grafting yield can be explained by the enhancement of homopolymer formation at high-monomer concentrations.<sup>11</sup> The maximum grafting yield obtained was for the AAm at a 0.60 mol/L concentration.

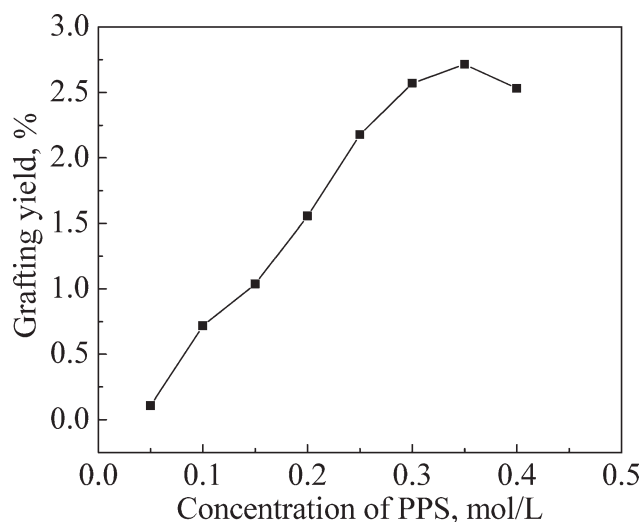
The effects of different concentration of PPS as initiator for the polymerization were investigated. It can be seen that the yield increased with increase of initiator concentration and then decreased. Initiator determines the grafting yield and possibly grafting sites. When the temperature is raised to above the decomposition temperatures of radical initiators, initiator radicals will be produced. To maximize the grafting efficiency, the initiator radicals are expected to abstract hydrogen atoms from cellulose rather than undergo radical addition to the monomers.<sup>3</sup> Figure 2 shows the influence of the concentration of initiator PPS on grafting yield. Evidently, the grafting percentage increased significantly as the PPS concentration increased, and a further increase in the PPS concentration decreased the grafting yield. The increase in PPS concentration increased the probability of both hydrogen abstractions from the cellulose backbone and chain-transfer reactions of

polyacrylamide, homopolymers with cellulose. So the grafting yield increased. However, the excessive increase in PPS concentration caused the formation of free-radical species. These free radicals reacted with cellulose macroradicals and growing polymer chains, which resulted in termination or combination reactions; consequently, the grafting yield decreased.<sup>11</sup> The maximum grafting yield obtained was for the PPS at a 0.35 mol/L concentration.

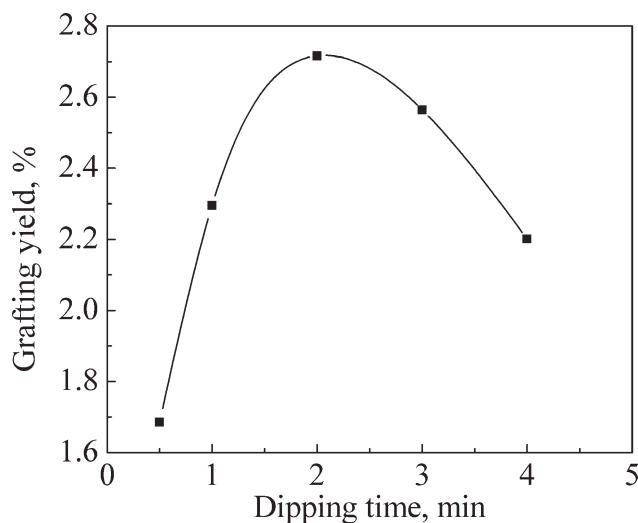
### Influence of dipping time and curing process on grafting yield

The effect of dipping time on the grafting yield was investigated by changing time (from 0.5 to 4 min) at room temperature and constant monomer–initiator concentrations. As shown in Figure 3, the grafting yields initially increased with time and then reached a saturation grafting value after 2 min. After 2 min, the grafting polymerization on cotton fabric was inhibited by the high molecular weight homopolymer, consequently decreased grafting yield.<sup>11</sup>

Curing temperature and time affected graft polymerization of monomers on the cellulose. The reaction was initially set at temperature much higher than the melt point of AAm at 84.5°C. The graft polymerization was conducted over a temperature range of 100–135°C. And under a higher temperature, the curing time was shorter and vice versa for lower temperature.<sup>8</sup> Effect of curing time and temperature on grafting yield were studied with AAm 0.6 mol/L, PPS 0.35 mol/L solution, dried at 60°C for 10 min. There was no significant difference in grafting yielding. The temperature was set at 120°C and the curing time was about 5 min.



**Figure 2** Effect of concentration of PPS on grafting yield. Acrylamide 0.6 mol/L, dried at 60°C for 10 min and cured at 120°C for 5 min.



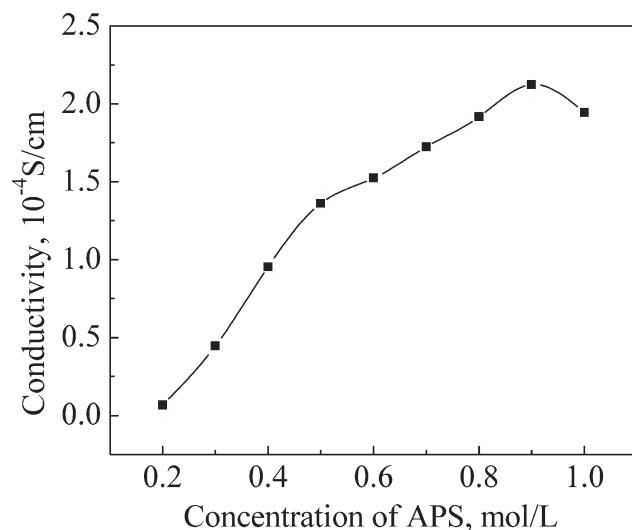
**Figure 3** Effect of dipping time on grafting yield. AAm 0.6 mol/L, PPS 0.35 mol/L solution, dried at 60°C for 10 min, and cured at 120°C for 5 min.

#### Influence of concentration of APS on conductivity

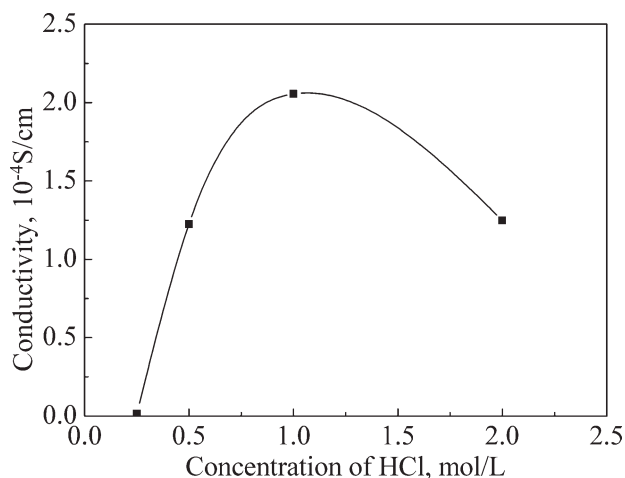
APS was used as oxidant in this reaction. As shown in Figure 4, it was clear that the conductivity of composite fabric increased, when the concentration of APS increased and it reached a maximum value at 0.9 mol/L, then decreased at higher concentrations. These behaviors arose from the formation of water-soluble oligomers and interruptions in conjugation, which may adversely affect the conductivity, due to over oxidation.

#### Influence of concentration of HCl on conductivity

Figure 5 showed that the conductivity of composite fabrics reached its highest value at 1M HCl and



**Figure 4** Effect of concentration APS solution on conductivity. HCl 1 mol/L, aniline 0.5 mol/L, then immersion in Bath 2 for 30 min, padded, dried at 60°C for 10 min.



**Figure 5** Effect of concentration of HCl solution on conductivity. APS 0.9 mol/L, aniline 0.5 mol/L, immersion in Bath 2 for 30 min, padded, dried at 60°C for 10 min.

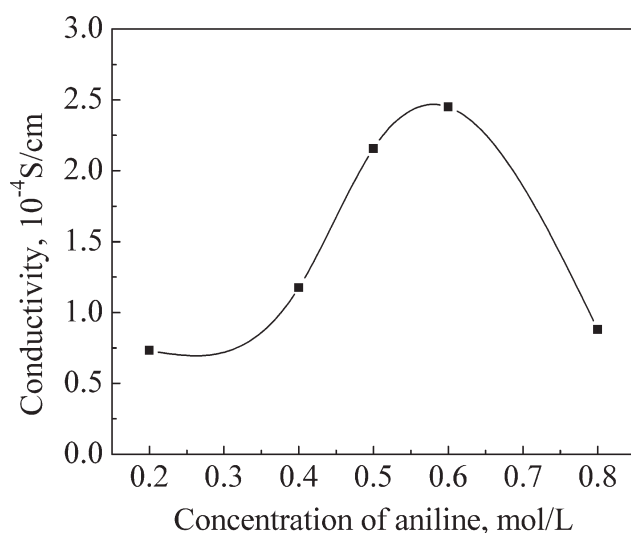
decreased at concentrations higher than that. This behavior could be attributed to the fact that H<sup>+</sup> ion could not be removed from the structure during head to tail coupling of aniline salt due to excessive salt formation at higher acid concentrations. If H<sup>+</sup> was not removed from the cation, the oligomer could not grow and dissociates with hydrolysis. The conductivity of composite decreased at higher acid concentrations could be explained with the increasing rate of hydrolysis of emeraldine chains formed under the polymerization conditions.

#### Influence of concentration of aniline on conductivity

The conductivity of PANI depended on the oxidation degree of PANI, which was mainly determined by the ratio of oxidant/aniline (mol ratio). Although the amount of APS on the fiber was constant after padded by the squeeze rolls of the laboratory padder, the concentration of aniline monomer became uppermost parameter and 0.6 mol/L was optimum as shown in Figure 6.

#### Influence of dipping time of aniline in HCl solution on conductivity

Figure 7 showed the effect of dipping time of Bath 2 on the conductivity of composite fabrics. The conductivity of composite fabrics increased rapidly with polymerization time at first but tended to have little change after 20 min. In the first stage, it seems that PANI is mainly polymerized in the outer layer of cellulose fiber and that this layer retarded the diffusion of aniline monomer and oligomer to the interior side and prohibited PANI from being polymerized inside. The absence of change after 20 min in the conductivity could be explained by this phenomenon.

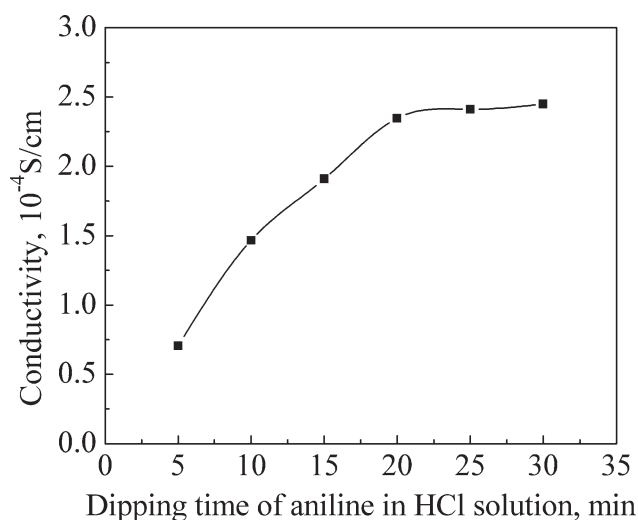


**Figure 6** Effect of concentration of aniline on conductivity. HCl 1 mol/L, APS 0.9 mol/L, immersion in Bath 2 for 30 min, padded, and dried at 60°C for 10 min.

#### Influence of graft to the conductivity of the composite fabric

There are two sets of absorption wavelength corresponding to green light, range from 360 nm to 500 nm and from 600 nm to 750 nm (Table I).  $K/S$  values provide more evidence that the composite fabric is dark green, which is characteristic color of doped PANI. And the corresponding relations between  $K/S$  values and conductivity are compatible.

Cotton fabric grafted by AAm has greater tendency to combine with PANI. One reason was that  $-\text{NH}_2$  on modified cotton participates in polymerization reaction and linked PANI molecular chain to cellulose molecular chain. The other reason was that



**Figure 7** Effect of dipping time of Bath 2 on conductivity. HCl 1 mol/L, APS 0.9 mol/L, aniline 0.6 mol/L, padded, and dried at 60°C for 10 min.

**TABLE I**  
Influence of Graft to the Conductivity of the Composite Fabric

Substrate materials	$K/S$ values	Conductivity (S/cm)
Pure cotton	15.358 (370 nm) 17.579 (730 nm)	$1.01 \times 10^{-5}$
Grafted cotton	37.063 (360 nm) 41.547 (610 nm)	$2.45 \times 10^{-4}$

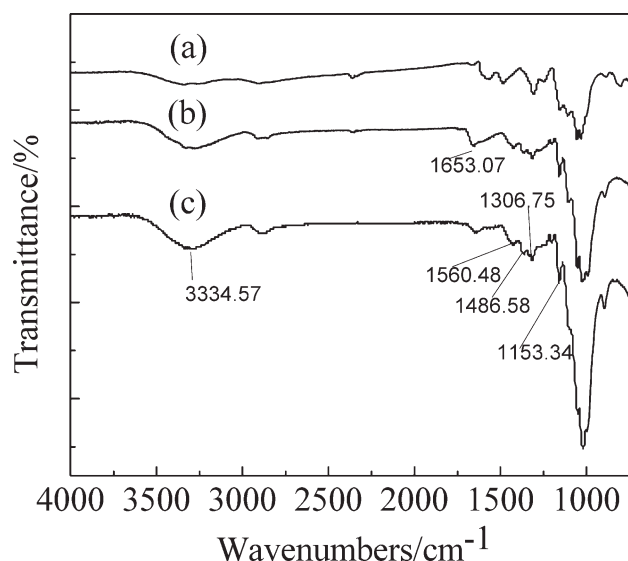
the presence of  $-\text{NH}_2$  and  $\text{C}=\text{O}$  increased the probabilities of forming hydrogen bond.

The composite fabric with the conductivity of  $2.45 \times 10^{-4}$  is used to following test.

#### FTIR-ATR study

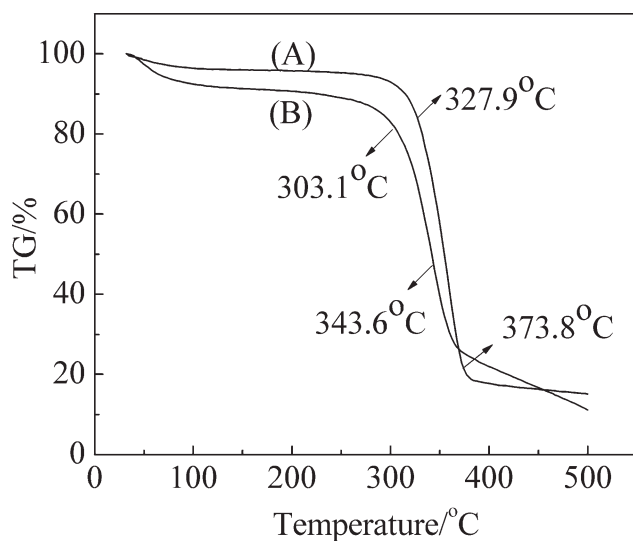
Figure 8(b) showed the FTIR-ATR spectra of cotton grafted by AAm. The band at  $1653.07 \text{ cm}^{-1}$  was characteristic of the  $-\text{CONH}_2$  group which proved that AAm was grafted onto cotton cellulose using a radical graft polymerization process.

The band observed at  $1486.58$  and  $1560.48 \text{ cm}^{-1}$  in Figure 8(c) corresponded to  $\text{C}-\text{N}$  and  $\text{C}=\text{N}$  group in the benzenoid and quinoid structures in PANI, respectively. The band at  $1306.75 \text{ cm}^{-1}$  corresponded to  $\text{N}-\text{H}$  bending and the broad band near  $3334.57 \text{ cm}^{-1}$  was characteristic of the  $\text{NH}_2$  groups corresponding to  $\text{N}-\text{H}$  stretching mode in PANI. Also characteristic band of the conductive form of PANI was observed at  $1153.34 \text{ cm}^{-1}$  in PANI/cotton composite fabric. The disappearance of prominent peak at  $1653.07 \text{ cm}^{-1}$  may be due to complete coating of PANI on surface of cellulose fiber.



**Figure 8** FTIR-ATR spectra of (a) pure cotton fabric, (b) cotton grafted by acrylamide and (c) PANI/cotton composite fabric.





**Figure 9** TG curves of (a) pure cotton and (b) PANI/cotton composite fabric.

#### TG analysis

TGA was used to measure the thermal properties of the composite fabric. Pure cotton fabric and PANI/cotton composite fabric decomposed at 327.9°C and 303.1°C, ended at 373.8°C and 343.6°C, respectively, as shown on Figure 9. The composite fabric decomposed at a lower temperature. This showed that the presence of PANI in the composite fabric reduced the thermal stability of cotton fabric corresponding to the removal of HCl from PANI molecular chain. The TG curve did not show the significant improvement in thermal stability which had been reported for other substrate materials.<sup>3</sup>

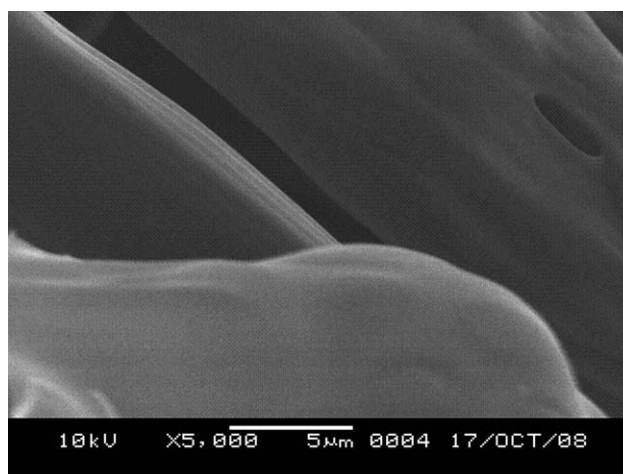
#### Tear strength

Oxidant (APS) and strong acid (HCl) may cause chemical damage to the cellulose. This could be the reason why the tear strength of PANI/cotton composite fabric reduced. So how to reduce the chemical damage to cellulose should be studied further Table II.

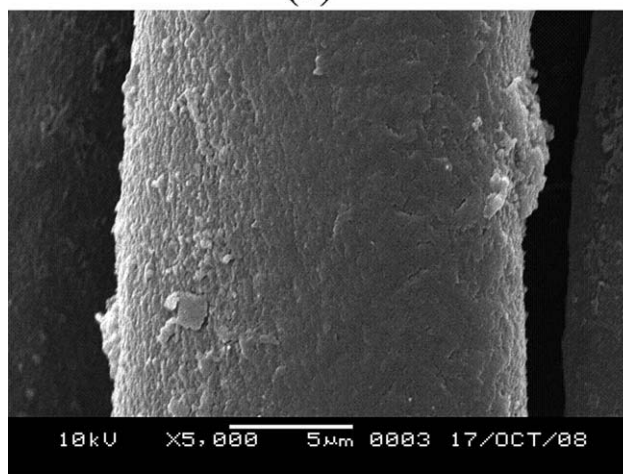
The surface morphology of the composite fabric was studied by SEM using an electron voltage of 10 kV and a magnification of 5000 as shown in Figure 10. The morphology of cotton fiber changed dramatically due to the addition of PANI. The surface exhibited a rough but uniform, coherent PANI coating

**TABLE II**  
Tear Strength of Pure Cotton and PANI/Cotton Composite Fabric

	Cotton	PANI/ cotton
Warp (mN)	11212.2	10066.6
Weft (mN)	8059.5	6463.1



(a)



(b)

**Figure 10** SEM micrographs of (a) pure cotton fabric and (b) PANI/cotton composite fabric.

and the conducting path was formed, which made the composite fabric had good conductivity.

#### CONCLUSION

AAM was grafted onto cotton cellulose using a radical graft polymerization process and the optimal reaction condition of graft copolymerization should be: the concentration of monomer and initiator were 0.6 mol/L and 0.35 mol/L, the reaction temperature and time were 60°C and 10 min, the curing temperature and time were 120°C and 5 min, respectively.

Then polyaniline/cotton conductive composite fabrics were prepared by *in situ* polymerization on the grafted cotton. The influences of the concentration of APS, aniline, hydrochloric acid, and the reaction time to the conductivity and *K/S* of composite fabric were studied. The optimal reaction condition of *in situ* polymerization on the grafted cotton should be: the concentration of APS was 0.9 mol/L,

HCl 1 mol/L, and aniline 0.6 mol/L. The dipping time of aniline in HCl solution was 30 min. By contrasting, graft brought on an improvement of about one order of magnitude to the conductivity of composite fabric. The strength, TG, FTIR-ATR, and SEM of prepared fabric were measured. The thermal stability and tear strength of composite fabric reduced, whereas PANI exhibited a rough but uniform, coherent PANI coating on surface of cotton fiber.

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