Fabrication and Characterization of Polyaniline on Cotton Fabric via Two-Step in-situ Polymerization

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Abstract. The conducting polyaniline (PANI) was fabricated with hydrochloric acid and ammonium persulfate (APS) as dopant and oxidant respectively on cotton fabric via two-step in-situ polymerization process. Effect of APS concentration on conductivity, EMI shielding effectiveness (SE) and weight gain rate of PANI coated on cotton fabric were investigated. FTIR spectra, crystallinity and morphology of resultant substrate were analyzed via attenuated total reflectance method (ATR), X-Ray diffraction (XRD), scanning electrical microscope (SEM) and optical microscope respectively. The result indicated that the optimum conductivity (0.5 kΩ) and SE (60%) of coated substrate were obtained at the concentration of APS 0.2 mol/L, and PANI had good combination with cotton substrate. The crystal structure of cotton fiber doped with PANI had no change with the increase of its crystallinity (up to (74.46±1)%).

1. Introduction
Conducting polymer could be divided into three categories: electronic conductive polymers (such as polyacetylene, polyaniline, polypyrrole, polythiophene), ionic conductive polymer(such as poly(2-vinylpyridine)) and oxidation reduction conductive polymer(such as Poly (2-ethylene ferrocene)). According to its structural characteristics, conduction mechanism and no any conductive materials adding, electronic conductive polymers were named intrinsically conductive polymers (ICPs). Among the ICPs, polyaniline attracted tremendous interest due to its easy in preparation, better atmospheric stability[1] and promising conductivity characteristics[2]. Flexible materials, such as fabrics and films, doped with PANI not only eliminate electrostatic interference in use, but also guarantee the integrity and conductivity of PANI film on substrate’s surface without changing its shape[3]. Compared with metal-based conductive materials, polyaniline modified materials were lightweight, breathability, anti-corrosion and tractable. At present, three methods to prepare PANI-coated substrates were widely used: interweave method, coating method and the in-situ chemical polymerization[4, 5]. Among the three techniques, the in-situ chemical polymerization of PANI onto substrate was certainly a simple and ecological process, which could obtain a large area adsorption of polynailine on the substrates[6].

In this article, two-step in-situ polymerization was adopted to produce polyaniline/cotton composite fabric. Aniline monomer was absorbed on cotton fabric followed by spraying medium solution containing oxidant, then, polyaniline film formed on the surface and internal of cotton fiber. Effect of oxidant concentration on conductivity, electromagnetic interference shielding effectiveness and PANI weight gain rate of PANI/cotton composite fabric were discussed. FTIR spectra, crystallinity and morphology of PANI/cotton composite fabric were also studied respectively.
2. Materials and Methods

2.1 Materials
Scoured without dyeing cotton fabrics (115±10 g/m²) were used as substrate. All chemicals used in this study including aniline distilled twice under vacuum, ammonium persulfate and hydrochloric were analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2 Deposition of aniline monomer
For polymerization, cotton fabric weighing m0 was treated in 100 mL monomer solution (0.5 mol/L aniline + 0.5 mol/L HCL) at 70 °C until it absorbed maximum of monomers. Then, the dipped substrate was taken out and immediately squeezed by a padder with a nip pressure in order to remove excess monomer solution.

2.3 Oxidative polymerization
After monomer deposition, oxidant solution (ammonium persulfate + HCl) pre-cooled at 0 °C was sprayed on the fabric homogeneously, and the amount of oxidant on each fabric was the same. The oxidation reaction was maintained at a low temperature for 2 h. Then, the composite fabrics were dried and weighted, which mass was signed as m1. Weight gain rate of PANI (P) on cotton fabric was calculated as Formula (1):

\[ P = \frac{m_1 - m_0}{m_0} \times 100\% \]  

In which:
- P—weight gain rate of PANI; m0—the weight of untreated cotton fabric; m1—the weight of PANI/cotton composite fabric

2.4 Characterization
Surface resistance (R) was determined by FLUKE 15B digital multimeter, then surface resistivity (\(\rho_s\)) could be obtained according to the Formula (2):

\[ \rho_s = \frac{R \times W}{L} \]  

Where: \(\rho_s\)—surface resistivity; R—surface resistance; W—width of testing area; L—length of testing area.

The structural characterization of the composite cotton fiber was analyzed by X-ray diffraction (XRD, Rigaku D/max-2550) spectra with the Cu Kα line of 1.5406Å. The morphology of cotton fabric observed by optical microscopy (LEICA DM500). Electromagnetic interference shielding effectiveness of the sample was measured using the flange coaxial transmission line method at 1 MHz to 1.5 GHz by Aglient equipment including Aglient E4447A spectrum analyzer and Aglient E8257D signal generator (Aglient Technologies Inc.). The surface IR analysis of cotton substrate was obtained from FTIR with Attenuated Total Reflectance (ATR) detector (Nicolet 380, Thermo Electron Corporation).

3. Results and Discussion

3.1 Surface morphology of PANI/cotton composite fabric
The effect of the polymerization reaction on morphology changes in polyaniline/cotton composite fabric was demonstrated by the optical microscopy.
The cross section of untreated cotton (showed in Fig. 1 (a)) was kidney shape and cottons’ middle was cavity. Fig. 1 (b) showed the color on the cross section of PANI/cotton composite fiber has changed from grey to green. And among fiber bundle there were obviously dark green border. From these image studies, it was clear that interior and surface of cotton fiber was evenly doped by PANI. Two-step in-situ chemical polymerization made the penetration of PANI monomers into the fiber easily. As a result, the PANI monomers could react with oxidant directly inside of the fibers which penetrates in the later time.

3.2 ATR-FTIR of PANI/cotton composite fabric

Figure 2 showed the ATR-FTIR spectra of cotton and PANI/cotton composite fabric.

The broad band in Curve (a) centered at 3294 cm\(^{-1}\) in the ATR spectra of cotton was due to the stretching vibrations of the -OH groups. The most intense peak in the spectrum of cotton sample was the peak at 2892 cm\(^{-1}\), which was the -CH stretching band of the glucose unites of cellulose. -CH\(_2\) symmetric bending vibrations were observed at 1430 cm\(^{-1}\) and the characteristic peak at 1020 cm\(^{-1}\) was due to the stretching vibration of C-O-C. C-H bending and –CH\(_3\) symmetric deformation vibrations, which normally occurred at the same peak, were seen at 1316 cm\(^{-1}\). The ring stretching vibration of the glucose of cellulose became at 1104 cm\(^{-1}\)[7, 8].

Curve (b) was similar to Curve (a). Because of doping of H\(^+\), the peak at 3294 cm\(^{-1}\) was disappeared. The peak at 1721 cm\(^{-1}\) corresponded to quinonoid and benzenoid ring stretching, respectively. The characteristic C-N stretching vibration of PANI was observed at 1458 cm\(^{-1}\), and the N=Q=N stretching of the quinoid units of PANI, which due to electron delocalization, was seen at 1296 cm\(^{-1}\). The C-H out-of-plane bending vibrations characteristic of 1,4-disubstituted compounds
were observed at 868 cm\(^{-1}\), with the plane bending vibration at 967 cm\(^{-1}\). It was proved that PANI had been deposited on the surface of cotton fabric adequately.

3.3 Crystallinity of PANI/cotton composite fiber
Cotton belongs to monoclinic crystal which is classified to cellulose\(^{[11]}\). Its lattice parameter as follows: \(a=0.834\text{nm}, b=1.04\text{nm}, c=0.789, \beta=83.2^\circ\). XRD spectra of PANI/cotton composite fiber was showed in Figure 3.

![XRD spectra of cotton fiber and PANI/cotton composite fiber](image)

**Fig.3. XRD spectra of cotton fiber and PANI/cotton composite fiber**

The (002) plane of cotton was found to give maximum XRD peak around 2\(\theta\) values of 22\(^\circ\). Compared with the spectra of cotton fiber, the XRD spectra of PANI/cotton composite fiber had no significant change in the positions and shapes, meaning that there was not any change in the crystal structure. The (101) plane value was slightly shift to higher value and the shape was sharp. The reason was that after doped PANI macromolecular chain combined with cotton fiber, improving the crystal order of cellulose fibers and reducing structure defects of crystalline region\(^{[12]}\), which decreased amorphous region and increased crystalline region. It could be confirmed from the crystallinity change between cotton and PANI/cotton composite fiber. The degree of crystalline of untreated cotton substrate was (73.82±1)\%, while the crystallinity increased to (74.46±1)\% after polymerization.

3.4 Effect of oxidant concentration on properties of composite fabric
Chemical polymerization of aniline conforms to aniline radical cation. When it was doped with a protonic acid, the imine nitrogen atom on the polymeric chain of PANI could be protonated preferentially. Hydron which generated by protonic acid (HA) ionization move to the polymeric chain of PANI, and combine with the nitrogen atom on amine and imine, forming polaron and bipolaron, forming polaron and bipolaron, which would delocalize conjugated \(\pi\)-bonds of the whole molecular chain. As a result the PANI had high electrical conductivity\(^{[13]}\).

Different from some intrinsically conductive polymers (such as polypyrrole, polythiophene), PANI had three oxidation states\(^{[14]}\). These states were highly reduced (leucoemeraldine), half oxidized-half reduced (emeraldine base) and highly oxidized (pernigraniline). In polymerization, the color of PANI changed from yellow, then green, blue until to black, as the oxidative reaction procedure\(^{[15]}\). Among these, except leucoemeraldine and pernigraniline, only emeraldine base is capable of electrical conduction after undergoing protonation. The oxidative concentration will affect the characteristic of PANI/cotton composite fabrics.
3.4.1 Oxidant concentration effect on fabrics’ electrical conduction and weight gain rate of PANI. In same concentration, cotton fabrics were treated with monomer solution, until reached the maximum absorption. Then fabrics were sprayed oxidant solution (nAPS:nHCL=1:1.) with different concentration (range from 0.1 M to 0.5 M). Effect of oxidant concentration on the electrical conduction of fabrics and PANI weight gain rate were shown in Figure 4.

![Figure 4. Effect of oxidant concentration on fabrics' electrical conduction and PANI weight gain rate](image)

Figure 4 showed that with the increase of oxidant concentration, the weight gain rate of PANI on cotton’s surface increased. However, the surface resistivity diminished to 0.5 kΩ when oxidant concentration was 0.2 M. It was indicated that after promoting oxidant concentration from 0.2 M, the weight gain rate of PANI was proportional to surface resistivity of composite fabric.

When the concentration of oxidant was lower than 0.2 M, cation radicals generated less. It is not conducive to produce activity center on the fiber surface at the preliminary stage of the polymerization, less PANI finally obtained. However, as high oxidation ability of ammonium persulfate, on contacting with oxidation solution, the oxidated reaction on the fabric absorbed monomer began. Polymer generated is completely oxidized PANI in the early, and the form is called as emeraldine base which has no conductivity\cite{15,16}. With the reaction continue, oxidant is exhausted completely, and the rest monomer of aniline reduces emeraldine base to pernigraniline which has higher conductivity. It is the reason the fabric obtained high conductivity with low oxidant concentration.

The reaction mechanism was showed as Figure 5\cite{17}:

![Figure 5. The reaction mechanism of polyaniline oxidative polymerization](image)

With higher oxidant concentration, more aniline monomer was exhausted to participate in polymerization of emeraldine base, less in reducing reaction, resulted in lower conductivity of composite fabric with higher PANI weight gain rate.

3.4.2 Oxidant concentration effect on fabrics’ electromagnetic interference shielding. Oxidant concentration was set from 0.1 M to 0.5 M, under this condition, electromagnetic interference
shielding and surface resistivity of PANI/cotton composite fabrics were tested. The testing result was shown as Figure 6:

![Figure 6. Effect of oxidant concentration on electromagnetic interference shielding and surface resistivity](image)

It can be noted that with increasing of oxidant concentration, electromagnetic interference shielding of PANI/cotton composite fabrics diminished after 0.2 M. Moreover, the contrary tendency of surface resistivity curve could also be found in Figure 6. It could be obtained that the better electrical conduction, the higher electromagnetic interference shielding.

According to the Schekunoff theory\[^{[18]}\], shielding effectiveness is the sum of reflection, absorption and internal reflection of the electromagnetic wave by the shielding layer. The shielding effect metal is mainly reflection loss, while the shielding effect of PANI depends on internal reflection mostly. The material with a high electrical conductivity has a big absorption loss, the composition of shielding material could reduce the domain wall, obtaining the increased magnetic permeability. The thicker of the material was, the more absorption lost. When oxidant concentration increased from 0.2 M to 0.5 M, the surface resistivity of PANI/cotton composite fabrics increased to 300%, however, the shielding effectiveness fell 14% merely. Compare with the curve of PANI weight gain rate, it was easy to know, with the increase of oxidant concentration, the weight of PANI on the surface of the cotton increased. The augment of the thickness of conductive molecular layer resulted in the enlargement of magnetic permeability. Consequently, it obtained the slight decline of shielding effectiveness of PANI.

4. Conclusion

(1) The optimal oxidant concentration was 0.2 M, lowest surface resistivity of 0.5 kΩ and best electromagnetic shielding effectiveness up to 60% could be gained under this condition.

(2) Two-step in situ polymerization made the penetration of PANI monomer into the fiber easily, and ensured that the PANI/cotton composites fabrics had good conductivity and electromagnetic interference shielding.

(3) After polymerization, the crystal structure of PANI/cotton composited fabrics had not change. And the crystallinity rise to (74.46±1)%, because of improving the crystal order of cellulose fibers and reducing structure defects of crystalline region.

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