Polyaniline/Poly(ethylene terephthalate) Conducting Composite Fabric with Improved Fastness to Washing

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ABSTRACT: In this article, we report a novel method for the design and development of a polyaniline (PANI)/poly (ethylene terephthalate) (PET) conducting composite fabric based on *in situ* polymerization. With the aim of improving fabric–PANI adhesion and good fastness to washing, we took some special steps: the alkali reduction pretreatment of the PET fabric before the polymerization of aniline onto the fabric, the introduction of squeezing the laboratory padder on the fabric to push the reagent into the inner part of the fabric, and short immersion time of the aniline-absorbed fabric in oxidant solution. Factors affecting the conductivity and fastness to washing, including the alkali reduction percentage, the wet pickup of the reagent-absorbed fabric, the immersion time in oxidant solution, and the reaction time, are discussed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5775–5780, 2006

Key words: conducting polymers; composites; polyesters

INTRODUCTION

In recent years, among all conducting polymers, polyaniline (PANI) has emerged as an important class of electronic materials because of its ease of synthesis, high conductivity, and excellent stability. However, the unprocessability and poor mechanical properties of PANI are the major problems that hinder it from successful commercialization. These problems can be tackled by the development of conductive composites by the blending of conductive PANI with conventional polymers, such as polypropylene, poly(methyl methacrylate), and polystyrene, where in the conductive composites, the mechanical strength is provided by the conventional polymers and conductive PANI provides electrical conductivity. However, conductive composites obtained by blending are not so satisfactory because of the structural homogeneity problem and the aggregation of conductive material.[1] The processability of PANI can also be achieved by the coating of conducting PANI onto flexible substrate such as insulated fabrics, where the coated fabrics retains the flexibility of the conventional fabrics and the electrical conductivity of the conducting polymers. There have been reports of the coating of PANI onto fabrics. Dhawan et al.[2] reported the coating of PANI onto a certain kind of fabric and gained a shielding effectiveness of more than 35 dB. Jin and Gong[3] observed that the dispersion of poly(ethylene tereph-

thalate) (PET) filaments or nylon fabrics in aniline solution for some time before polymerization occurred could produce a PANI composite with improved adhesion and a high electric conductivity. However, the preparation procedure of the PANI composite was more or less the same: the fabrics or fibers were immersed in an aniline monomer solution of HCl or other acid for some time, and then, successive polymerization was initiated by the addition of an oxidant solution dropwise into the aniline solution. Polymerization was carried out at a low temperature, such as 5°C or lower, for 1 h or even longer.[2–8] After the reaction was finished, the composite fabrics were carried out, rinsed by HCl solution or water, and dried. However, this kind of preparation method has some shortcomings that need to be overcome. First, the polymerization took place in solution, and the fabrics with aniline absorbed on them were usually dipped in the oxidant solution for a long time. Hence, the aniline monomer absorbed came out from the inner of the fabric to the oxidant solution. Most PANI deposited in the solution and not on the fabric. The conductive ability of the fabric was not so ideal. Second, although some PANI did deposit on the fabric, there was just loose sedimentation on the surface, and firm adhesion did not occur. As a result, the fastness to washing was not satisfactory because fabrics were inevitably subjected to washing and rubbing in practice.

To solve such problems, we took some special steps to prepare PANI conducting composite fabrics by *in situ* chemical polymerization with PET fabrics as the substrate. First, we aimed for improved adhesion of PANI onto PET fabrics: the fabrics were pretreated

with alkali, and a rough surface was obtained before the polymerization. Second, after being immersed in an aniline solution, the fabrics were taken out and squeezed by a laboratory padder (see Fig. 1) to push the monomer into the inner part of the fiber by the mechanical pressure caused by the squeeze rolls of the padder. Third, to avoid the loss of aniline monomer caused by diffusion from the fabric to the oxidant solution, the squeezed and dried fabric with aniline absorbed on it was dipped in the oxidant solution for a very short time, taken out, and squeezed by the padder. The oxidant was pushed into the interstice and inner part of the fabric fiber and reacted with aniline monomers not only on the surface of the fabric but also in the inner part of the fabric fiber.

Kim et al.[9] prepared polypyrrole/PET conducting fabric by electrochemical polymerization after chemical polymerization to improve the conducting ability of their composite fabric. Although in the chemical polymerization the pyrrole monomer solution was sprayed onto the PET fabric and the fabric was squeezed by a two-roller mangle to ensure the uniform diffusion of pyrrole to the fabric, the effect of the squeezing conditions on the conducting ability of the composite fabric were not mentioned. That article was mainly concerned with how the chemical polymerization laid a solid foundation for the following electrochemical polymerization; the adhesion between polypyrrole and the PET fabric and the fastness to washing of the composite fabric was not considered. Actually, the squeezing conditions did have a great effect on the conducting ability. In this study, the most important problem was how to improve the adhesion between PANI and the PET fabric to obtain a good fastness to washing of the composite fabric; so, the squeezing conditions were systematically studied.

Also, the alkali reduction pretreatment had a great effect on the improvement of the adhesion, which was a key problem that we studied.

Some results are given here.

EXPERIMENTAL

Materials

Aniline and hydrochloric acid were used as received. Water was purified by distillation. Ammonium peroxydisulfate was selected as an oxidant for aniline. Dodecylbenzene sulfonic acid (DBSA) was used as the secondary dopant. PET fabrics were washed with detergent, rinsed thoroughly with water, and air-dried.

Alkali reduction pretreatment of the PET fabrics

PET fabrics with an initial weight of w_1 were treated at 95°C for certain time in a 0.25 mol/L aqueous sodium hydroxide solution, and the mass ratio of the sodium hydroxide solution to the fabric (liquor ratio) was 20 : 1. The contents were cooled to ambient temperature and neutralized with acetic acid. The pretreated fabrics were thoroughly rinsed with water and then washed twice with 5% acetic acid for 20 min. Finally, the fabrics were thoroughly rinsed, dried, and weighed. The weight after the alkali reduction pretreatment was denoted as w_2. The weight reduction percentage by alkali hydrolysis was determined gravimetrically and was calculated by the following equation:

$$\text{Reduction}(\%) = \frac{w_1 - w_2}{w_1} \times 100$$

In this experiment, the alkali reduction percentage was controlled by the adjustment of the alkali reduction time.
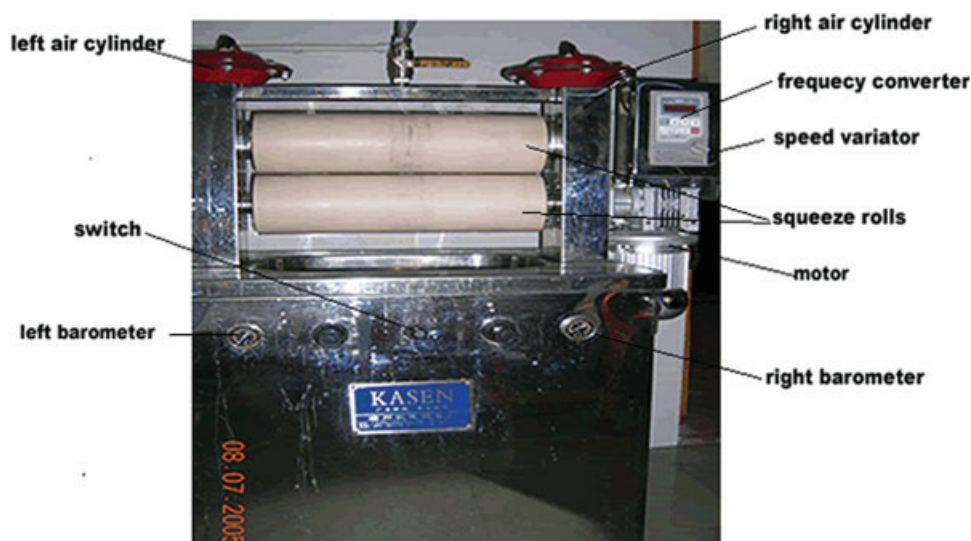
Figure 1 Laboratory two-roller padder. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Polymerization of the monomer onto the fabrics

The polymerization of aniline onto the PET fabrics was carried out by chemical oxidative polymerization. After immersion in a 0.75M solution of aniline in 1M hydrochloric acid for 10 min, the PET substrate was taken out, squeezed by the squeeze rolls of the laboratory padder (Fig. 1) to push the aniline monomer into the interstice and the inner part of the fabric, and finally dried at 80°C in a laboratory oven. Then, the whole process mentioned previously was repeated. The polymerization was initiated by immersion of the fabric in a 0.17M oxidant solution containing 1M HCl for a short time. The dipped fabric was taken out and immediately squeezed by the padder (Fig. 1) to push the reagent into the interstice and inner part of the fabric fiber by the mechanical pressure caused by the squeeze rolls. Then, the squeezed fabric was placed at ambient temperature to allow the polymerization to continue. After some time, the composite fabric was washed with a 1M HCl solution and then with distilled water and dried at 80°C in an oven. Finally, the fabric was doped with a 1M aqueous ethanol solution of DBSA with DBSA as a secondary dopant for 20 min, rinsed, and dried at 80°C in an oven. The ratio of water and ethanol by volume was 1 : 1.

After the fabric was squeezed, an amount of solution was picked up by the fabric, which is called wet pickup in the dyeing and finishing industry. The wet pickup is usually expressed as a percentage of the weight of the dry fabric:

$$\text{Wet pickup}(\%) = \frac{A_2 - A_1}{A_1} \times 100$$

where A_1 is the weight of the dry fabric before immersion and A_2 is the weight of the fabric after immersion and squeezing.

Surface conductivity measurement of the treated fabric

The surface conductivity of the PANI/PET conducting composite fabric was measured by a two-probe method with a multimeter, and the surface specific conductivity (ρ_s) was calculated according to the following equation:

$$\rho_s = RW/L$$

where W is the width, L is the length of the fabric sample and R is the resistance of the fabric sample according to the multimeter.

Measurement of the fastness to washing

The conducting fabric sample was subjected to a washing test as follows: the fabric sample was immersed in a detergent solution with a pH lower than 7 and with a liquor ratio of 30 : 1. The temperature was held at 40°C, and the fabric sample was washed in a washing machine at a normal rotation speed for 5 min. Then, the fabric sample was taken out, extracted to remove the detergent solution, rinsed in water for 2 min, and extracted. The mentioned procedure was repeated. Finally, the fabric was dried at 80°C in an oven. The surface conductivity measurement of the fabric was then carried out.

RESULTS AND DISCUSSION

Effect of the alkali reduction pretreatment

It was difficult for PANI to firmly deposit onto PET fiber due to the fiber's smooth and impact surface [see Fig. 2(a)].

To solve this problem and improve the adhesion between PANI and PET fiber, we introduced NaOH to pretreat the PET fabric. The hydrophobic PET fiber with a smooth and compact surface reacted with the NaOH solution at a certain concentration and at a certain temperature. Hydrolysis of the ester groups of the macromolecules on the surface of the PET fiber
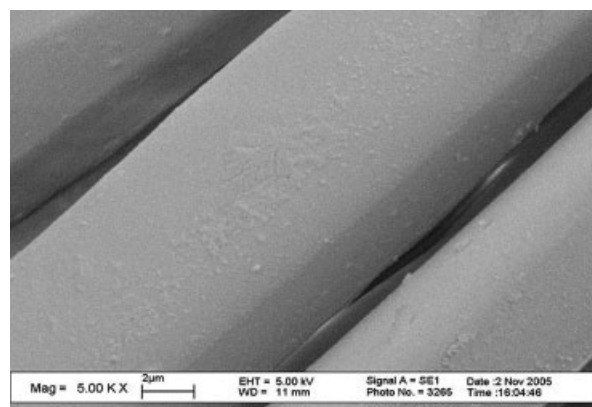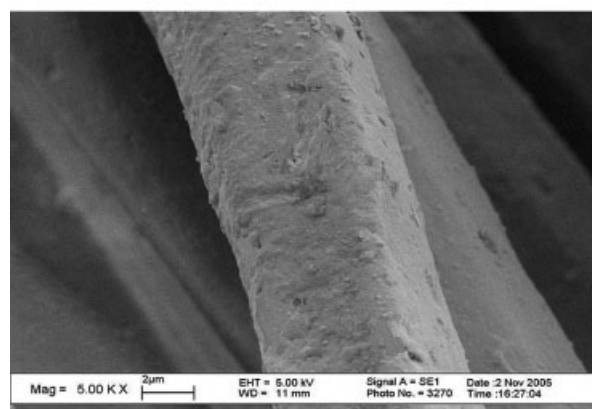
Figure 2 SEM micrographs of the PET fabric: (a) blank and (b) after alkali pretreatment.

occurred and produced hydrolysate. Eventually, the hydrolysate decomposed and dissolved in the solution, whereas the inner fiber was almost not affected by control of the reasonable alkaline condition and reaction time. After the alkali pretreatment, the smooth surface of the fiber became very rough; this was favorable for the adhesion between PANI and the PET fiber. Figure 2(b) shows the rough surface of the PET fiber after alkali treatment. The dissolution reaction of PET is represented in Scheme 1.

In the first step, OH^- in aqueous sodium hydroxide solution attacked $-\overset{\overset{\text{O}}{\|}}{C}-$ with a lower electron cloud density, and an intermediate was produced. In the second step, further reaction between OH^- and $-C-$ broke the macromolecular chain and produced $-COOH$ and $O^- -CH_2CH_2-$; the final product was $-COONa$ in alkaline solution.

The investigation showed that the alkali reduction pretreatment had a great influence on the ρ_s of the PANI/PET composite fabric, as shown in Table I.

ρ_s of the fabric without pretreatment of alkali was 1.06×10^4 Ω, and after washing, it became 2.56×10^6 Ω because of the smooth surface and compact structure of PET fiber; it was not easy for PANI to firmly deposit on it. When the polymerization reaction was finished, the PANI/PET conducting composite fabric prepared without alkali reduction pretreatment was rinsed in water, and we could see many green granules dropping off of it, whereas the fabric samples with alkali reduction pretreatment showed lower ρ_s and better fastness to washing. When the reaction was finished, the composite fabric with alkali reduction pretreatment was rinsed in water, and few dropping PANI granules could be observed. When the reduction percentage increased, ρ_s decreased constantly. However, when the reduction percentage was larger than 20%, ρ_s did not show an apparent decrease anymore. We suspected that by alkali reduction pretreatment, the smooth surface of the fabric fiber become rough, which was favorable to the deposition of PANI onto the fiber and improved adhesion between the fabric and PANI. However, excessive alkali reduction pretreatment would damage the struc-
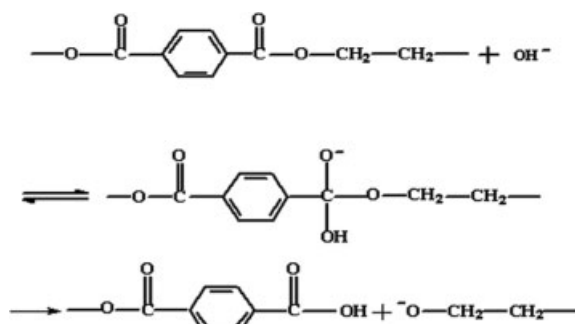
TABLE I
Effect of Alkali Reduction Pretreatment on ρ_s

| Reduction (%)	ρ_s (Ω)	ρ_s after washing (Ω)
0	1.06×10^4	2.56×10^6
4.4	9.51×10^3	8.61×10^5
9.1	2.89×10^3	9.84×10^4
14.8	5.45×10^2	7.23×10^3
19.3	3.92×10^2	4.52×10^3
25.8	3.03×10^2	4.32×10^3
30.0	4.76×10^2	5.17×10^3

ture of the fabric and do harm to the mechanical properties. With the strength and other mechanical properties of the fabric taken into consideration, a reduction percentage between 15 and 20% was appropriate. Moreover, improved adhesion between PANI and the rough surface of the fabric endowed the composite fabrics with improved fastness to washing. As shown in Table I, after washing, ρ_s of the fabric that was not pretreated by alkali increased sharply to 10^6 Ω by two orders of magnitude, whereas those with alkali reduction pretreatment increased only one order of magnitude when the alkali reduction percentage was about 9.1% or higher.

The effect of alkali reduction pretreatment on the PANI/PET conducting composite fabric is shown in Figure 3.

Figure 3(a) shows the SEM graph of the PET fabric without alkali reduction pretreatment with PANI deposited on it. The PANI that coated on the fabric was loosely deposited due to the smooth surface of PET fabric, and the conducting path was hard to form, whereas the alkali pretreated fabric with a uniform and coherent PANI coating showed good adhesion with PANI, and the conducting path was formed, as shown in Figure 3(b).

Immersion time in the oxidant solution

In our experiment, the aniline-absorbed fabric was dipped in the oxidant solution for some time before it was subjected to the squeeze rolls. The time of the aniline-absorbed fabric immersion in the oxidant solution was a key factor in the preparation of the PANI/PET conducting composite fabric, and the immersion indicated the start of polymerization. Table II shows the influence of the immersion time in the oxidant solution on the conductivity. Clearly, when the immersion time increased from 2 to 60 s, ρ_s increased sharply from 3.92×10^2 to 2.86×10^4 Ω. A short immersion time brought in a lower ρ_s. A long immersion time was disadvantageous to the polymerization on the fabric due to the fact that the aniline monomer absorbed by the fabric diffused into the oxidant solution, and the amount of PANI that formed on and in

Scheme 1
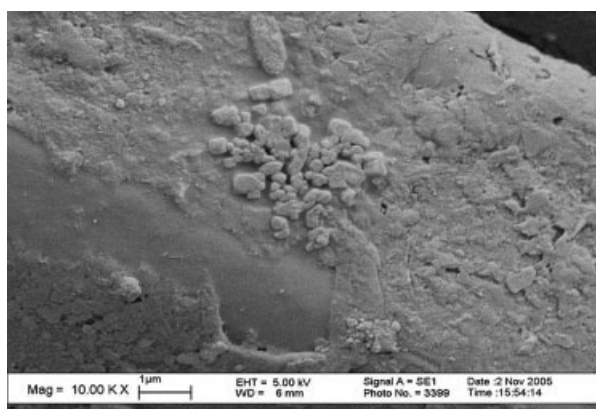
(a)
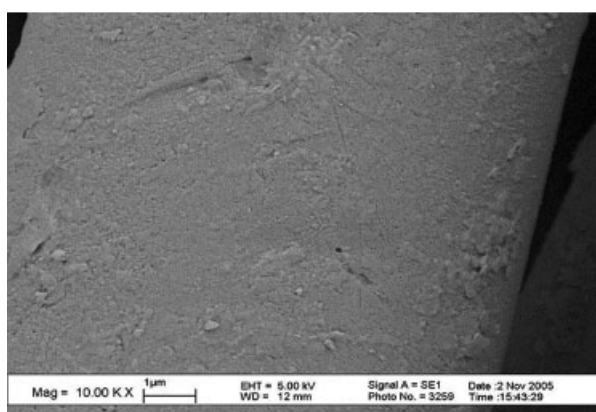
(b)

Figure 3 SEM micrographs of the PANI/PET composite fabric (a) without and (b) with alkali pretreatment.

the fabric decreased and caused a reduction in the conductive ability. In the preparation process, when the aniline-absorbed fabric was dipped in the oxidant solution for more than 5 s, the colorless oxidant solution became a little red, which was caused by the aniline monomer that diffused to the oxidant solution and was oxidized into a quinoid structure. When the immersion time was increased, the color of the oxidant solution gradually changed to green, and a lot of sediment was formed, which indicated that lots of aniline monomers diffused from the fabric to the oxidant solution and that polymerization occurred in solution. To overcome such drawbacks and to obtain a good

conductive ability, we reduced the immersion time in the oxidant solution. After being squeezed and dried, the fabric with aniline monomer absorbed on it was immersed in the oxidant solution for a very short time, taken out, and squeezed by the squeeze rolls to push the oxidant into the interstice and the inner part of the fabric fiber. As a result, the polymerization occurred on the fabric fiber but not in the solution.

Effect of the wet pickup of oxidant solution

After the procedure of immersion in aniline solution and drying was finished, the aniline-absorbed fabric was immersed in the oxidant solution for a very short time, taken out, and subjected to the squeeze rolls of the padder. The pressure between the squeeze rolls controlled the amount of oxidant solution absorbed by the fabric (wet pickup). The wet pickup had a great influence on the conductivity and fastness to washing of the fabric.

A shown in Table III, when compared with that of the squeezed fabrics, ρ_s of the one that was not squeezed was parallel with the squeezed ones with a wet pickup between 100 and 120%. However, this fabric sample possessed poor fastness to washing. As shown in Table III, after washing, ρ_s of the fabric that was not squeezed increased dramatically. We concluded that the squeezing played an important role in the improvement of fastness to washing. We assumed that when the immersed fabric was subjected to the squeeze rolls, the pressure of the rolls forced the reagent into the interstice and the inner fabric fiber. As a result, PANI formed in the interstice and the inner part of the fiber. When the fabric was subjected to washing and rubbing, the PANI was not likely to drop off. This implied an improved adhesion between PANI and the fabric.

Comparing fabric samples squeezed to different wet pickup, we found that a low wet pickup was not favorable to the formation of PANI/PET composite fabric with a good conductive ability. This could be explained by the fact that the polymerization of aniline to PANI was an oxidation polymerization, and too low amount of oxidant was disadvantageous to the formation of PANI with a high molecular weight. Hence, the composite fabric obtained with a low wet

TABLE II
Effect of Immersion Time in the Oxidant Solution on ρ_s

Immersion time (s)	ρ_s (Ω)
2	3.92×10^2
5	5.88×10^2
10	8.87×10^2
30	5.76×10^3
60	2.86×10^4

TABLE III
Effect of Wet Pickup on ρ_s

Wet pickup (%)	ρ_s (Ω)	ρ_s after washing (Ω)
Not squeezed	4.39×10^2	6.50×10^4
119	3.52×10^2	7.80×10^3
100	3.92×10^2	4.52×10^3
80	7.71×10^2	5.02×10^3
60	6.74×10^3	4.76×10^4
50	5.86×10^5	$> 10^7$

pickup showed a high ρ_s. When the wet pickup of oxidant solution increased from 50 to 80%, ρ_s dropped sharply from 5.86×10^5 to 7.71×10^2 Ω. However, when the wet pickup increased to higher than 80%, the ρ_s of the fabric samples was maintained at a certain level.

From both ways, a wet pickup between 100 and 120% was optimum according to our experimental results.

Reaction time

The immersion of the fabric in the oxidant solution was the beginning of polymerization, and the time that was taken in squeezing the fabric and placing it at ambient temperature to let the polymerization continue before rinsing with HCl and distilled water was the reaction time.

Table IV shows the effect of the reaction time on ρ_s. After 4 min, the fabric became green, but ρ_s was high because polymerization was not yet finished. With increasing time, ρ_s decreased. After 6 min, the polymerization was finished, and ρ_s became stable. Even when the fabric was placed in air for 60 min, ρ_s showed little change because the polymerization of aniline to PANI occurred very quickly at ambient temperature, which was initiated by ammonium peroxydisulfate. We noticed that the fabric squeezed by the padder almost have dried at ambient temperature when it was placed in the air for more than 1 h. Without water, the polymerization could not occur, so there was no need to prolong the reaction time. According to our experimental results, the polymerization was finished in 6 min, and we did not need to prolong the reaction time.

Effect of ethanol in the secondary doping acid

It is known that PANI/PET composite fabrics doped by HCl readily to lose their conductive ability when subjected to water. To improve the fastness to washing of the conducting composite fabric, DBSA was used as the secondary dopant. As shown in Table V, ρ_s of the fabric that was doped by an aqueous ethanol solution of DBSA was lower than that doped without ethanol.

TABLE IV
Effect of Reaction Time on ρ_s

Reaction time (min)	ρ_s (Ω)
2	8.50×10^4
4	3.58×10^3
6	3.92×10^2
10	4.21×10^2
20	3.80×10^2
60	5.34×10^2

TABLE V
Effect of Ethanol in the DBSA Solution on ρ_s

Solvent	ρ_s (Ω)
Without ethanol	1.07×10^3
With ethanol	3.92×10^2

This could be explained by the fact that DBSA is a viscous surfactant that can be used as detergent, and the aqueous DBSA solution was very foamy. Hence, ethanol was introduced as a secondary solvent[10] and defoaming agent. The addition of ethanol into the doping DBSA aqueous solution not only worked in defoaming but also enhanced the solubility of DBSA, which was favorable to the release of H^+ to dope.

CONCLUSIONS

In this study, a novel method of preparing PANI/PET composite fabrics by *in situ* polymerization was developed, and composite fabrics with good conducting ability and improved fastness to washing were prepared in a short time. The results show that the alkali reduction pretreatment on the fabric before the polymerization of aniline onto the fabric, the use of padder, a short immersion time in the oxidant solution, and the use of aqueous DBSA as secondary dopant with ethanol as a cosolvent helped to produce a PANI/PET conducting composite fabric with good conductivity, improved adhesion between the fabric and PANI, and enhanced fastness to washing. The optimum conditions for the preparation of the PANI/PET conducting composite fabric were a reduction percentage of the alkali reduction pretreatment between 15 and 20%, a wet pickup of oxidant solution between 100 and 120%, an immersion time in the oxidant solution of 2 s, a reaction time of 6 min, and a ratio of water to ethanol by volume of 1 : 1 in the secondary doping.

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