Preparation of Polyaniline/Nylon Conducting Fabric by Layer-by-Layer Assembly Method

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ABSTRACT: In this article, layer-by-layer assembly technology was used to prepare polyaniline (PANI)/nylon conducting fabrics. PANI/nylon conductive composite fabrics were prepared by deposition of polyanion (PSS) and polycation (aniline cation) alternately. The pretreatment with PSS was discussed. The influence of the reaction time, aniline concentration, acid concentration and assembly time on the conductivity, and K/S values of composite fabric was studied. The optical reaction condition of assembly should be: the concentration of PSS was 20 g/L, the PSS-treated nylon immersion in blended bath for 24 min, ammonium persulfate 0.1 mol/L, aniline 0.1 mol/L, p-toluene sulfonic acid 0.3 mol/L. In the end, the conductive composite fabrics were characterized by fourier transformed Infrared-attenuated total reflection spectroscopy and compared with pure nylon fabrics. At the same time, scanning electron microscopy, atomic force microscope (AFM), thermogravimetric analysis (TG), and mechanical properties were studied. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Since intrinsically conducting polymers, especially π-electron conjugate polymers, including polythiophene, polyaniline (PANI), and polypyrrole, were found in 1977 by MacDiarmid, Shirakawa, Heeger, et al,[1–4] they have been extensively studied for their promising applications. Among those organic conducting polymers, PANI is regarded as the most commercial promising conducting polymer because of inexpensive monomers, being easy to produce, high yield, and thermal, chemical stabilities.[5]

Recently, conductive textiles are widely used as filters, electromagnetic interference shielding materials, antimicrobial, and flame retardancy materials. Traditionally, conductive textiles can be produced either by coating of intrinsically conducting polymers, carbon, or by *in situ* polymerization of various monomers. Many quite valuable reports have been published about the electrically conductive textiles made by PANI, polyester (PET),[5] nylon,[6] and cotton.[7]

The layer-by-layer (LbL) assembly method, since it had been developed by Decher,[8] has become very popular over the past few years as it allows the fabrication of ultrathin, organized multilayers of polymeric materials. Decher's method can be outlined as charged substrate absorbing polyanion (PSS)/polycation

consecutively until the fabrication of the desirable films. Because the process only involves adsorption from solution, there are in principle no restrictions with respect to substrate size, which will offer prospects for many new applications not only in basic research but also in industrialization. Some researchers have used this method on textile substrates to achieve various properties, such as superhydrophobicity,[9] antibacterial,[10] and flame-retardant property.[11] The LbL molecular-level manipulation of conjugated polymers had been successfully used to fabricate ultrathin multilayer films.[12–15] Many reports have been illustrated PANI assembled on hydroxyl-terminated surfaces, such as quartz, glass, indium tin oxide, and native oxide on Si.[16] Unfortunately, no one use textiles as substrate to complete this assembly reaction.

Nylon is a kind of polymer with amide groups, which link together the segment of its polymer chain, and the amino groups and carboxylic acid groups. In the isoelectric condition, the fiber is neither positively nor negatively charged. If pH is under the isoelectric point, the fiber is positively charged, which can attract anions, such as PSS.

Our objective in this article is to develop a new and simple method to prepare PANI conductive fabrics by LbL assembly

method with nylon as substrate. The process involves the repeated dipping of nylon into the polyaniline solution followed by a solution of a PSS with rinsing in between each polymer deposition step. In this case, the cationic nature of partially doped polyaniline promotes multilayer assembly via the electrostatic attractions developed with the PSS.[14] Fourier transformed Infrared- Attenuated Total Reflection Spectroscopy, scanning electron microscopy (SEM), AFM, TG, conductivity, and strength of PANI/nylon composite were studied.

EXPERIMENTAL

Materials

We used a fluorescent whitening agents-free, 100% nylon weaving fabric (nylon taffeta, 210 T) with a density of 70D in the warp and 70D in the weft direction throughout this study.

Aniline, p-toluene sulfonic acid (PTS), hydrochloric acid, and ammonium persulfate (APS) are A. R. grade (analytical reagent) and provided by Shanghai Handa Chemicals, P. R. China.

PSS solution is provided by Shanghai Xirun Chemicals, P. R. China with average molecular weight 5000–60,000.

Activation of the Substrates

The nylon fabrics were first washed with deionized water, and later treated with aqueous HCl (pH = 3.5) for 5 min to create the positively charged surface. Such substrates were preserved in deionized water before the deposition of in situ self-assembled LbL films.[17]

PSS-Treated Nylon

The sodium salt of poly(styrene sulfonate) (PSS, M_w: 5000–60,000) at a certain concentration was dissolved in water, and adjusted to pH 1 by addition of HCl. The positively charged substrate was dipped into PSS solution for 10 min to obtain a negatively charged surface. 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 was called "two-dip two-nip" process. After the fabric was padded, an amount of solution was picked up by the fabric, which was called pickup in the dyeing and finishing industry. The pickup was calculated as follows:

$$Pickup\% = (A_2 - A_1)/A_1 \times 100\% \qquad (1)$$

where A_1 was the weight of the dry fabric before immersion and A_2 was the weight of the fabric after immersion and padded.

The padded fabrics were dried at 60°C for 10 min, and then washed in a large amount of deionized water. Afterward, the fabrics were dried. The PSS-coated substrate was suitable to fabricate the PANI film, where simultaneous polymerization of the aniline monomer and oxidation of the PANI molecules occurred.

In Situ LbL Assembly of PANI on PSS-Treated Nylon

The polymerization of aniline onto the PSS-treated nylon was carried out by chemical oxidative polymerization. The active

solution for PANI contained the oxidizing agent APS and PTS, followed by the addition of aniline monomer. The various concentrations of the dipping solutions of aniline monomer along with PTS and APS were tested. The active solution was stirred after the addition of the aniline monomer. Such solutions were used for the deposition of the PANI film. A single layer of PANI was obtained in several minutes by the in situ polymerization. Alternating the dipping of the protonated substrate in PSS and PANI solutions produced bilayered structures. The alternate bilayers of PSS/PANI were fabricated by dipping the protonated substrates in PSS solution for 5 min, and several minutes in PANI active solution followed by washing and drying in each step of deposition. After each immersion in PSS solution, the substrate was taken out, padded by the squeeze rolls of the laboratory padder with take-up 70% and then immersion in PANI solution. The 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 PTS as a secondary dopant for 30 min, rinsed, and dried.[7]

Surface Conductivity Measurement of the Treated Fabric

The surface conductivity of the PANI/nylon conducting composite fabric was measured with a multimeter. Ten readings at different locations were taken randomly and carefully and the average was recorded. The conductivity (σ) was calculated according to the following equation:

$$\sigma = 1/(L \times R) \qquad (2)$$

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[7] and then reflects the LbL assembly reaction process.

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.

Morphology

The morphology of surfaces of composites was examined with a Hitachi TM-1000 SEM at an accelerating voltage of 15 kV. The surfaces were coated with thin layers of gold before the observation.

The surface morphologies and surface roughness of the samples were characterized by an AFM (NanoScope IV) in air under ambient condition, and the characterization was made in a non-contact mode.
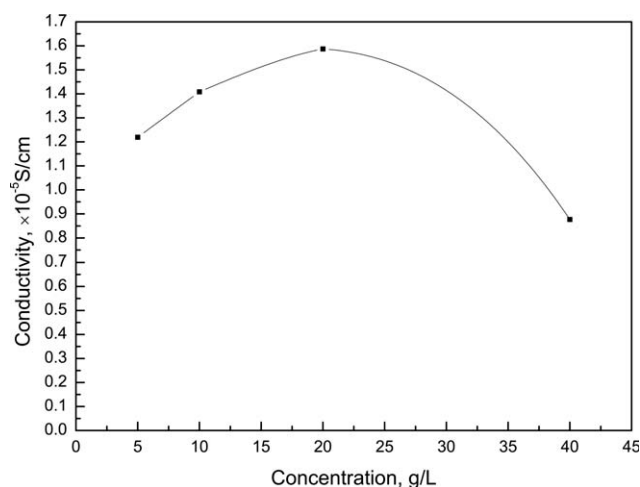
Figure 1. Effect of concentration PSS solution on conductivity.

Table I. Effect of Concentration PSS Solution on K/S Value

The concentration of PSS (g/L)	The maximum K/S value
0	15.308
5	21.625
10	25.336
20	27.079
40	24.900

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 fabric was measured with China National Standard GB/T 3917.2-1997[18] by Elmendorf tearing tester (Thwing-Albert).

RESULTS AND DISCUSSION

Influence of Concentration of PSS on Conductivity

Nylon fabric contains primary amino groups and carboxylic acid groups situated at the ends of the polyamide chains —CONH—. The nylon exists in specific ionic states according to the pH of the surrounding aqueous solution. Below pH 3.5, nylon behaves as if it possesses a net positive charge and exhibits a strong attraction for anions such as sulphonated groups.[19] Before immersed in PSS solution, treated the nylon fabric with acid made it show strong attraction for PSS.

The effects of different concentration of PSS as polyelectrolyte for the LbL assembly *in situ* polymerization were investigated. The nylon fabric first was immersed in PSS solution with concentration ranges from 0 to 40 g/L for 10 min. Then, the PSS-treated nylon was immersed in bath composed with APS 0.1 mol/L, aniline 0.1 mol/L, and PTS 0.2 mol/L for 20 min. The composite fabric was padded and dried at 60°C for 10 min. Then, the treated fabric was immersed in 1 mol/L of PTS as a secondary dopant for 30 min. It can be seen from Figure 1 that the maximum conductivity obtained was for the PSS at a 20 g/L concentration. As PSS concentration increased, the attraction of the PSS molecules onto the fiber surface and the trend to formation of PANI on the surface of nylon fabric also increased, which led to a higher conductivity.

To monitor the LbL deposition of the PANI, we used the K/S value provided by a spectrophotometer. This K/S value is calculated from the reflectance and scattering data and is commonly used in textile-related research to characterize the amount of dye fixation on the fiber. Higher dye content leads to an increase in absorbance, and therefore to a lowering of the reflec-

tance of the corresponding wavelength. PANI has a shade of dark green color. The formation of PANI on nylon surface can be illustrated by the K/S value. As can be seen from Table I, K/S value increased with the concentration of PSS increasing from 5 to 20 g/L and then decreased from the maximum value of 27.079. The corresponding relations between K/S values and conductivity were compatible. The optimal concentration of PSS should be 20 g/L.

Influence of Dipping Time of PSS-Treated Nylon in Blended Solution on Conductivity

The nylon fabric was immersed in 20 g/L PSS solution for 10 min. Then, the PSS-treated nylon was immersed in the blended solution with dipping time ranging from 4 to 26 min. The blended solution composed with APS 0.1 mol/L, aniline 0.1 mol/L, and PTS 0.2 mol/L. The composite fabric was padded and dried at 60°C for 10 min and then, was done second dopant. The effect of dipping time of PSS-treated nylon in blended solution on conductivity was shown in Figure 2, which showed that the conductivity increased significantly as the reaction time increased, and a further increase in the reaction time decreased the conductivity. The maximum conductivity was obtained at 24 min, and there was little change after 22 min. In the first stage, it seemed that PANI was mainly polymerized in the outer layer of nylon 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
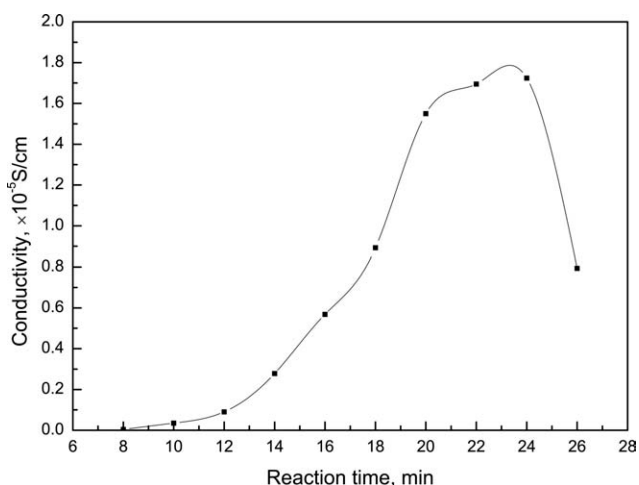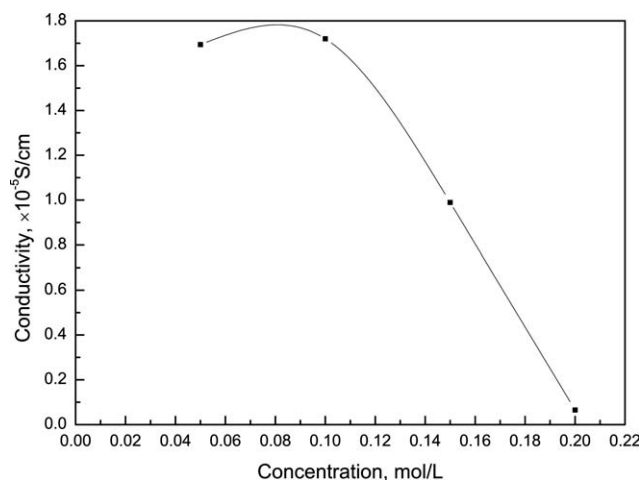

Figure 2. Effect of dipping time of PSS-treated nylon in blended solution on conductivity.

Table II. Effect of Dipping Time of PSS-Treated Nylon in Blended Solution on K/S value

Reaction time (min)	The maximum K/S value
4	1.312
6	2.336
8	4.268
10	6.833
12	8.053
14	9.587
16	11.497
18	14.406
20	27.079
22	26.463
24	25.053
26	18.748

Table III. Effect of Concentration of Aniline on K/S Value

The concentration of aniline (mol/L)	The maximum K/S value
0.05	17.224
0.1	25.053
0.15	21.418
0.2	14.310

change after 22 min in the conductivity could be explained by this phenomenon. Taken measuring error of electrical resistance into account, it could be considered that PANI obtained maximum absorption on fabric as reaction time exceeded 24 min. Thus, 24 min was selected for the experiments.

Table II showed that K/S value increased until maximum value obtained at 24 min and then decreased, which was in accordance with that effect on conductivity. The difference of K/S value was suggested to be due to the changing color of the solution during different polymerization stages. The chain initiation started with the addition of APS, which resulted in the color of active solution for PANI being darkened gradually. The temperature increased after 10 min, and the color of solution changed from violet to blue until it turned to dark blue and presented luster on the surface. The above process experienced chain growth during oxidative polymerization—an exothermic process. As the chain termination process occurred, the temperature began to fall after 20 min along with the color of solution turning to dark green. Therefore, all of the experiments were performed at 24 min.

Influence of Concentration of Aniline on Conductivity

The PSS-treated nylon was immersed in the blended solution for 24 min. The blended solution was composed with aniline ranging from 0.05 to 0.2 mol/L, APS with the same mol ration as aniline, and PTS 0.2 mol/L. The composite fabric was padded and dried at 60°C for 10 min and then, was done second dopant. The conductivity of PANI depends on the oxidation degree of PANI, which is mainly determined by the molar ratio of oxidant/aniline. The effect of concentration of aniline on conductivity was shown in Figure 3, where the highest conductivity was obtained at 0.1 mol/L. A continuous increase in the concentration of aniline resulted in a decrease adversely on conductivity. This behavior can be illustrated by that when the concentration of aniline monomer increased to the certain extent, the PANI chain would not keep growing and tend to be over oxidation, which was not conducive to the formation of high conductivity of PANI. As listed in Table III, the K/S value increased first and then decreased with the increase of the concentration of aniline. The concentration of PSS reaching the maximum on K/S value was corresponding to that effect on conductivity, which indicated that the color yield of fabric could be characterized by the level of conductivity. The concentration of aniline was chosen to be 0.1 mol/L.

Influence of Concentration of PTS on Conductivity

The PSS-treated nylon was immersed in the blended solution for 24 min. The blended solution composed with aniline 0.1 mol/L, APS 0.1 mol/L, and PTS ranging from 0.1 to 0.5 mol/L. The composite fabric was padded and dried at 60°C for 10 min and then, was done second dopant. Acidity plays a critical role
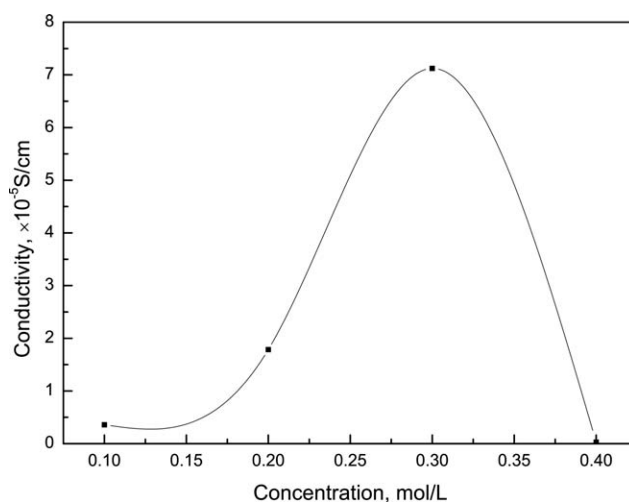
Figure 3. Effect of concentration of aniline on conductivity.

Figure 4. Effect of concentration of PTS solution on conductivity.

Table IV. Effect of Concentration of PTS on K/S Value

The concentration of PTS (mol/L)	The maximum K/S value
0.1	17.898
0.2	25.053
0.3	27.111
0.4	9.643

Table V. Effect of Assembly Times of Composite Fabric on K/S Value

Assembly times	The maximum K/S value
1	27.111
2	28.051
3	30.464
4	23.544

in the preparation of the PANI, for acid has two main functions here: one is to provide acidic environment for reaction medium; the other is to participate in reaction as doped acid and impart conductivity to PANI. Figure 4 showed that the conductivity of composite fabrics reached its highest value at 0.3 mol/L and decreased at concentration higher than that. This behavior was attributed to the fact that when the acidity was low at first, the aniline was polymerized by two means—head to tail and head to head which led to low reaction efficiency and poor conductivity. As the increasing concentration of H^+, the aniline was polymerized only by the form of head to tail which caused rapid increase in conductivity. However, H^+ 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^+ was not removed from the cation, the oligomer could not grow and dissociates with hydrolysis. The conductivity of composite decreased sharply at higher acid concentrations was explained with this. Furthermore, PTS as a doped acid obtained maximum conductivity and K/S value among various organic acids, for it was conducive to the delocalization of charge by decreasing the interaction of PANI molecules. On the basis of above discussion, a PTS concentration of 0.3 mol/L was selected for the experiment. Besides, the K/S value possessed similar trends with conductivity as shown in Table IV.

Influence of Assembly Times of Composite Fabric on Conductivity

The PSS-treated nylon was immersed in the blended solution for 24 min. The blended solution composed with aniline
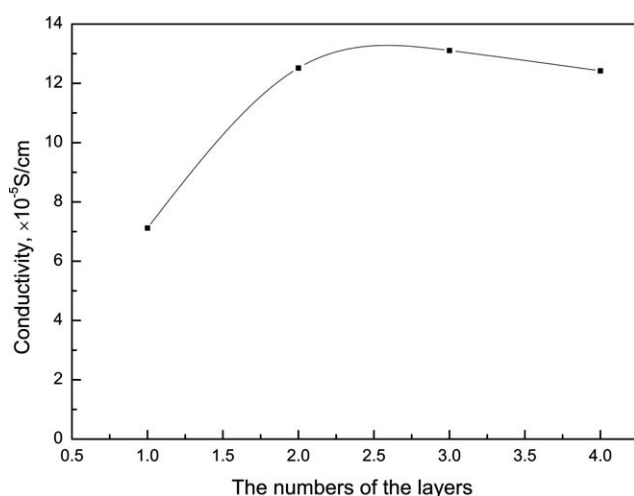
0.1 mol/L, APS 0.1 mol/L, and PTS 0.3 mol/L. The composite fabric was padded and dried at 60°C for 10 min and then, was done second dopant. A multi-assembly composite fabric can be prepared by repeating the above fabricated method. Figure 5 and Table V showed that the conductivity increased with the number of assembly times, which implied that the nylon absorbed more amount of PANI. However, the conductivity began to decrease with assembly times exceeding four. This phenomenon was attributed to over oxidation by APS when composite fabric had attained saturated absorption.

FTIR-ATR Study

Compared to Figure 6(a), not only the characteristic peaks of nylon, but also those of polyaniline could be noted obviously in Figure 6(b). The wide and strong peak at 3295.8 cm^{-1} in Figure 6(b) was assigned to N—H stretching vibration. The band observed at 1490.73 and 1540.87 cm^{-1} corresponded to C—C and C=N group in the benzenoid and quinoid structures in PANI, respectively. The band at 1305.59 cm^{-1} was attributed to C—N stretching, and the band at 804.18 cm^{-1} was characterized as 1,4-substituted phenyl stretching, which were identical to the emeraldine salt from PANI.[20]

The band at 1540.87 cm^{-1} in Figure 6(b) became wider compared to (a). This phenomenon was because part of positive charge of —N^+H— delocalized on benzene ring, which resulted in decrease in electron density of aromatic ring and vibration frequency. The conjugation effect due to rearrangement of electron cloud also was the reason. Therefore, it was assumed that
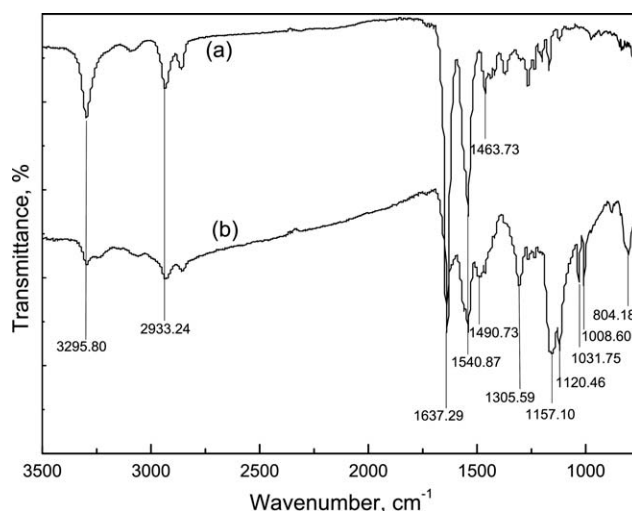

Figure 5. Effect of assembly times of composite fabric on conductivity.

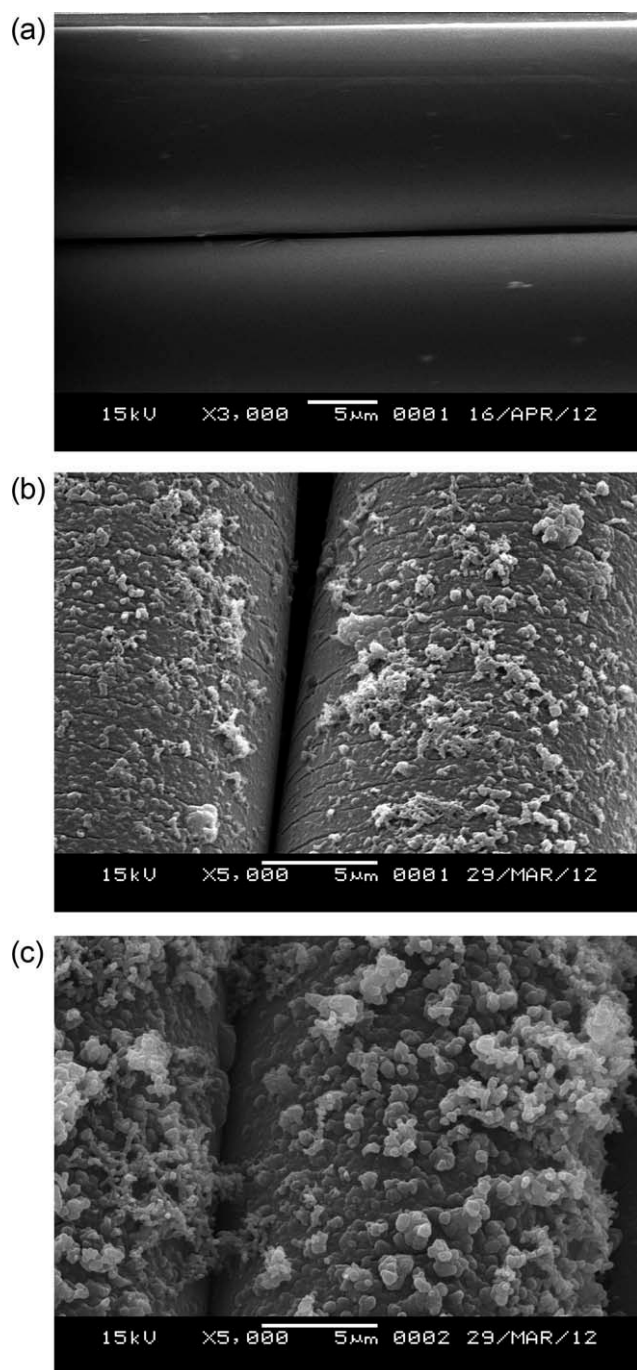**Figure 6.** FTIR-ATR spectra of (a) nylon fabric, (b) PANI/Nylon composite fabric.

Figure 7. SEM of (a) nylon fabric, (b) PANI/Nylon composite fabric, one cycle of LbL, (c) PANI/Nylon composite fabric, four cycles of LbL.

seen from Figure 7(b), the surface exhibited a rough but coherent PANI coating and the conducting path was formed, which made the composite fabric had good conductivity. Compared to Figure 7(b), Figure 7(c) shows that more PANI coated on the surface of Nylon fabric because it undergo four cycles of assembly.

AFM images of pure nylon, PANI/Nylon composite fabric (one cycle of LbL), and PANI/nylon composite fabric (four cycles of LbL) are shown in Figure 8. Untreated nylon has flat surface, which becomes rougher after the one cycle of LbL. PANI/nylon
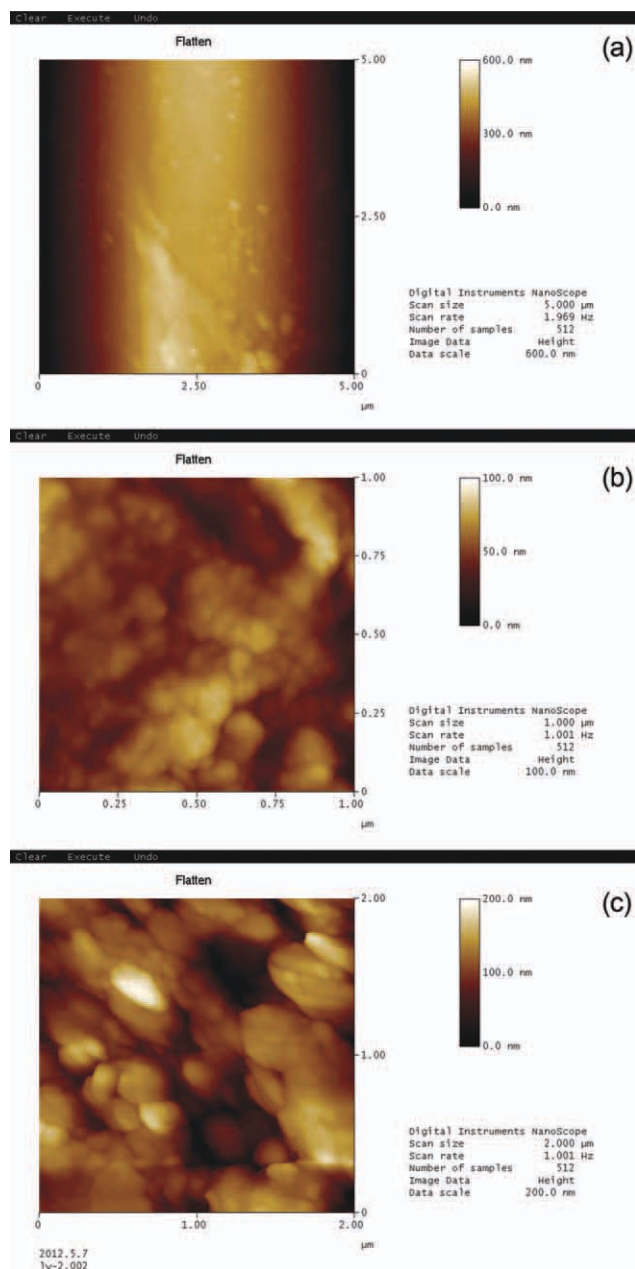

Figure 8. AFM images of (a) nylon fabric, (b) PANI/Nylon composite fabric, one cycle of LbL, (c) PANI/Nylon composite fabric, four cycles of LbL. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the overlap of the electron cloud resulted in the formation of the conjugated structure of polyaniline doped with proton acid, which contributed to the conductivity of the polyaniline.

Morphology

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 7. The morphology of Nylon fiber changed dramatically due to the addition of PANI. It can be

with four cycles of LbL shows many isolated rough spots, which are even larger than those found on PANI/nylon with one cycle of LbL.

TG Analysis

In Figure 9, the thermal stability of PANI/nylon composite fabric was compared with those of pure nylon. Pure nylon and PANI/nylon decomposed at 395.1 and 394.8°C, respectively. The composite fabrics doped by PTS were significantly damaged, as indicated by reduction of the temperature of maximum rate of degradation ($T_m = 408$°C) compared to that of the pure nylon fabrics ($T_m = 438$°C) because strong acid deteriorated the nylon substrate. The residue left at 550°C increased for the PANI/nylon composite fabric (residue 20.97%) in comparison with that of the pure nylon fabric (residue 7.60%). PANI/nylon composite fabric showed a small initial weight loss between 100 and 300°C, which is attributed by the evaporation of water and the loss of dopant. The major weight loss observed between 300 and 500°C in sample is the decomposition of nylon and PANI backbone.

Tear Strength

The composite fabric was prepared by the optimal conditions: APS 0.1 mol/L, aniline 0.1 mol/L, PTS 0.3 mol/L, immersion in blended bath for 24 min, assembly times three. Table VI showed that the tear strength of composite fabric reduced in comparison with pure nylon. PSS and polycation may cause damage to the hydrogen bond of nylon molecular because crystallinity reduced. This was the reason why the tear strength of composite fabric reduced. So how to reduce the chemical damage to composite fabric should be studied further.

CONCLUSIONS

In this article, LbL assembly technology was used to prepare polyaniline/nylon conducting fabrics. Polyaniline/nylon conductive composite fabrics were prepared by deposition of PSS and polycation (aniline cation) alternately. First, the pretreatment with PSS was discussed, and then the influence of the reaction time, aniline concentration and acid concentration, assembly

Table VI. Tear Strength of Pure Nylon and PANI/Nylon Composite Fabric

	Nylon	PANI/Nylon
Warp (mN)	19,111.2	14,780.6
Weft (mN)	11,987.65	10,198.95

times on the conductivity, and K/S values of composite fabric were studied, and the optimal reaction condition was determined. The optical reaction condition of assembly should be: the concentration of PSS was 20 g/L, the PSS-treated nylon immersion in blended bath for 24 min, APS 0.1 mol/L, aniline 0.1 mol/L, PTS 0.3 mol/L. The conductive composite fabrics were characterized by FTIR-ATR, SEM, AFM, TG, and mechanical properties were compared with nylon fabrics. The band at 1540.87 cm^{-1} in FTIR-ATR of polyaniline/nylon fabric became wider compared to pure nylon.

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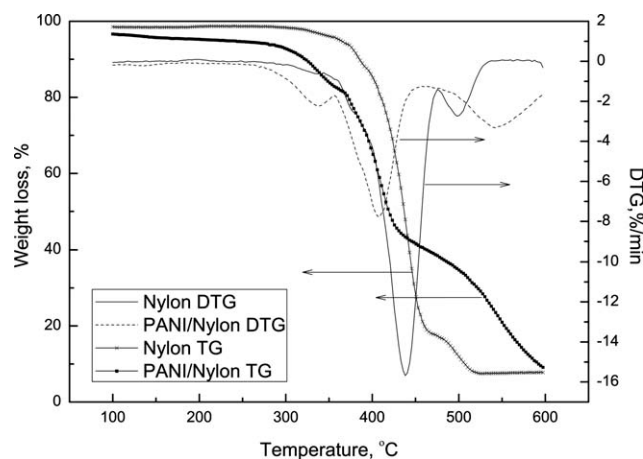
Figure 9. Thermogravimetric analysis curves of the samples.