

Conductive Fibers Based on Poly(ethylene terephthalate)–Polyaniline Composites Manufactured by Electrochemical Polymerization

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ABSTRACT: A novel method of manufacturing composite conductive fibers was developed through electrochemical polymerization with an apparatus consisting of insulating fibers, cotton fabrics as electrolytic solution holders, an electrolytic solution, and planer electrodes. By this method, poly(ethylene terephthalate) (PET) fibers coated with polyaniline (PAN) were prepared readily and yielded PET–PAN composite conductive fibers (PPCFs). The content of PAN in PPCFs increased with an increase in both the aniline concentration in the electrolytic solution and the polymerization voltage, although it did not depend on the load applied to the electrodes. Observations of the PPCF surface by scanning electron microscopy confirmed that the formation pro-

cesses of PPCFs could be divided into three steps: (1) fine (nanometer-size) granular PAN was generated from the anode and adsorbed onto the PET fiber surface, (2) the size of the granular PAN increased up to about 90 nm in a short time, and (3) the granular PAN was linked together to form networks. The conductivity of PPCFs increased with an increasing content of PAN networks. The surface resistance of the PPCF fabric was about $3 \times 10^5 \Omega/\square$ at a PAN content of approximately 2 wt %. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1073–1078, 2003

Key words: polyesters; conducting polymers; composites; coatings; electrochemistry

INTRODUCTION

Conductive polymers have widely been applied in various industrial fields. The preparation of fibers from conductive polymers allows their range of use to be expanded. For example, conductive fibers have been used in electromagnetic wave attenuation,^{1,2} static dissipation,² and chemical sensing.³

Because conductive polymers are usually infusible and insoluble, conductive fibers have been prepared by unique techniques.^{4–8} Techniques based on the coating of conductive polymers onto insulating fibers should be noted in terms of the facility and low cost of the preparation. Fibers coated with conductive polymers have mostly been prepared by the polymerization of aniline or pyrrole in a solution with oxidizing agents in the presence of fibers.^{9–13} With this technique, conductive polymers are deposited on the fiber surface.

However, there have been few studies using an electrochemical method for the preparation of insulating fibers coated with conductive polymers, except for conductive carbon fibers,^{14–16} which could also be em-

ployed for electrodes. Bhadani and coworkers^{17–20} prepared conductive fibers with cylindrical platinum electrodes. Insulating fibers were wound around the anode, and the polymerization was carried out in an electrolytic cell charged with a solution of aniline in aqueous HBF₄.

Here we report a novel system for preparing the conductive fibers electrochemically with the apparatus illustrated in Figure 1. In this system, insulating fibers, cotton fabrics as electrolytic solution holders, and an electrolytic solution were held between planer electrodes. A load was applied to an electrode, and a current was impressed. This method had advantages in the simplicity of the system and no limitation on insulating fiber materials. In this study, the effects of the load, voltage, and monomer (aniline) concentration on the properties of composite fibers and on the formation mechanism of polyaniline (PAN) coatings were investigated.

EXPERIMENTAL

Materials and reagents

Aniline (Kishida Chemical, Osaka, Japan) and water were purified by distillation. Hydrochloric acid (HCl; Kishida Chemical) of a special reagent grade was used as received. Carbon plates (100 mm × 100 mm × 5

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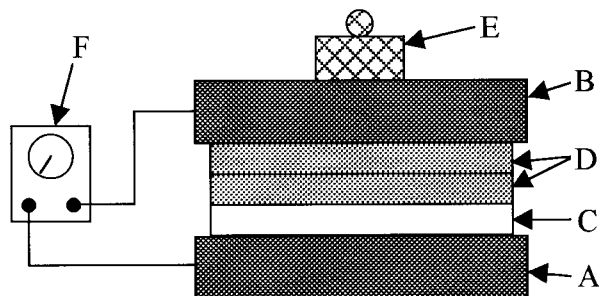


Figure 1 Outline of the apparatus: (A) anode, (B) cathode, (C) PET fabric, (D) cotton fabrics, (E) load, and (F) direct-current power supply.

mm; Yamamoto–Metkishikenki, Tokyo, Japan) were employed as electrodes. Poly(ethylene terephthalate) (PET) fabrics (fineness = 114 μm ; warp density = 210 ends/5 cm; weft density = 191 ends/5 cm; plain weave) and cotton fabrics (warp fineness = 275 μm ; warp density = 141 ends/5 cm; weft fineness = 220 μm ; weft density = 135 ends/5 cm; plain weave) were obtained from the Japanese Standards Association (Tokyo, Japan). PET fabrics were rinsed with methanol before use.

Processing method

PET fabric (100 mm \times 100 mm) and two sheets of cotton fabric (100 mm \times 100 mm) were placed on the anode. The electrolytic solution, prepared by the addition of aniline to 0.5N HCl, was poured on fabrics sufficiently. The cathode was placed on the cotton fabric, and a load was applied to the cathode, as shown in Figure 1. The polymerization was carried out from 2.0 to 3.5 V at room temperature with a direct-current power supply. After the polymerization, the carbon plates and cotton fabrics were taken off, and the PET fabric was rinsed with water and then dried in a hot-air dryer at 80°C. The same process was repeated for the untreated side of the PET fabric. After the completion of the polymerization, the fabric was washed with water, soaked in 0.5N HCl for 5 min, and dried in a hot-air dryer at 80°C. The PET fabric was colored green. The processing time was determined as the total polymerization time in a series of operations. For the next processing, the anode surface was polished with emery paper for the removal of PAN adhering to the anode.

Measurements of the ratio of the electrolytic solution to the fabric

The weight of the whole apparatus in a dry state (W_{DA}) was measured. The electrolytic solution was poured on the fabrics. After a load was applied to the electrode, the apparatus was left for 1 min. The oozing electrolyte was wiped out, and the whole apparatus

weight in a wet state (W_{WA}) was measured. The ratio of the electrolytic solution to the fabric was calculated as follows:

Electrolytic solution ratio to fabric

$$= (W_{WA} - W_{DA})/W_F \quad (1)$$

where W_F was the weight of the PET fabric.

Measurements of the PAN content

After the composite fabric was dried in a hot-air dryer at 105°C for 30 min, the weight (W_P) was measured. The PAN content in the composite fabric was calculated as follows:

$$\text{PAN content (wt \%)} = (W_P - W_N)/W_N \times 100 \quad (2)$$

where W_N was the dried weight of the untreated PET fabric.

Measurements of the surface resistance

The surface resistance of the composite fabric was measured with a Yokogawa–Hewlett–Packard 4329A high-resistance meter (Tokyo, Japan) when the surface resistance was greater than $2 \times 10^6 \Omega/\square$ and with a Hioki (Nagano, Japan) digital hi tester when the resistance was lower than $2 \times 10^6 \Omega/\square$. In both cases, a Yokogawa–Hewlett–Packard 16008A electrode was employed.

Scanning electron microscopy (SEM)

The PET–PAN composite conductive fiber (PPCF) surface was observed with a Hitachi S-800 scanning electron microscope (Tokyo, Japan) operating at 10 kV after being coated with Pt and Pd. The average size of granular PAN, except for other forms (fiber, rod, or network), on a PET fiber was estimated from the SEM micrographs.

Durability tests of the composite fabrics

A washing test was performed by the composite fabric being washed with water for 5 min. A rubbing test was achieved with a color fastness tester (Showa Juki, Tokyo, Japan). A PPCF fabric was rubbed horizontally with an untreated PET fabric at a 4.9-N load, 20°C, and 65% relative humidity.

RESULTS AND DISCUSSION

To obtain uniform PPCF fabrics with the apparatus shown in Figure 1, we needed to solve two problems. One problem was that sufficient amounts of the elec-

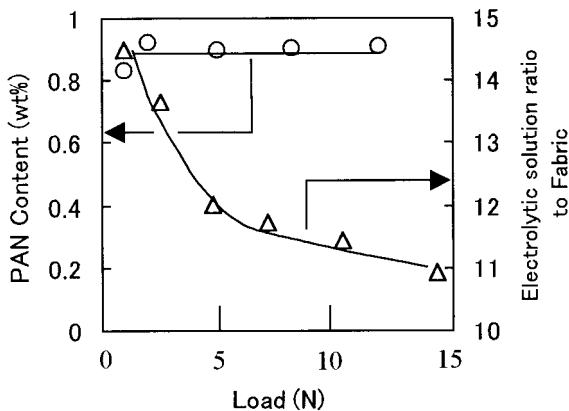


Figure 2 (○) PAN content of the composite fabric (aniline concentration = 0.05 mol/L; polymerizing voltage = 2.4 V; processing time = 12 min) and (△) the ratio of the electrolytic solution to the fabric versus the load.

trolytic solution had to be held between the electrodes. This was accomplished with cotton fabrics as electrolytic solution holding materials. When the fiber sample could hold the electrolytic solution sufficiently, the cotton fabrics were not necessary. Second, the PET fabric and the anode had to be close enough to each other. This was achieved by the application of a load to the electrodes.

The effects of the load applied to the electrodes on the PAN content in the PPCF fabrics and the ratio of the electrolytic solution to the fabric are shown in Figure 2. Because the PAN contents in the PPCF fabrics did not depend on the load, the PET fiber and anode were close enough to form PAN on the fiber surface even at a low load. As the load increased, the ratio of the electrolytic solution to the fabric decreased, suggesting that the amount of the electrolytic solution between the electrodes decreased with the load.

Figure 3 shows the relationship between the polymerization voltage and the PAN content in a PPCF fabric. The PAN content reached the maximum value

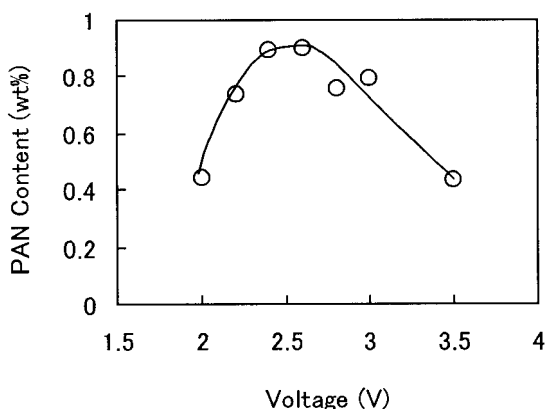


Figure 3 PAN content versus the voltage for the composite fabric (aniline concentration = 0.05 mol/L; load = 4.9 N; processing time = 12 min).

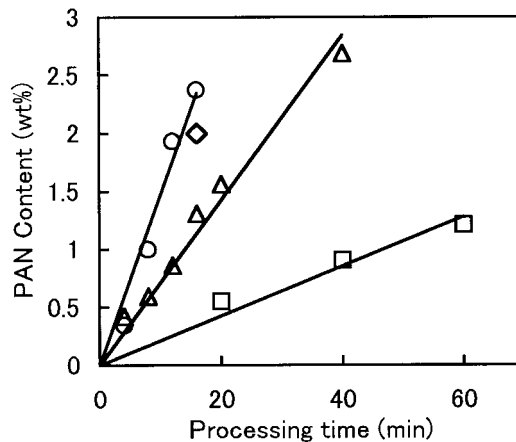


Figure 4 PAN content versus the processing time for the composite fabric prepared with (◇) 0.2, (○) 0.1, (△) 0.05, and (□) 0.025 mol/L aniline (polymerizing voltage = 2.4 V; load = 4.9 N).

at 2.6 V. At lower voltages, it was concluded that the slow rate of PAN formation made the PAN content decrease. At higher voltages, the evolution of bubbles was observed to increase at the gap between the electrodes. The amount of the hydrogen gas generated from the cathode increased with increasing voltage. The gas restricted the formation of PAN on PET fibers because the accumulated gas induced the formation of spaces between the PET fibers and the cathode.

The PAN content linearly increased with the processing time, as shown in Figure 4, suggesting that the generated PAN was quantitatively adsorbed onto the PET fiber surface. The rate of PAN formation increased with increasing aniline concentration in the electrolytic solution, except for 0.2 mol/L. The PAN content at the processing time of 16 min has been plotted as a function of the aniline concentration in Figure 5. The PAN content linearly increased with aniline concentrations of 0.025–0.1 mol/L. However, the PAN content decreased at an aniline concentration

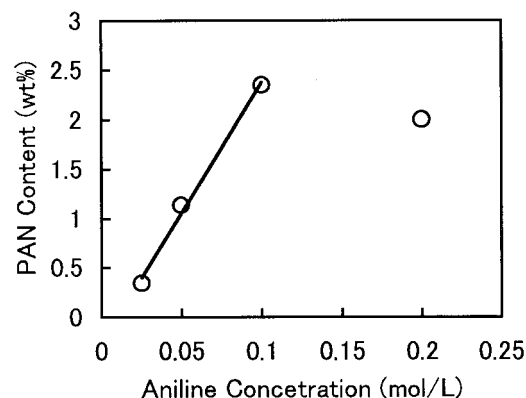


Figure 5 PAN content versus the aniline concentration (polymerizing voltage = 2.4 V; processing time = 16 min; load = 4.9 N).

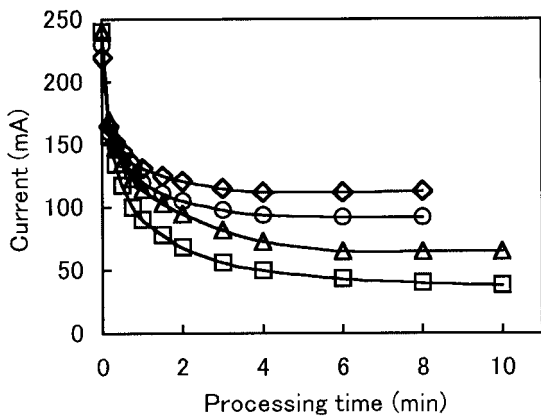


Figure 6 Current versus the processing time [aniline concentration = (\diamond) 0.2, (\circ) 0.1, (\triangle) 0.05, and (\square) 0.025 mol/L; polymerizing voltage = 2.4 V; load = 4.9 N].

of 0.2 mol/L. The decrease in the PAN content was attributable to the formation of spaces between the fibers and cathode due to an excess accumulation of hydrogen generated from the cathode. As shown in Figure 6, the current increased with increasing aniline concentration in the electrolytic solution because the anodic oxidation of aniline increased with the aniline concentration. Because the generation of hydrogen from the cathode occurred in agreement with the anodic oxidation of aniline, the amount of hydrogen increased with increasing aniline concentration.

The surface resistance of the composite fabrics is plotted against the PAN content in Figure 7. All the data points could be approximated by one curve. This result indicates that the PAN coatings on the fibers had the same morphology in all the composite samples. The surface resistance decreased with increasing PAN content and reached a plateau at a PAN content greater than 2 wt %.

An SEM micrograph of a typical PPCF is shown in Figure 8. The PET fiber surface was uniformly coated

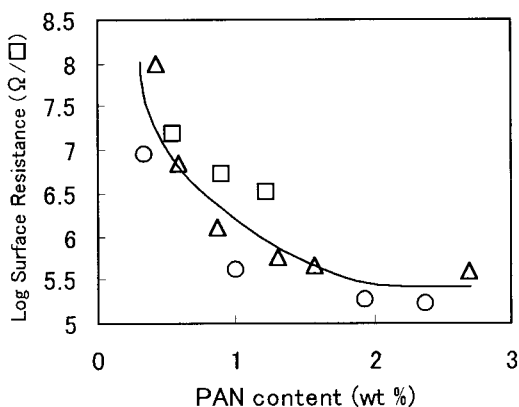


Figure 7 Surface resistance versus the PAN content for the sample shown in Figure 4 [aniline concentration = (\circ) 0.1, (\triangle) 0.05, and (\square) 0.025 mol/L].

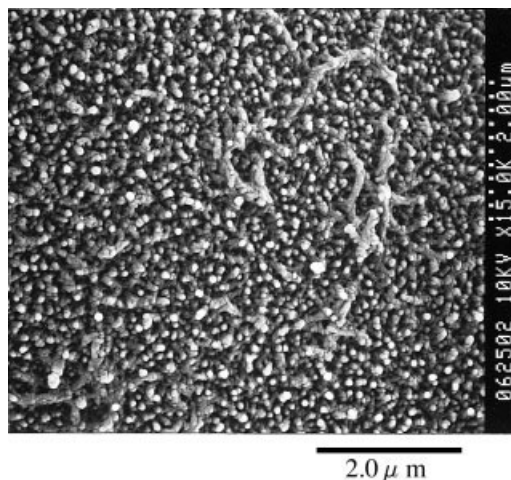
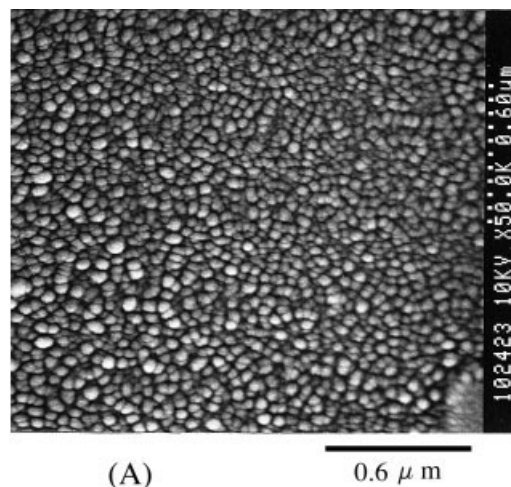
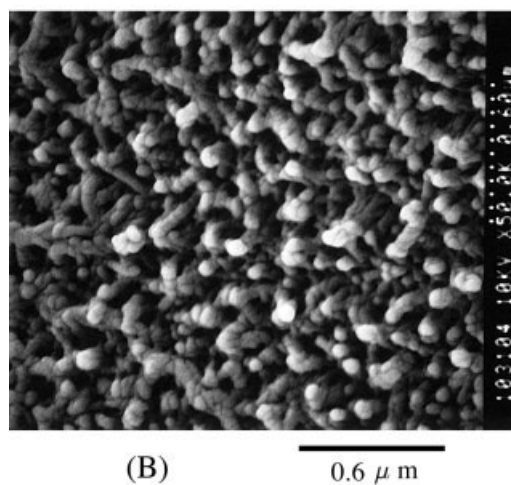


Figure 8 SEM micrograph of the composite fabric (aniline concentration = 0.05 mol/L; polymerizing voltage = 2.4 V; load = 4.9 N; processing time = 15 min).



(A)



(B)

Figure 9 SEM micrographs of the composite fabric prepared with (A) 30 s and (B) 8 min of processing (aniline concentration = 0.05 mol/L; polymerizing voltage = 2.4 V; load = 4.9 N; only a single side was treated).

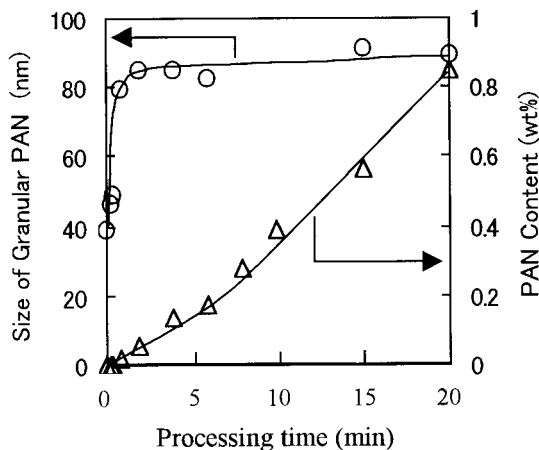


Figure 10 (○) Size of granular PAN and (△) PAN content versus the processing time (aniline concentration = 0.05 mol/L; polymerizing voltage = 2.4 V; load = 4.9 N; only a single side was treated).

with granular or fibrous PAN, and no PAN occupied the interstices of the PET fibers.

The changes in the PPCF surface with the processing time were observed by SEM. Typical SEM micrographs of PPCFs, with only a single side of the PET fabric treated (aniline concentration = 0.05 mol/L; voltage = 2.4 V; load = 4.9 N), are shown in Figure 9. The sizes of the granular PAN were measured from SEM micrographs and are plotted against the processing time in Figure 10. After a very short processing time such as 10 s, fine, granular PAN deposited uniformly on the PET fibers. During this stage, the deposition of PAN occurred not only on areas of PET fiber surfaces in contact with the anode but also on areas not in contact with the anode. Then, the granular PAN enlarged rapidly (within 2 min) to about 90 nm [Fig. 9(A)]. After that, the formation of PAN networks was observed [Fig. 9(B)]. During this stage, no significant changes in the sizes of the granular PAN and PAN networks occurred, whereas the PAN content in the PPCF fabric increased with the processing time. This result suggests that thickness growth occurred for the PAN coatings on the PET fiber.

From these findings, it is clear that the formation of PAN coatings on PPCFs was accomplished by three successive steps. Each step is illustrated in Figure 11. In the initial step of the processing, very fine, granular PAN was generated near the anode, migrated into the electrolyte, and was adsorbed onto the fiber surface [Fig. 11(I)]. In the second step, the growth of granular PAN adsorbed onto the fiber surface occurred by the transfer of an electron from the anode-contacted fiber to the anode [Fig. 11(II)]. In the final step, the PAN networks were formed by linkages in the granular PAN [Fig. 11(III)].

The durability of PAN coatings on PPCFs was tested through washing with water and rubbing with

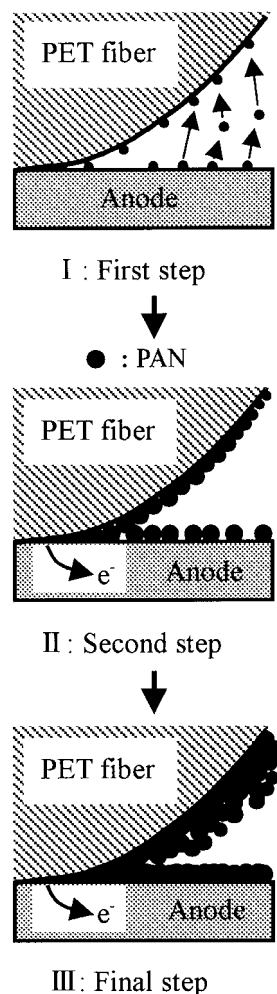


Figure 11 Formation mechanism of the PAN coatings.

an untreated PET fabric. As shown in Table I, the PAN coating was stable for a washing test. SEM micrographs of the rubbed PPCFs are shown in Figure 12(A,B). Although the PAN coating was not peeled off from the PPCFs after rubbing for 10 times, the coating was partly peeled off after rubbing for 100 times [Fig. 12(B)]. As shown in the SEM micrographs in Figures 9(B) and 12(A), the granular and network PAN on the fiber was squashed flat by the friction, and this suggested that the PAN on the fiber was soft. The high frictional durability of the PAN coatings was due their excellent flexibility.

TABLE I
Durability of the PAN Coatings

Testing type	Durability
Washing ^a	Nonpeeling
Rubbing ^b	
10 times	Nonpeeling
100 times	Partly peeling

^a Washed with water for 5 min.

^b Rubbed with PET fabric at 4.9 N.

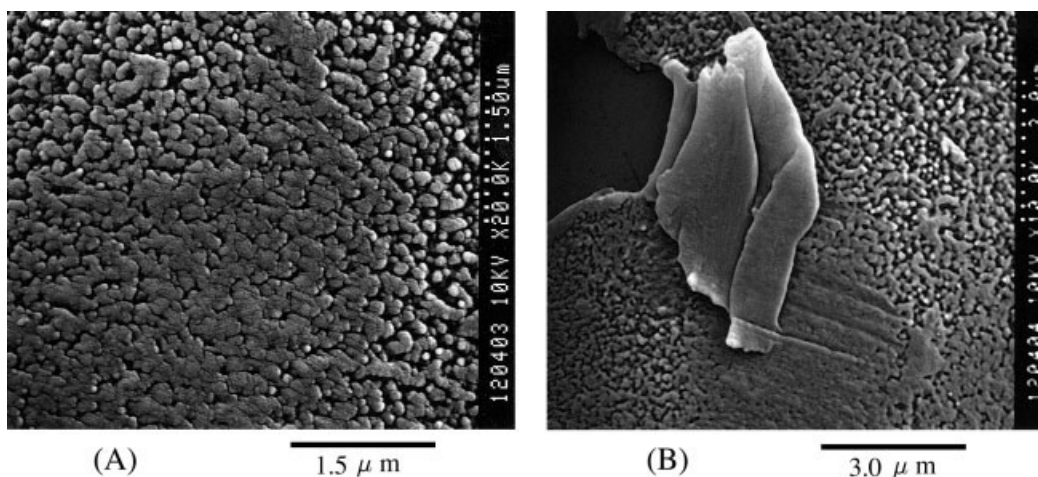


Figure 12 SEM micrographs of the composite fabric rubbed (A) 10 times and (B) 100 times at 4.9 N (aniline concentration = 0.05 mol/L; polymerizing voltage = 2.4 V; load = 4.9 N; processing time = 16 min).

This method could be applied to other fibrous materials such as nylon, wool, silk, cotton, vinylon, and acrylic fibers.

CONCLUSIONS

In this work, a novel method of manufacturing PET-PAN composite fibers by electrochemical polymerization was developed. The important features of this method were the simplicity of the system and its applicability for various fiber materials.

In this system, composite fibers could be prepared in a short time because PET fibers in the vicinity of the anode began to be coated with PAN immediately after the polymerization began. Therefore, this system will be applicable to a continuous process.

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