

Preparation and Properties of Electrically Conducting Textiles by *In Situ* Polymerization of Poly(3,4-ethylenedioxythiophene)

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ABSTRACT: Poly(3,4-ethylenedioxythiophene) (PEDOT) was *in situ* polymerized on nylon 6, poly(ethylene terephthalate) (PET), and poly(trimethylene terephthalate) (PTT) fabrics using ferric *p*-toluenesulfonic acid (FepTS) and ferric chloride (FeCl₃) as oxidants. The effect of the organic solvents used in the polymerization bath was investigated. Prepared PEDOT/nylon 6 composite fabrics have superior electrical conductivity (0.75 S/cm, in ethanol solvent) compared to those of the other PEDOT composite fabrics. In particular, after five cycles of polymerization, the electrical conductivity of the composite fabric reached about 2 S/cm. However, the nylon 6 fabric was damaged by EDOT radical

cations and the strong acidity of FepTS during the polymerization process. It was concluded that PTT fabric, which has excellent elastic recovery and acid resistance, is a suitable substrate for *in situ* polymerization of PEDOT, because the PEDOT/PTT composite fabric was hardly damaged during the polymerization process and its electrical conductivity is comparatively good (0.36 S/cm, in butanol solvent). © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1326–1332, 2005

Key words: electrical conducting fabrics; poly(3,4-ethylenedioxythiophene); nylon 6; poly(trimethylene terephthalate); poly(ethylene terephthalate); *in situ* polymerization

INTRODUCTION

Electrically conductive fabrics are mainly used for industrial applications like filters, deelectrifying and electromagnetic interference shield materials, and special purpose clothing, which is dust and germ free. The demand for them has strongly increased in recent years. The reason is that electrostatic and electromagnetic interference have proliferated and become commonplace because of human lifestyle changes and the increasing sophistication of industrial technology.^{1,2}

Among the manufacturing processes used to produce conductive materials, there have been great expectations for π -electron conjugate polymers, such as polythiophene, polyaniline, and polypyrrole. Such conducting polymers have been the subject of much interest, not only from a fundamental scientific interest viewpoint but also from a practical viewpoint for various functional applications. Within the class of conducting polymers, polythiophene is unique among other conducting polymers because of its environmental stability.^{3–5} However, the high oxidation potential of the monomer and the possible α , β and β , β linkages

in the polymer lead to inferior properties. Therefore, a derivative of thiophene that has low oxidation potential and is free from the possible α , β and β , β linkages would be an ideal material for industrial applications. In this direction, Jonas et al.^{6,7} synthesized 3,4-ethylenedioxythiophene (EDOT), which has low oxidation potential and is free from the possible α , β and β , β linkages^{8,9} as shown in Figure 1. Prepared poly(EDOT) (PEDOT) has a low-bandgap polymer ($E_g = 1.5$ eV in the undoped state, where E_g is band gap energy), it shows high electrical conductivity (up to 550 S/cm) in the doped state, and it has good thermal and chemical stability with promising properties for applications such as transparent electrode materials or electronic devices.^{4,10,11} Therefore, many studies on PEDOT have recently been done to enhance its conductivity and stability and to extend its fields of application. Kudoh et al.¹² found that when PEDOT was prepared in an aqueous medium containing Fe₂(SO₄)₃ and alkyl naphthalenesulfonate as an oxidant and dopant, respectively, the addition of *p*-nitrophenol leads to improved moisture stability of PEDOT as well as an increase in yield. Aleshin et al.¹³ studied the temperature dependences of the conductivity [$\sigma(T)$] and magnetoconductivity of PEDOT doped with PF₆, BF₄, and CF₃SO₃. In addition, there are various studies to prepare new forms of PEDOT. Duvail et al.³ synthesized electrochemical PEDOT nanofibers by using the template method, and Choi et al.¹⁴ prepared PEDOT

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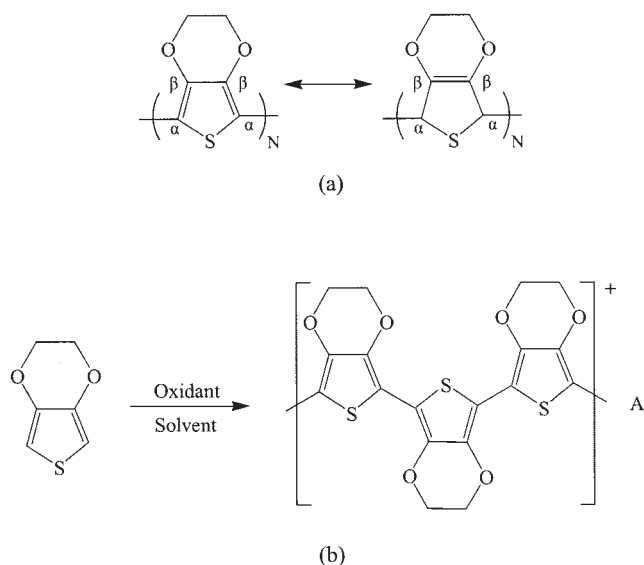


Figure 1 (a) The molecular structures of PEDOT and (b) the chemical synthesis of PEDOT.

nanoparticles with enhanced conductivity and processibility by oxidative polymerization in dodecylbenzene sulfonic acid micellar solution.

In this study, PEDOT/fabrics composites were prepared by *in situ* polymerization of EDOT monomer on nylon 6, poly(ethylene terephthalate) (PET), and poly(trimethylene terephthalate) (PTT) fabrics. To investigate the optimum condition of PEDOT polymerization for improving the conductivity and adhesion of PEDOT/fabric composites, we used ferric *p*-toluenesulfonic acid (Fe_pTS) and ferric chloride ($FeCl_3$) as an oxidant because Fe_pTS and $FeCl_3$ are known as the prominent oxidants for EDOT polymerization. We used ethanol and butanol as solvents because they are thought to be reasonable solvents that can solve EDOT monomer as well as the oxidants. After producing the PEDOT/fabric composite, their electrical and mechanical properties were examined.

EXPERIMENTAL

Materials

Scoured nylon 6 plain weave fabrics (7.8 tex, 43×30 /cm) and PET plain weave fabrics (8.3 tex, 42×38 /cm) were obtained from KATRI, and PTT plain weave fabrics (112 denier (De), 38×36 /cm) supplied by Huvis Co. Ltd. were washed with distilled water and dried prior to use. EDOT monomer and Fe_pTS were purchased from Bayer AG, and $FeCl_3$ was obtained from Ducksan Pure Chemical Co., Ltd. The reagents were used as received without further purification.

Fabric treatment

Electrically conducting PEDOT/fabric composites were prepared by the following process. Fabrics were

immersed in the freshly mixed solution of EDOT, oxidant, and organic solvent for 20 min. At this time, the solution had to be maintained at about $0\text{--}3^\circ\text{C}$ for delaying the polymerization of the solution during immergence. Subsequently, the fabrics were dried under atmospheric conditions (25°C , relative humidity = $65 \pm 5\%$) for 24 h, and then the EDOT on the surface of the fabrics was polymerized to PEDOT during the drying time. After the polymerization step, the fabrics were washed with distilled water and dried.

Evaluation

The electrical surface conductivity of the composite fabric was measured by four straight lines and equidistant points, taking the thickness as that of the fabric.¹⁵ A constant current source was used to pass a steady current through the two outer probes in the surface of a specimen, and the voltage drop across the inner two was measured by a Kithley 2400 digital source meter. The conductivity of the sample was given by the following formula:

$$\sigma \text{ (S/cm)} = \frac{Z}{dW} \cdot \frac{I}{V}$$

where σ is the electric conductivity, Z is the spacing between probes (0.3 cm), d is the thickness of the sample, W is the length of the line probe (1 cm), I is the current passed through outer probes, and V is the voltage drop across inner probes.

Fourier transform IR spectroscopy (FTIR) was performed with a Perkin-Elmer Spectrum 2000 FTIR spectrometer with a resolution of 4 cm^{-1} , and the measurement was carried out with a KBr support. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA apparatus at a heating rate of $10^\circ\text{C}/\text{min}$ from 30 to 600°C under a nitrogen atmosphere. A Jeol JSM-6340F field emission scanning electron microscope (SEM) was used for high-magnification observation.

RESULTS AND DISCUSSION

Effect of polymerization condition

Figure 2 presents the changes in the electrical conductivities of PEDOT/nylon 6 composite fabrics with various EDOT concentrations. When $0.5M$ Fe_pTS was used as an oxidant, the conductivity of the PEDOT/nylon 6 composite fabrics was increased with increasing EDOT concentration. In particular, when the conductivities of PEDOT/nylon 6 composite fabrics are plotted as a function of the EDOT concentration, a shape change in conductivity is observed at about $0.2M$ EDOT in $0.5M$ Fe_pTS plus butanol solvent.

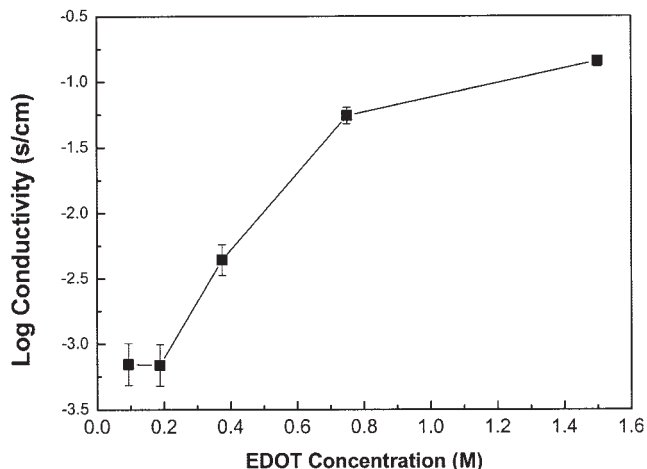


Figure 2 The effect of the EDOT concentration on the electrical conductivity of PEDOT/nylon 6 composite fabrics; diffusion temperature/time = 0–3 °C/20 min; polymerization temperature/time = 25 °C/24 h; oxidant (FepTS) concentration = 0.5M.

Figure 3 shows that the conductivity variation of PEDOT/nylon 6 composite fabrics with the oxidant (FepTS) concentration (EDOT concentration = 1.0M). When butanol was used as the solvent (Fig. 3, curve b), the conductivity of PEDOT/nylon 6 composite fabrics was steeply increased until 0.7M and then the increasing rate of the conductivity was reduced. Therefore, it is concluded that the PEDOT polymerization condition in butanol solvent was optimized at about a 1:1.5 molar ratio of FepTS/EDOT. However, when the PEDOT/nylon 6 composite fabrics were treated in etha-

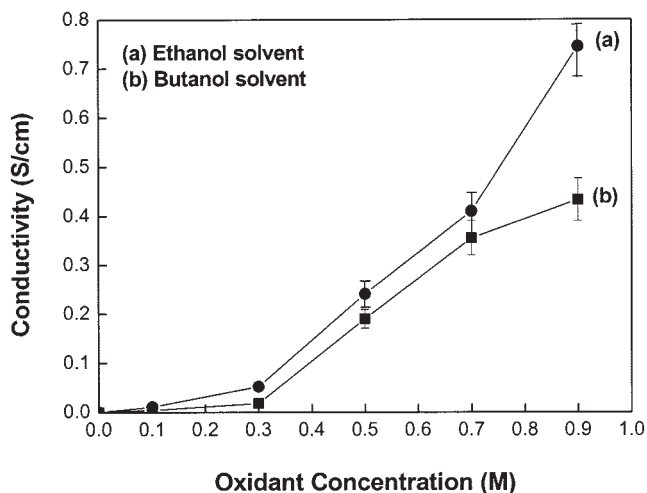


Figure 3 The effect of the oxidant (FepTS) concentration on the electrical conductivity of PEDOT/nylon 6 composite fabrics prepared in ethanol solvent (curve a) and butanol solvent (curve b); diffusion temperature/time = 0–3 °C/20 min; polymerization temperature/time = 25 °C/24 h; monomer (EDOT) concentration = 1.0M.

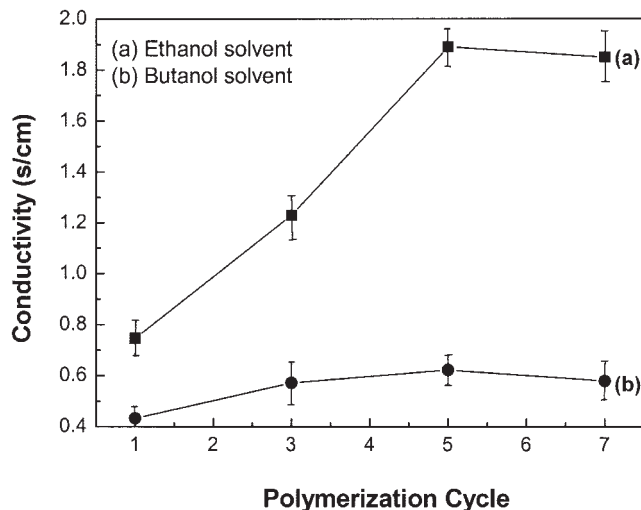


Figure 4 The effect of the polymerization cycles on the electrical conductivity of PEDOT/nylon 6 composite fabrics prepared in ethanol solvent (curve a) and butanol solvent (curve b); diffusion temperature/time = 0–3 °C/20 min; polymerization temperature/time = 25 °C/24 h; monomer (EDOT) concentration = 1.0M; oxidant (FepTS) concentration = 0.7M.

anol solvent (Fig. 3, curve a), the conductivity of the PEDOT/nylon 6 composite fabrics was higher overall than that of the fabrics treated in butanol solvent and the conductivity was increased continuously until a 1.0M FepTS concentration. It is assumed that the relatively long alkyl chains (C_4H_9-) of butanol molecules surrounded the EDOT monomer and sometimes formed micelles; therefore, they hindered EDOT from contacting the oxidant. Thus, because ethanol has only $-CH_3$, the FepTS in ethanol solvent can easily access the EDOT existing on the nylon 6 fabrics and sufficiently oxidize the EDOT monomer. Therefore, the yield and conductivity of PEDOT/nylon 6 composite fabrics treated in ethanol solvent are higher than those of the composite fabrics treated in butanol solvent. However, an excess amount of FepTS was found to damage the nylon 6 fabrics because of its strong acidity.

Figure 4 reveals the effect of PEDOT repeat treatments in ethanol solvent and butanol solvent on the conductivities of PEDOT/nylon 6 composite fabrics. The concentrations of the polymerization solutions were fixed at 1.0M PEDOT and 0.7M FepTS. The conductivities of the PEDOT/nylon 6 composite fabric treated in ethanol solvent (Fig. 4, curve a) increased with increasing polymerization cycles and reached a maximum value (1.89 S/cm) at five cycles, then it tended to level off or decrease somewhat (1.85 S/cm). However, the conductivities of PEDOT/nylon 6 composite fabrics treated in butanol solvent (Fig. 4, curve b) hardly changed with the cycles of PEDOT polymerization repeat treatment. This is presumably because

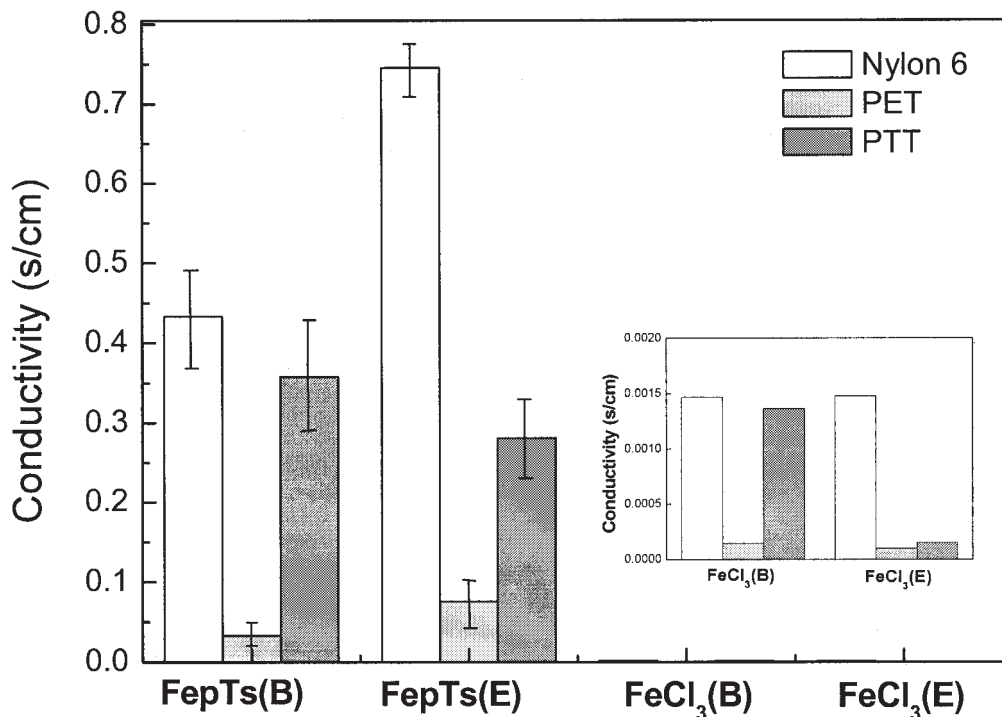


Figure 5 The effects of the fabric species on the electrical conductivity as a function of oxidant and solvent species; solvent species, ethanol (E) and butanol (B); diffusion temperature/time = 0–3 °C/20 min; polymerization temperature/time = 25 °C/24 h; monomer (EDOT) concentration = 1.0M; oxidant concentration = 0.7M.

the amount of PEDOT formed on the fabric surface increased, and the conductivity of the PEDOT/nylon 6 composite fabric treated in ethanol solvent increased at the first stage. However, after five cycles the excessively treated PEDOT became an uneven structure form and impurities, such as unreacted EDOT monomer, oligomer, and oxidant molecules, piled up in various places in PEDOT so the current of the electric charges was disturbed.¹⁶ On the other hand, when the repeat treatment was done in butanol solvent, the alkyl chains of the butanol molecules were arranged and absorbed on the surface of the PEDOT/nylon 6 composite fabrics because of their hydrophobic character; therefore, the butanol molecules as well as the above impurities existed among the PEDOT layers and acted as electrical resistance.

Effect of fabric substrates

The effects of the fabric substrates on the fabric conductivity were determined as a function of the oxidant and solvent species as shown in Figure 5. Overall, the conductivities of PEDOT/fabric composites polymerized with FepTS are higher than those of the PEDOT/fabric composites polymerized with FeCl₃. It is assumed that the oxidative power of FepTS is stronger than that of FeCl₃ because the C₇H₇SO₃— of FepTS withdrew more electrons from the EDOT monomer

than the Cl— of FeCl₃. On the other hand, among the various fabric substrates, nylon 6 shows the best electrical conductivity (0.43 S/cm in butanol, 0.75 S/cm in ethanol), followed by PTT (0.36 S/cm in butanol, 0.28 S/cm in ethanol) > PET (0.03 S/cm in butanol, 0.07 S/cm in ethanol) in decreasing order. It is thought that nylon 6 has an amide group (—NHCO—), which can serve as sites for hydrogen bonds in its backbone, and thus the adhesion between the substrate and PEDOT is superior to that of the other fibers. In addition, PTT has more amorphous regions than PET; hence, more PEDOT diffused and adhered on the PTT fabric than that on PET. However, we observed that the electrical conductivity of the PET fabric was relatively inferior compared to nylon 6 and PTT and was hardly influenced by the solvent species.

Figure 5 also shows that the conductivity of PEDOT/nylon 6 composite fabrics treated in ethanol solvent was superior to that of the composite fabric treated in butanol solvent. Presumably, the relatively long alkyl chains (C₄H₉—) of butanol molecules surrounded the EDOT monomer and hindered it from contact with the oxidant. Because ethanol has only —CH₃, the FepTS in ethanol solvent can easily access the EDOT existing on nylon 6 fabrics and sufficiently oxidize the EDOT. However, the conductivity of the PEDOT/PTT composite fabric treated in butanol solvent was superior to that of the composite fabric

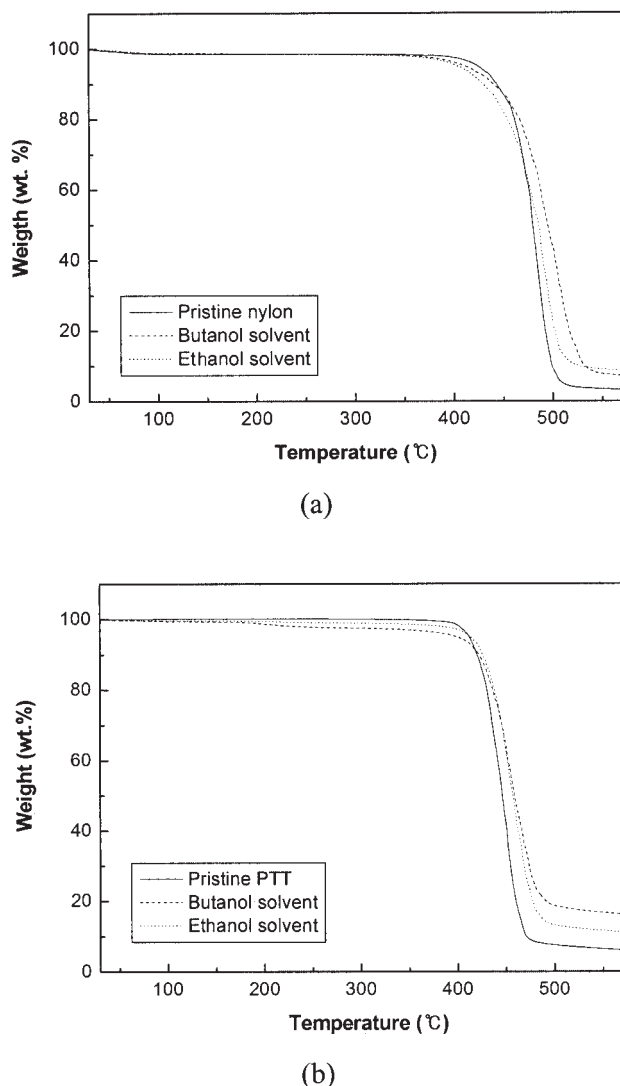


Figure 6 The TGA curves of (a) PEDOT/nylon 6 composite fabrics and (b) PEDOT/PTT composite fabrics; solvent species, ethanol and butanol; diffusion temperature/time = 0–3 °C/20 min; polymerization temperature/time = 25 °C/24 h; monomer (EDOT) concentration = 1.0M; oxidant (Fe p TS) concentration = 0.7M.

treated in ethanol solvent, as shown in Figure 5. It is assumed that because the viscosity of the PEDOT/butanol solution is higher than that of the PEDOT/ethanol solution, the PEDOT in butanol solution could adhere more to the PTT fabric, which has excellent elastic recovery and hydrophobicity. Conversely, because PTT fabric is not only hydrophobic but also more amorphous and has better elastic recovery than PET fabric, the PTT fabric could contain more PEDOT than the PET fabric. Therefore, it is assumed that the electrical conductivity of the PTT fabric treated with PEDOT/butanol was superior to that of the PET fabric treated with PEDOT/butanol. This is supported by the TGA results of the PEDOT composite fabrics as shown in Figure 6. The percentage of residue of PE-

DOT/PTT composite fabrics treated in butanol is greater than that of the fabrics composite treated in ethanol [Fig. 6(b)]. However, the TGA residue (%) of PEDOT/nylon 6 composite fabric [Fig. 6(b)] shows a reverse tendency to that of PEDOT/PTT composite fabric. On the other hand, Kudoh et al.¹² reported that, although the reaction for the difference between the solvent species is not clear, the vaporization rates of the solvent seem to play some significant roles in the conductivity and yield of PEDOT.

Fabric damage

The SEM morphologies of the PEDOT/fabric composites are shown in Figure 7. Observe that the surfaces of PEDOT/nylon 6 composite fabrics treated in butanol [Fig. 7(b)] and ethanol [Fig. 7(c)] were dissolved and thus the woven structure of the fabrics was transformed to almost a film form. Whereas PEDOT/PTT composite fabrics were not significantly damaged because the PTT fibers resist acid degradation, it was not dissolved by the acidity of the oxidant (Fe p TS). The only observation is that there is more PEDOT adhered on the PTT fabric treated in butanol [Fig. 7(e)] than on the fabric treated in ethanol [Fig. 7(f)], as expected. PTT fibers are aromatic polyesters made by the polycondensation of 1,3-propanediol and terephthalic acid, but they also offer their own unique performance attributes. The polymer's helical molecular configuration results in greater fiber elasticity, stretch, and recovery. Consequently, PTT unifies the main and best characteristics of nylon and polyester for the most disparate application. Therefore, we concluded that PTT fabric is a more suitable substrate for *in situ* polymerization of PEDOT than the other fabrics.

The FTIR spectra for PEDOT, PEDOT/nylon 6 composite fabric, and pristine nylon 6 fabric are shown in Figure 8. The spectral features of pure PEDOT (Fig. 8, spectrum a) at 1430, 1260, 1150, and 1110 cm^{-1} are related to the doped polythiophene main chain and the bands at 1560 and 993 cm^{-1} are related to the oxygen containing substitution of PEDOT rings.¹⁷ On the other hand, in the spectrum of pristine nylon 6 fabric (Fig. 8, spectrum c), the peaks at 1600 and 1550 cm^{-1} can be assigned to the C=O stretching in amide and the N–H bending in secondary amide (–NH) and the C–N stretching peak was also observed at 1400 cm^{-1} , which is due to the amide group in nylon 6. However, the peaks at 3140 and 3010 cm^{-1} were oriented from primary amine (–NH₂) stretching, and the peak at 2890 cm^{-1} was oriented from aldehyde hydrogen (–CHO) stretching that was newly occurring in the spectrum of PEDOT/nylon 6 composite fabric (Fig. 8, spectrum b). It is supposed that the amide group in the backbones of nylon 6 were hydrolyzed by EDOT radical cations and the strong acidity oriented from the Fe p TS during the polymerization

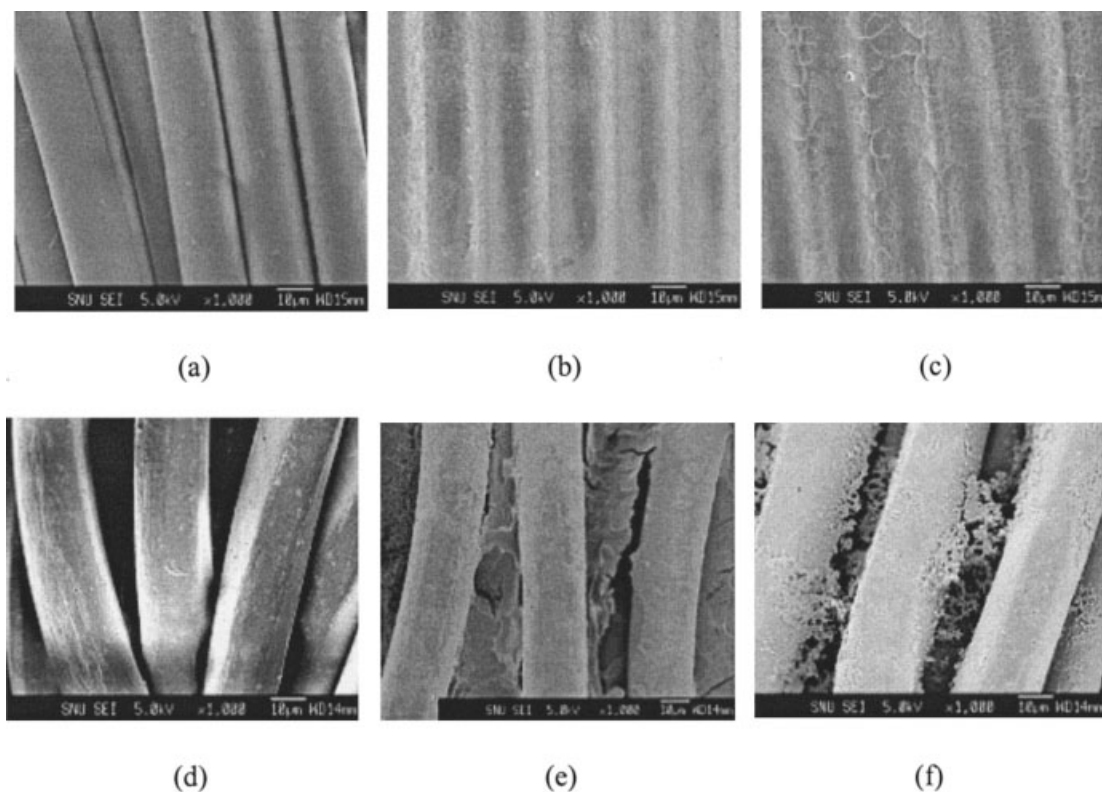


Figure 7 SEM morphologies of PEDOT/nylon 6 composite fabrics and PEDOT/PTT composite fabrics; solvent species, ethanol and butanol; diffusion temperature/time = 0–3 °C/20 min; polymerization temperature/time = 25 °C/24 h, monomer (EDOT) concentration = 1.0M; oxidant (FepTS) concentration = 0.7M; (a) pristine nylon 6 fabric, (b) PEDOT/nylon 6 composite fabrics (butanol solvent), (c) PEDOT/nylon 6 composite fabrics (ethanol solvent), (d) pristine PTT fabric, (e) PEDOT/PTT composite fabrics (butanol solvent), and (f) PEDOT/PTT composite fabrics (ethanol solvent).

process.¹⁸ On the other hand, the FTIR spectra for PEDOT/PTT composite fabric (Fig. 8, spectrum d) and pristine PTT fabric (Fig. 8, spectrum e) display similar pattern and peak positions. Therefore, we believe that PEDOT did not damage the PTT fabric matrix and thus the PTT fabric is more a suitable substrate for *in situ* polymerization of PEDOT than nylon 6.

CONCLUSION

PEDOT/fabric composites were prepared by *in situ* polymerization of PEDOT on nylon 6, PET, and PTT fabrics using FepTS and FeCl₃ as oxidants. The effect of the organic solvent (butanol or ethanol) was also investigated. The oxidative power of FepTS was found to be stronger than that of FeCl₃. Conversely, the conductivities of PEDOT/nylon 6 composite fabrics treated in ethanol were generally higher than those of the fabrics treated in butanol. Moreover, the conductivities of PEDOT/nylon 6 composite fabrics treated in ethanol increased with increasing polymerization cycles and reached a maximum value (1.89 S/cm) at five cycles. However, the conductivities of PEDOT/nylon 6 composite fabrics treated in butanol hardly changed

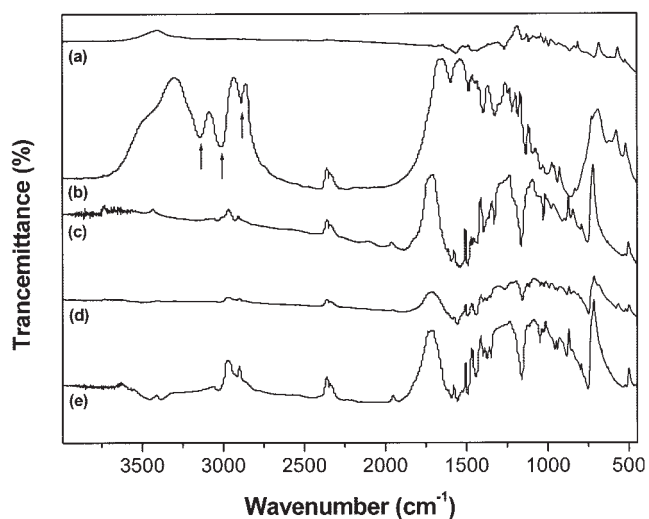


Figure 8 FTIR spectra for PEDOT (spectrum a), PEDOT/nylon 6 composite fabric (spectrum b), pristine nylon 6 fabric (spectrum c), PEDOT/PTT composite fabric (spectrum d), and pristine PTT fabric (spectrum e); diffusion temperature/time = 0–3 °C/20 min; polymerization temperature/time = 25 °C/24 h; monomer (EDOT) concentration = 1.0M; oxidant (FepTS) concentration = 0.7M; solvent, ethanol.

with the cycles of PEDOT polymerization repeat treatment, but butanol was more effective in improving the electrical conductivity of PEDOT/PTT composite fabric than ethanol. Among the various fabric substrates, nylon 6 fabric showed the best electrical conductivity, followed by PTT > PET in decreasing order. However, nylon 6 fabric was decomposed by EDOT radical cations and the strong acidity oriented from the oxidant (FepTS). Therefore, we concluded that PTT fabric was a more suitable substrate for *in situ* polymerization of PEDOT than nylon 6.

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