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Article

An Effective Surface Modification of Polyester Fabrics for Improving the Interfacial Deposition of Polypyrrole Layer

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Abstract: A simple and effective surface modification of polyester fabrics with sulfuric acid to improve the interfacial deposition of polypyrrole was presented in our work. A range of sulfuric acid concentrations were analyzed by studying water contact angle. Effect of sulfuric acid modification on the deposition of polypyrrole was investigated by sheet resistance and color depth of fabric samples. Polyester fabrics coated with polypyrrole layer were confirmed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-Ray diffraction spectra (XRD), Fourier transform infrared spectroscopy (FTIR). XPS showed that sulphur containing functional groups were obviously appeared on the polyester fiber surface after modification, which were advantageous to promote the deposition of polypyrrole onto polyester fabrics. The improved deposition increased electrical conductivity of fabric samples.

Keywords: polyester fabrics; surface modification; sulfuric acid; polypyrrole; deposition; conductivity

1. Introduction

Polyester fiber (PET), as a very important textile fiber, has been widely used in clothing, home furnishings and some industrial areas due to its superiorities of high strength, mechanical stability and low cost[1, 2]. Electroconductive polyester fibers have received increasing attention over the last few years, because of their potential applications in electromagnetic shielding clothing[3], medical therapeutics devices[4], supercapacitors[5, 6], chemical and biological sensors[7-10]. Therefore, it is desirable to synthesize conductive polypyrrole (PPy) as thin layers on the PET fabrics by chemical method or by electrochemical method[11-13]. The two methods are in-situ polymerization of pyrrole molecules from aqueous solution onto fibers surface[14, 15]. However, the in-situ polymerization of pyrrole on commercial textile fibers surface is mainly designed for cellulose-based fibers[16-18] and for animal fibers[19] because of excellent affinity of these fibers' surface to PPy layers. On the contrary, it is very difficult for hydrophobic surface of polyester fibers to be wetted, which will retard the absorption and deposition of polypyrrole onto PET fiber surface[20, 21]. Consequently, increasing hydrophilic property of PET fiber surface could increase the pyrrole–fiber interaction and improve the deposition of polypyrrole.

In recent years, many attempts have been made to overcome the problem. A. Kaynak[22-24] treated polyester fabrics with atmospheric plasma glow discharge to increase the wettability and surface energy of the fiber substrate. N.D. Gupta[25] found that well-formed and continuous polypyrrole films were deposited on polyester substrate which was pretreated with cetyl trimethylammonium bromide (CTAB) as adhesion promoter.

In this paper, we adopted a new technique of surface modification of the PET fabrics for enhancing deposition amount of PPy, by simply treating the hydrophobic substrate with dilute sulfuric acid at high temperature prior to polymerization of pyrrole monomer. The color and electroconductivity of modified PET fabrics with sulfuric acid were significantly different from those of original fabrics after PPy layers were deposited on samples.

2. Experiment

2.1. Materials

The plain polyester (PET) fabrics (104 g·m^{-2}) were cleaned by 1 % (w/w) of sodium carbonate (Na_2CO_3) at 80 ºC for 1 h, washed by distilled water and dried. Pyrrole (Py) was purchased from Aladdin Chemical Reagent Co, China. Hydrogen chloride (HCl), ferric trichloride hexahydrate ($FeCl_3{\cdot}6H_2O$) were purchased from Sinopharm Chemical Reagent. Sulfuric acid (H_2SO_4, 98%) were purchased from Chongqing Chuandong Chemical (group). All reagents were of analytical grade and were used without any further process.

2.2. Surface modification of PET fabric

A series of PET fabrics were immersed in H_2SO_4 aqueous solution in the bath ratio of 1:40 at room temperature for 15 min and cured at 110 °C for 6 min in heat-setting machine. The concentration of H_2SO_4 aqueous solution ranged from 2 g·L^{-1} to 25 g·L^{-1}. The fabrics with H_2SO_4 modification but without PPy deposition were called "modified samples".

2.3. Deposition of PPy layers on PET fabrics

The PPy layers were polymerized and deposited on PET fabrics via chemical oxidative polymerization. The fabric samples were immersed in 100 ml of aqueous solution containing pyrrole (Py) monomer and HCl in the bath ratio of 1:50 for 1 h at room temperature. The solution was added 20 ml of $FeCl_3{\cdot}6H_2O$ aqueous solution dropwise slowly under stiring and the polymerization was performed at 0 ºC for 2 h. After that, immersing fabrics in 0.1 M H_2SO_4 solution for 10 h was conducted in order to make PPy layer doped. The concentration of pyrrole monomer ranged from 0.0175 M to 0.0275 M. The molar ratio of Py:HCl:$FeCl_3{\cdot}6H_2O$ was 2:2:1. The finishing samples were finally rinsed several times by distilled water and dried at room temperature.

2.4. Sheet resistance

The PPy-deposited PET fabrics were measured by a four points probe resistivity system (RTS-9, four probes Tech., China). These samples were all kept in room temperature for 24 h prior to measurements. Each sample was measured for ten times and the average of the ten values was used in further analysis.

2.5. Water contact angle

Water contact angle (WCA) measurements were conducted using a contact angle instrument (OCA15EC, GER). 2 cm^2 of samples were cut and put on a glass slide without any press or pull. The water droplet of 3 μl and water contact time of 10 s were adopted. The original sample and the modified sample were tested, and each one was performed on three different positions to obtain the average value.

2.6. Scanning electron microscopy

The surface morphologies of the original, modified and PPy-deposited (with treated by 10 g·L^{-1} of H_2SO_4 solution) samples were examined by scanning electron microscope (FEI Quanta-250, USA). All sample surfaces were sputtered with gold.

2.7. Fourier transforms infrared

Fourier transforms infrared (FTIR) spectra of PET samples were obtained by the ALPHA German Brooke Fourier Infrared Spectrometer. The wavenumber was over the range of 4000-400 cm^{-1} for 16 scans with a resolution of 4 cm^{-1}.

2.8. X-ray photoelectron spectroscopy

Spectra were performed using a K-Alpha X-ray photoelectron spectrometer (Thermo ESCALAB 250XI, USA) with monochromatic X-rays focused to a 500 mm spot size. An achromatic Al (Ka) X-ray source operating at 15 kV (300 W) was used, and the spectrometer was operated in CAE mode with 100 eV pass energy. Data acquisition was taken with a pressure lower than 10^{-6} Pa. The C1s binding energies of the samples were accurately established by charge shift correcting the lowest binding energy peak of the C1s to 284.8 eV.

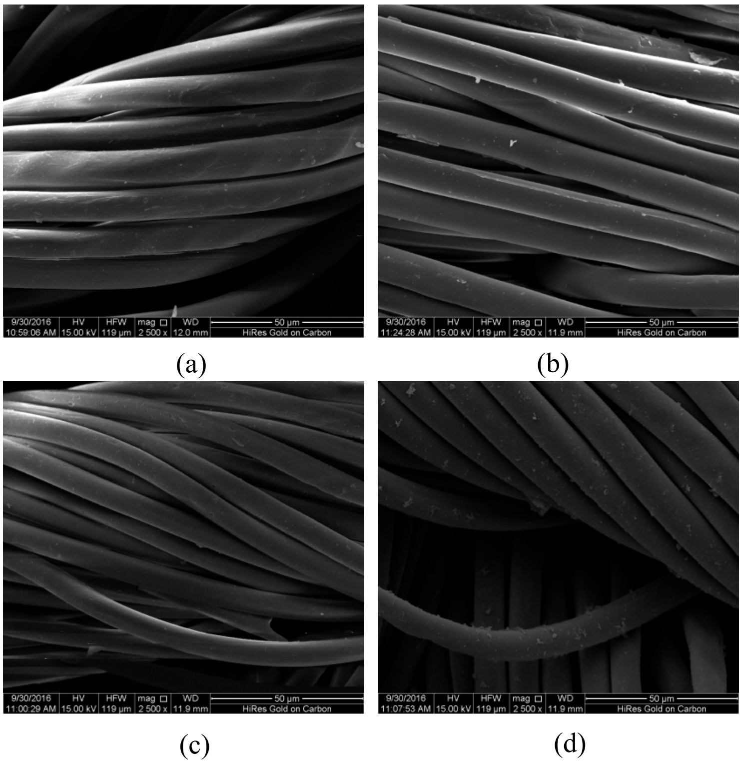
2.9. X-ray diffraction spectroscopy

The XRD diffractogram of the PET samples were determined with a TD-3500 diffraction system. It used a monochromatized Cu Kα1 radiation (λ = 0.154 nm) at 30 kV and 20 mA. The angle was from 5º to 50º in steps of 0.02º.

3. Results and discussion

3.1. Scanning electron microscopy

The surface morphologies of the original, modified and PPy-deposited samples were observed in Fig.1. The surface of the original PET fiber (Fig.1a) and the modified PET fiber (Fig.1b) were smooth. After deposition process of PPy layers, the surface of PET fibers without modification by H_2SO_4 was still smooth (Fig.1c), however, the surface of the modified PET fibers (Fig.1d) became obviously coarse with some granules, indicating the modification of PET with H_2SO_4 could improve the deposition of PPy layers.



(a) (b)

(c) (d)

Fig.1 SEM images of (a) the original sample, (b) the PPy-deposited sample without modification by H_2SO_4 (the concentration of Py was 0.0175 M), (c) the sample with modification by H_2SO_4 (10 g·L^{-1}), (d) the PPy-deposited sample with modification by H_2SO_4 (the concentration of H_2SO_4 and Py were 10 g·L^{-1} and 0.0175 M, respectively).

3.2. Optical images of PPy-deposited PET fabrics

The optical images of the PPy-deposited PET samples with modification by different concentrations of H_2SO_4 were shown in Tab.1. The fabric samples all appeared black because PPy was black. The samples modified with dilute H_2SO_4 solutions were apparently darker as compared with the unmodified samples. The color depth of fabrics increased with the increase of concentration of H_2SO_4 solution. The results suggested that surface modification of PET fabrics with H_2SO_4 solution facilitated PPy deposition.

Tab.1 PPy-deposited PET fabrics (concentration of Py monomer was 0.0175 M) with modification by different concentrations of H_2SO_4

Concentrations of H_2SO_4 ($g\cdot L^{-1}$)	**0**	**2**	**4**	**6**	**8**	**10**
Photographs						

3.3. Water Contact Angle Measurement

The effects of H_2SO_4 concentration on the hydrophilicity of PET fabrics were studied. The water contact angle (WCA) of the original and modified samples (without deposited with PPy) were shown in Fig.2. The WCA decreased rapidly with the H_2SO_4 concentration increasing. The WCA of original sample was 131.9 °, but the sample modified with 10 $g\cdot L^{-1}$ H_2SO_4 solution had an angle of 31.4 ° and the sample modified with 25 $g\cdot Lu^{-1}$ H_2SO_4 solution had an angle of only 5.45 °. It confirmed that surface modification with dilute H_2SO_4 under high temperature improved the wettability of PET fabric. As a result of the better wettability, more Py monomer could adhere onto the fabrics.

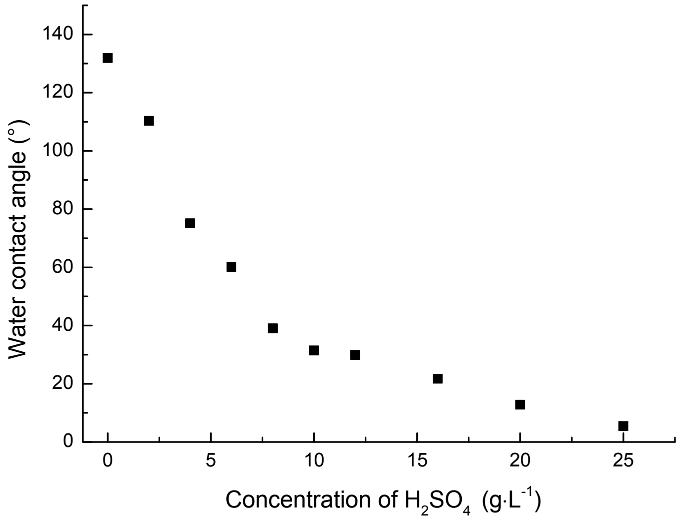


Fig.2 Water contact angles for the original and modified PET samples.

3.4. FTIR Spectra

Fig.3 presented the FTIR spectra of the original, modified and PPy-deposited (treated by 10 $g\cdot L^{-1}$ of H_2SO_4 solution) samples. It revealed that their characteristic peaks were almost the same. The same bands observed were assigned as follows. A peak at 1719 cm^{-1} comed from the –C=O stretching of –COO. A peak at 1506 cm^{-1} was assigned to the vibration of benzene ring. A peak at 1409 cm^{-1} was contributed to aromatic C-C stretching and C-H in-plane bending, a peak at 1345 cm^{-1} is contributed to CH_2 wagging. Peaks at 1244 and 1094 cm^{-1} were contributed to C-O vibration. The peak at 1044 cm^{-1} was due to aromatic =C-O bending

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In the spectrum of the surface modified PET fabric, peaks at 3558, 3426 and 1610 cm^{-1}, assigned to hydroxyl groups, bending and stretching vibration of O-H of H_2O, became stronger compared with those of the original sample because treatment with dilute H_2SO_4 increased bound water. Peaks at 1244 cm^{-1} and 1094 cm^{-1} became wider than those of the original PET samples, which were assigned to S=O stretching. The new peak at 630 cm^{-1} corresponded to the C-S stretching. The results confirmed that S=O functional groups were introduced into the polyester macromolecules.

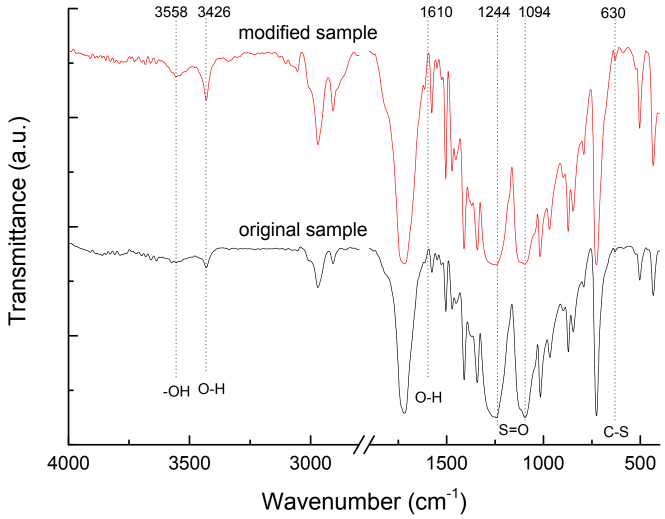

Fig.3 FTIR spectra of the original and modified PET samples (treated by 10 g·L^{-1} of H_2SO_4).

3.5. XPS spectra

X-ray pohotelectron spectroscopy (XPS) measurements were conducted for the original, modified and PPy-deposited PET samples (the concentrations of H_2SO_4 solution and Py were 10 g·L^{-1} and 0.025 M, respectively). The wide scan (0-1400 eV) spectra were shown in Figs.4. Carbon and oxygen were detected in all the samples whereas nitrogen was detected only in the PPy-deposited sample. Compared with the original sample, the S2s and S2p peaks of the modified and PPy-deposited samples increased apparently due to the modification with H_2SO_4. The N1s peak was observed only in the spectrum of PPy-deposited sample owing to the introduction of PPy layers.

The high resolution S2p scan was shown in Fig.5. In the spectrum of the modified sample, the new peak at 168.7 eV demonstrated that $-SO_3H$ (or $-SO_3^-$) groups were introduced to polyester macromolecules by modification process with H_2SO_4. The peak of $-SO_3H$ or $-SO_3^-$ in the PPy-deposited sample spectrum shifted higher which was caused by the interaction between doping anion and the amine nitrogen sites of PPy. Besides, the intensiy of the peak increased, further indicating the introduction of $-SO_3H$ (or $-SO_3^-$) groups to fibers and the doping of PPy layers by H_2SO_4.

The relative concentrations of C functionalities were studied by means of XPS-peak-differenating analysis, as shown in Fig.6. The sub peaks at 284.8 eV, 286.5 eV and 289 eV are assigned to O-C=O, C-O and C-C/C-H groups respectively, and their relative concentrations were shown in Tab.2. The O-C=O group concentrations of the three samples were almost the same. The C-C/C-H concentration increased from 70.78 % for the original sample to 71.57 % for the modified sample, and the C-O concentration decreased from 17.30 % to 16.50 %. The increase of C-C/C-H concentration was caused by the appearance of $C_6H_5-SO_3H$ or $C_6H_5-SO_3^-$ peak which locates at around 289 eV and is near the C-C/C-H peak. It demonstrated sulfonic groups were introduced to benzen rings of polyester macromolecules as shown in Fig.7. Under high temperature, dilute H_2SO_4 aqueous solution left in PET fibers gradually got concentrated, and the sulfonation reaction could take place in polyethylene terephathalate macromolecules.

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The concentration of C-O increased from 16.50 % for the original sample to 21.55 % for the PPy-deposited sample, and the C-C/C-H concentration decreased from 70.78 % to 66.48 %. The N functionalities are around at 286 eV which are close to C-O peak (Fig.6), therefore, the C-O peak seemed to increase due to the coating of PPy. The surface modification introduced sulfonic groups in polyester macromolecules, improving the hydrophilicity of fabrics. In addition, the electrophilic sulfonic groups can attract nucleophilic N of pyrrole ring. The enhancement of polar groups, surface hydrophilicity and intermolecular attraction were contributed to a larger absorption of pyrrole monomer on polyester fibers[26, 27].

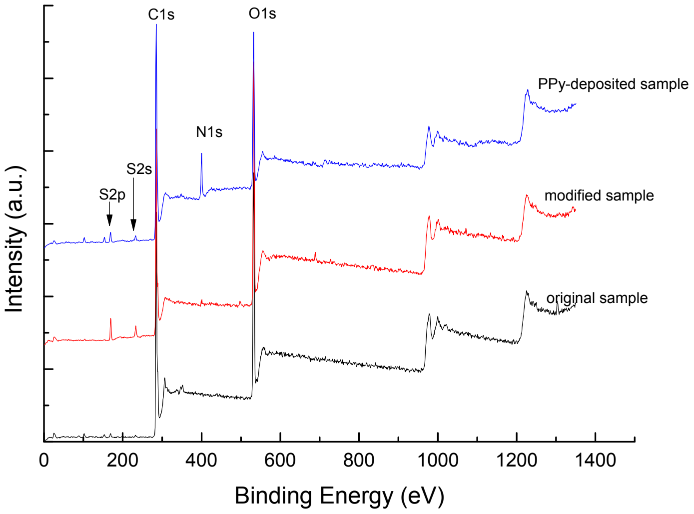

Fig.4 Wide-scan XPS spectra of the original, modified and PPy-deposited PET samples.

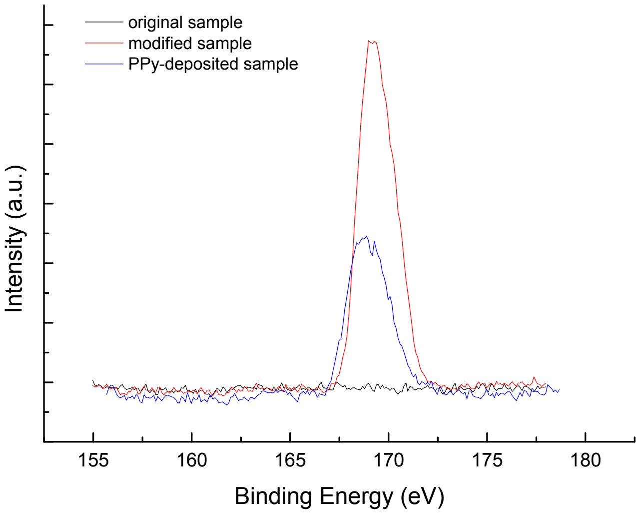

Fig.5 S2p scan of the original, modified and PPy-deposited samples.

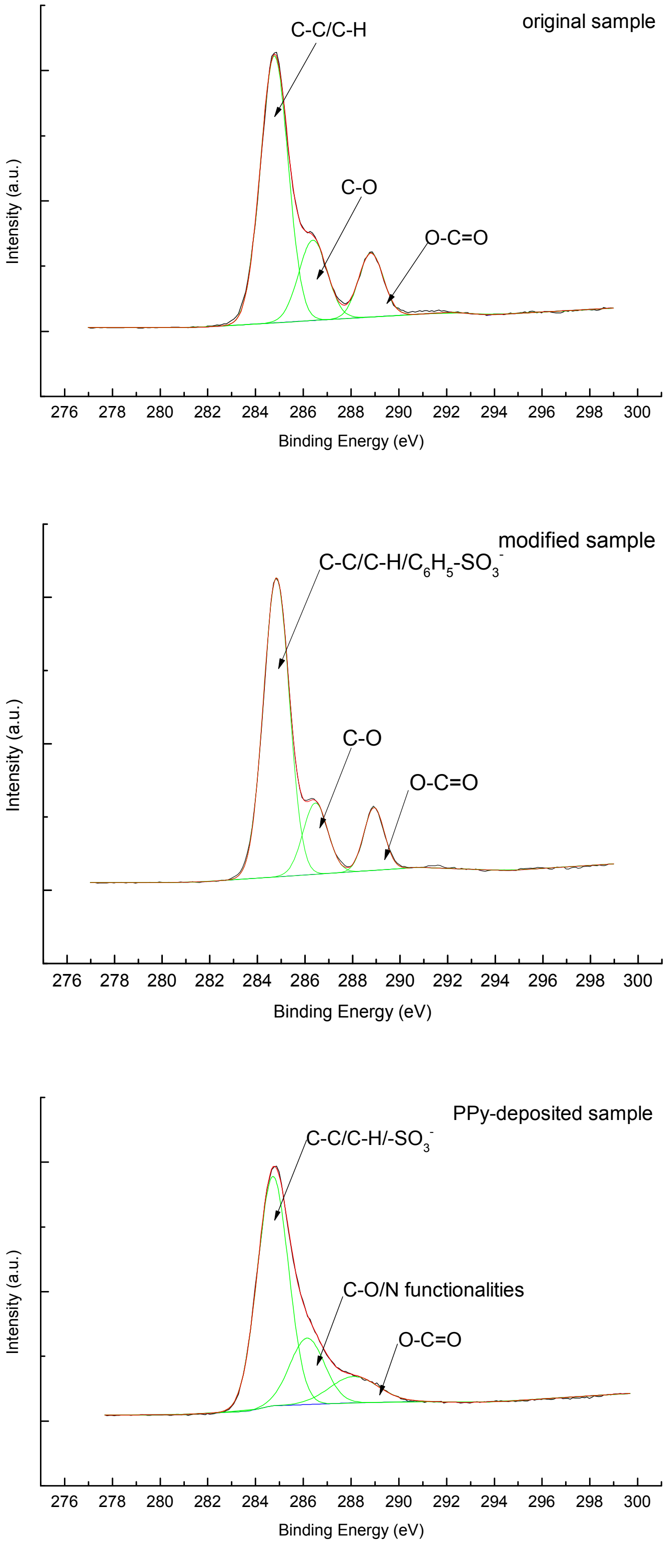

Fig.6 C1s scan of the original, modified and PPy-deposited samples.

Tab.2 The relative concentrations of C containing functional groups of the original, modified and PPy-deposited PET samples

	O-C=O	**C-O/C-N**	**C-C/C-H/Ar-SO_3^-**
Original PET	11.92%	17.30%	70.78%
Modified PET	11.93%	16.50%	71.57%
PPy-deposited PET	11.96%	21.55%	66.48%

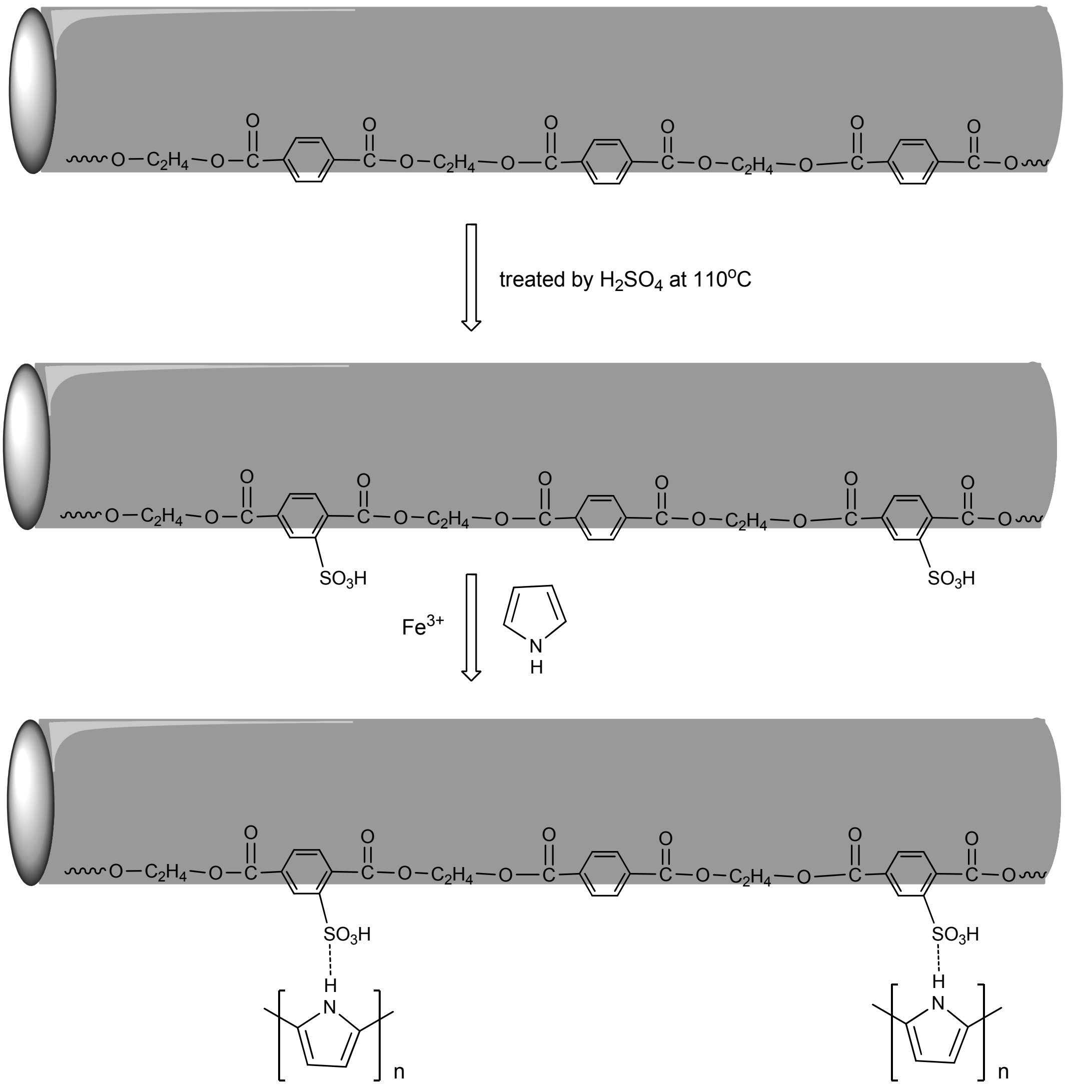

Fig.7 Scheme of improving the interfacial deposition of polypyrrole layer on modified PET fiber by H_2SO_4.

3.6. Sheet Resistance

The sheet resistance of PPy-deposited PET samples was shown in Fig.8 and the concentration of Py monomer was 0.0175 M. It is reported that the conductivity of the PPy-deposited fabrics were nearly proportional to the depositon of PPy[28, 29]. After deposition process of PPy on PET fabrics, the sheet resistance decreased distinctly with the concentrations of H_2SO_4 solution increasing. The sheet resistance of the PET sample modified with 10 $g \cdot L^{-1}$ H_2SO_4 solution was 5 kΩ·cm, while the sheet resistance of unmodified sample was 10 kΩ. The sheet resistance of modified PET fabric decreased by about 50 % as compared with that of unmodified sample. When the concentration of H_2SO_4 solution exceeded 8 $g \cdot L^{-1}$, the sheet resistance tended to a steadiness. It indicated that the surface modification method using H_2SO_4 solution at high temperature was efficient in improving electrical conductivity of the PPy-deposited PET fabrics.

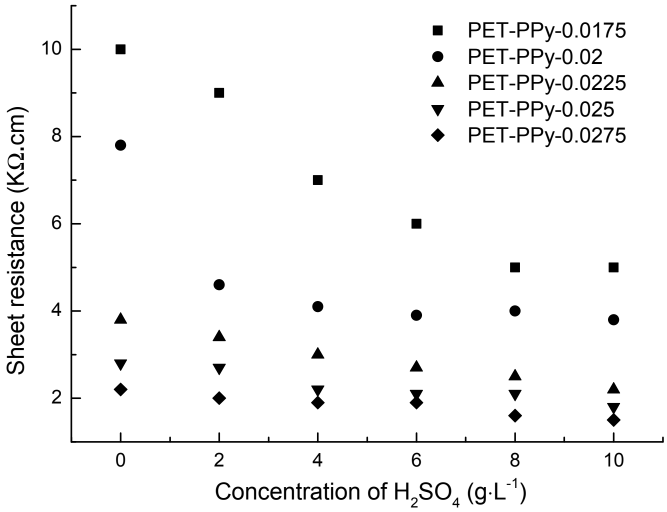

Fig.8 Sheet resistance of the PPy-deposited PET samples.

3.7. XRD patterns

The X-ray diffraction patterns of the original, modified (H_2SO_4 concentration of 10 g·L^{-1}) and PPy-deposited (after modified with 10 g·L^{-1} of H_2SO_4) PET samples were shown in Fig.9. The peaks at 16.39 °, 17.64 °, 21.79 °, 22.79 ° and 26.12 ° (JCPDS No.49-2301) were typical of polyester fabrics. There were no obvious differences in the three patterns. It showed that the major structure of fibers was undamaged when original PET fabrics were modified with dilute H_2SO_4 and deposited with PPy layer. This was because only a small amount of H_2SO_4 was left in PET fibers during the modification process[30].

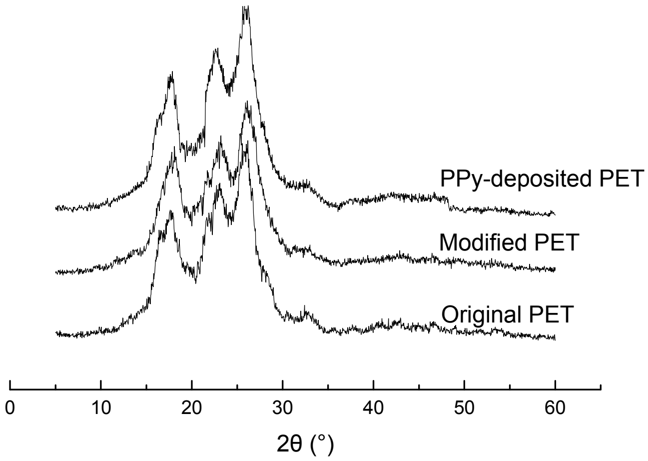

Fig.9 The X-ray diffraction patterns of the original, modified, PPy-deposited PET samples.

4. Conclusion

The surface modification with H_2SO_4 allowed the incorporation of sulfonic groups onto PET fiber surface, as seen by FTIR and XPS analyses. The introduction of polar groups improved the hydrophilicity of PET fabrics and the absorption of pyrrole from water phase onto PET substrates. Hence, the higher deposition of PPy layers was obtained under the same conditions. Besides, the affinity between electrophilic sulfonic groups and nucleophilic N of pyrrole ring was contributed to the deposition of PPy layers on fibers surface. The surface modification of PET fibers with dilute H_2SO_4 prior to polymerization of pyrrole improved the deposition of PPy, resulting in better electrical properties.

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Reference

1. Varesano, A., et al., *A systematic study on the effects of doping agents on polypyrrole coating of fabrics.* Journal of Applied Polymer Science, 2016. **133**(1).
2. Yu, J., et al., *Flame retardancy and conductive properties of polyester fabrics coated with polyaniline.* Textile Research Journal, 2016. **86**(11): p. 1171-1179.
3. Schreuder-Gibson, H.L., et al., *Chemical and biological protection and detection in fabrics for protective clothing.* Mrs Bulletin, 2003. **28**(8): p. 574-578.
4. Curto, V.F., et al., *Concept and development of an autonomous wearable micro-fluidic platform for real time pH sweat analysis.* Sensors and Actuators B-Chemical, 2012. **175**: p. 263-270.
5. Firoz Babu, K., S.P. Siva Subramanian, and M. Anbu Kulandainathan, *Functionalisation of fabrics with conducting polymer for tuning capacitance and fabrication of supercapacitor.* Carbohydrate Polymers, 2013. **94**(1): p. 487-495.
6. Marquez-Herrera, A., et al., *Facile Synthesis of SrCO3-Sr(OH)(2)/PPy Nanocomposite with Enhanced Photocatalytic Activity under Visible Light.* Materials, 2016. **9**(1).
7. Kincal, D., et al., *Conductivity switching in polypyrrole-coated textile fabrics as gas sensors.* Synthetic Metals, 1998. **92**(1): p. 53-56.
8. Do, J.-S. and S.-H. Wang, *On the sensitivity of conductimetric acetone gas sensor based on polypyrrole and polyaniline conducting polymers.* Sensors and Actuators B: Chemical, 2013. **185**: p. 39-46.
9. Jadon, N., et al., *Recent trends in electrochemical sensors for multianalyte detection – A review.* Talanta, 2016. **161**: p. 894-916.
10. Su, P.-G., C.-T. Lee, and C.-Y. Chou, *Flexible NH3 sensors fabricated by in situ self-assembly of polypyrrole.* Talanta, 2009. **80**(2): p. 763-769.
11. Molina, J., et al., *Electrochemical polymerisation of aniline on conducting textiles of polyester covered with polypyrrole/AQSA.* European Polymer Journal, 2009. **45**(4): p. 1302-1315.
12. Maiti, S., D. Das, and K. Sen, *Characterization of electro-conductive fabrics prepared by in situ chemical and electrochemical polymerization of pyrrole onto polyester fabric.* Materials Science and Engineering: B, 2014. **187**: p. 96-101.
13. Hakansson, E., A. Kaynak, and A. Kouzani, *Change in Dielectric Properties in the Microwave Frequency Region of Polypyrrole-Coated Textiles during Aging.* Materials, 2016. **9**(7).
14. Molina, J., et al., *Stability of conducting polyester/polypyrrole fabrics in different pH solutions. Chemical and electrochemical characterization.* Polymer Degradation and Stability, 2010. **95**(12): p. 2574-2583.
15. Kaynak, A., et al., *Study of Radio Frequency Plasma Treatment of PVDF Film Using Ar, O-2 and (Ar + O-2) Gases for Improved Polypyrrole Adhesion.* Materials, 2013. **6**(8): p. 3482-3493.
16. Bober, P., et al., *The deposition of globular polypyrrole and polypyrrole nanotubes on cotton textile.* Applied Surface Science, 2015. **356**: p. 737-741.
17. Hebeish, A., et al., *Advancement in conductive cotton fabrics through in situ polymerization of polypyrrole-nanocellulose composites.* Carbohydrate Polymers, 2016. **151**: p. 96-102.
18. Lu, M., et al., *Enhancement in electrical conductive property of polypyrrole-coated cotton fabrics using cationic surfactant.* Journal of Applied Polymer Science, 2016. **133**(32).
19. Varesano, A., L. Dall'Acqua, and C. Tonin, *A study on the electrical conductivity decay of polypyrrole coated wool textiles.* Polymer Degradation and Stability, 2005. **89**(1): p. 125-132.
20. Cho, G.J., et al., *Preparation and characterization of polypyrrole-coated nanosized novel ceramics.* Langmuir, 2001. **17**(2): p. 456-461.
21. Dall'Acqua, L., et al., *Performances and properties of intrinsic conductive cellulose-polypyrrole textiles.* Synthetic Metals, 2004. **146**(2): p. 213-221.
22. Garg, S., C. Hurren, and A. Kaynak, *Improvement of adhesion of conductive polypyrrole coating on wool and polyester fabrics using atmospheric plasma treatment.* Synthetic Metals, 2007. **157**(1): p. 41-47.

doi:10.20944/preprints201705.0008.v1

23. Mehmood, T., et al., *Improved Bonding and Conductivity of Polypyrrole on Polyester by Gaseous Plasma Treatment.* Plasma Processes and Polymers, 2012. **9**(10): p. 1006-1014.
24. Mehmood, T., et al., *Study of oxygen plasma pre-treatment of polyester fabric for improved polypyrrole adhesion.* Materials Chemistry and Physics, 2014. **143**(2): p. 668-675.
25. Gupta, N.D., et al., *Improvement of adhesion and continuity of polypyrrole thin films through surface modification of hydrophobic substrates.* Journal of Applied Polymer Science, 2014. **131**(2): p. n/a-n/a.
26. Doddi, G., et al., *NUCLEOPHILIC-SUBSTITUTION AT PYRROLE RING - COMPARISON WITH FURAN, THIOPHENE, AND BENZENE RINGS IN PIPERIDINODENITRATION.* Journal of Organic Chemistry, 1976. **41**(17): p. 2824-2826.
27. Gerenser, L.J., *PHOTOEMISSION INVESTIGATION OF SILVER POLY(ETHYLENE-TEREPHTHALATE) INTERFACIAL CHEMISTRY - THE EFFECT OF OXYGEN-PLASMA TREATMENT.* Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films, 1990. **8**(5): p. 3682-3691.
28. Agnhage, T., A. Perwuelz, and N. Behary, *Eco-innovative coloration and surface modification of woven polyester fabric using bio-based materials and plasma technology.* Industrial Crops and Products, 2016. **86**: p. 334-341.
29. Eren, E., et al., *Atmospheric pressure plasma treatment of wool fabric structures.* Journal of Electrostatics, 2015. **77**: p. 69-75.
30. Xu, F., et al., *Facile preparation of super-hydrophilic poly(ethylene terephthalate) fabric using dilute sulfuric acid under microwave irradiation.* Applied Surface Science, 2015. **349**: p. 437-444.