PREPARATION OF POLYPYRROLE/SILVER CONDUCTIVE POLYESTER FABRIC BY UV EXPOSURE

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Abstract:

In this study, polypyrrole/silver (PPy/Ag) conductive polyester fabric was synthesized via an in-situ polymerization method under UV exposure, using silver nitrate ($AgNO_3$) as an oxidizing agent in the presence of sodium dodecyl benzene sulfonate (SDBS) and polyvinylpyrrolidone (PVP). The effect of the preparation processes on the properties of the conductive fabric was studied experimentally, and the optimal preparation process of the conductive fabric was obtained. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) showed the chemical structural properties of the PPy/Ag conductive polyester fabric. X-ray diffraction (XRD) confirmed the presence of silver nanoparticles in the prepared material. Furthermore, subsequent test results proved that the PPy/Ag conductive polyester fabric prepared by UV irradiation had good electrical conductivity and antibacterial property. The sheet resistance of the prepared conductive fabric was $61.54 \ \Omega \cdot sq^{-1}$.

Keywords:

UV exposure, polypyrrole, conductive polyester fabric, in-situ polymerization, nano silver particles

1. Introduction

Conductive polymer-modified synthetic textiles are important emerging materials with the potential of varied applications, for example, electromagnetic shielding, biosensors, electron charge dissipation, pressure sensors, semiconductor materials, transistors, lightweight batteries [1]. Among the existing conductive polymers, polypyrrole (PPy) has received extensive attention due to its excellent stability under environmental conditions, conductivity, biocompatibility, reversible protonation, and the ease with which it is synthesized [2].

Polyester (polyethylene terephthalate [PET]) fiber is inexpensive, environmentally and chemically stable, but does not contain a hydrophilic group, and the adhesion of the pyrrole to the surface of the polyester fabric is poor. Plasma technology can be used to change the physical and chemical properties of polyester fabric surfaces and to improve the bonding fastness between PPy and polyester fabrics [3].

Silver nanoparticles have been studied extensively due to their unique physical and chemical characteristics, such as the large surface-to-volume ratio and the increased surface activity [4]. For example, a PPy/silver polymer is used to prepare gas sensor [5], novel low-humidity sensors [6], electrochemical sensor [7], and so on. At the same time, due to the excellent antibacterial effect of silver, when used as a wearable flexible sensor, a certain antibacterial effect can also be achieved. In recent studies, PPy/Ag nanocomposites have been produced via in-situ polymerization [8], chemical polymerization [9], interfacial polymerization [10], screen printing [11], inkjet printing [12], and so on. Compared with other methods, in-situ polymerization has been considered as the most suitable method due to its simplicity and suitability for large-scale production [13]. However, the selection of oxidant concentrations, dopant concentrations, and reaction time for in-situ chemical polymerization has been random so far [14, 15]. The optimum preparation conditions of PPy/Ag conductive polyester fabric by in-situ polymerization method under UV exposure has not been reported yet.

In this paper, we have synthesized the PPy/Ag conductive polyester fabric by in-situ polymerization method under UV exposure using silver nitrate ($AgNO_3$) as an oxidizing agent in the presence of sodium dodecyl benzene sulfonate (SDBS) and polyvinylpyrrolidone (PVP). We obtained optimum preparation process and studied the effects of different parameters on the electrical conductivity of the composite fabric: $AgNO_3$ concentration, SDBS concentration, PVP concentration, and reaction time under UV irradiation. The surface morphology of the composite fabric was analyzed and its structure and composition were characterized. The antibacterial and durability test, that is, the resistance of composite fabric to abrasion was tested. The results indicated that PPy/Ag conductive polyester fabrics have good application potential in flexible sensors and intelligent garment.

2. Experimental

2.1. Materials

Sodium hydroxide, absolute ethanol, and $AgNO_3$ used in the experiment were AR grade reagents. PVP and SDBS were

GR grade reagents. All the solutions were prepared using deionized water during the synthesis. Polyester warp knitted fabrics (5 cm x 5 cm) with areal density 10^3 g/m² were used in this study.

2.2. Preparation of PPy/Ag conductive polyester fabric

PPy/Ag was used to synthesize the polyester fabric by in-situ polymerization method under UV exposure as shown in Figure 1. First, the polyester warp knitted fabric was put into 5 g/l sodium hydroxide to remove impurities. The dried fabric was subsequently subjected to plasma treatment for 4 min (using an oxygen low-temperature vacuum plasma apparatus, 220 W).

In a beaker, $AgNO_3$, PVP, and SDBS were added sequentially. The fabric padding 1.5 ml of pyrrole monomer was then added to the above solution under constant stirring for 5–9 h using magnetic stirrer at room temperature. The reactions were carried out under a 365 nm UV lamp at room temperature. After UV exposure, the samples were removed and cleaned with ethanol and deionized water. The fabrics were dried in the oven at 60°C for 1 h.

2.3. Characterization tests

The morphology of composites was observed using a SU1050 scanning electron microscopy (SEM). The crystal structure of the samples was characterized by D2-PHASER X-ray diffraction (XRD) operating at 40 kV and 40 mA, using Cu Kα radiation. The samples were scanned in 2θ orientation ranged from 9° to 10°. The Fourier transform infrared (FTIR) spectrum of PPy/Ag conductive polyester fabrics was recorded using Perkin-Elmer-Spectrum 2000 Spectrophotometer between 1,000 and 4,000 cm⁻¹. X-ray photoelectron spectroscopic measurements were carried out with a AXIS Supra by Kratos Analytical Inc. using monochromatized Al Ka radiation (hv = 1,486.6 eV, 225 W) as X-ray source with a base pressure of 10^{-9} torr. The analyzed area of all X-ray photoelectron spectroscopy (XPS) survey spectra was 300 x 700 µm². A charge neutralizer was used throughout as the samples were mounted in such a way that they were electrically isolated from the sample bar.

The sheet resistance was determined using four probe electrical meter (Quanzhou Fengyun Testing Equipment Co., Ltd.); every measurement was repeated five times; and the average value was calculated [16]. GB/T 20944.1 2007 "Evaluation of Antibacterial Properties of Textiles Part 1: Agar Plate Diffusion Method" can be referred to test and evaluate the antibacterial properties of the samples. The test strains were *Escherichia coli* and *Staphylococcus aureus*. The resistance of samples was tested after subjecting them to cycles of rubbing using Martindale abrasion test, and the sheet resistance values after 100, 500, 1,000, 1,500, and 2,000 times of rubbing were then recorded respectively.

3. Results and discussion

According to the experiment, in the absence of UV light, the fabrics started to turn black after 48 h. In order to obtain the optimal preparation process of the PPy/Ag conductive polyester fabric under UV exposure, the effect of the reaction time, SDBS concentration, PVP concentration, and $AgNO_3$ concentration on the properties of the conductive fabric was studied experimentally as shown in Figure 2.

The effect of reaction time on the sheet resistance of the composite fabric is shown in Figure 2a. As the reaction time increased, the sheet resistance recorded an initial decrease followed subsequently by an upsurge. In the initial stage of the reaction, the polymerization reaction was not complete due to the short reaction time. At this time, only the pyrrole on the surface of the fabric reacted, so the sheet resistance of the fabric was large and the surface of the fabric was gray. As the reaction time increased, the pyrrole monomer had been oxidatively polymerized to form PPy, the fabric appeared black, and it was observed that the surface of the fabric has reduced Ag particles. As the reaction time continued to increase, the PPy oxidized excessively, and the macromolecular chain was destroyed. Thus the resistance of the fabric sheet began to increase at the reaction time beyond 8 h.

The other reaction conditions remained unchanged, and the concentration of the dopant SDBS was changed to investigate its effect on the electrical conductivity of PPy/Ag conductive polyester fabric. It can be seen from Figure 2b) that as the concentration of SDBS increased, the sheet resistance of the composite fabric continued to increase. This may be due to the fact that as the concentration of SBDS increased, the excessive anions in the SDBS hindered other reactions in the solution [1].
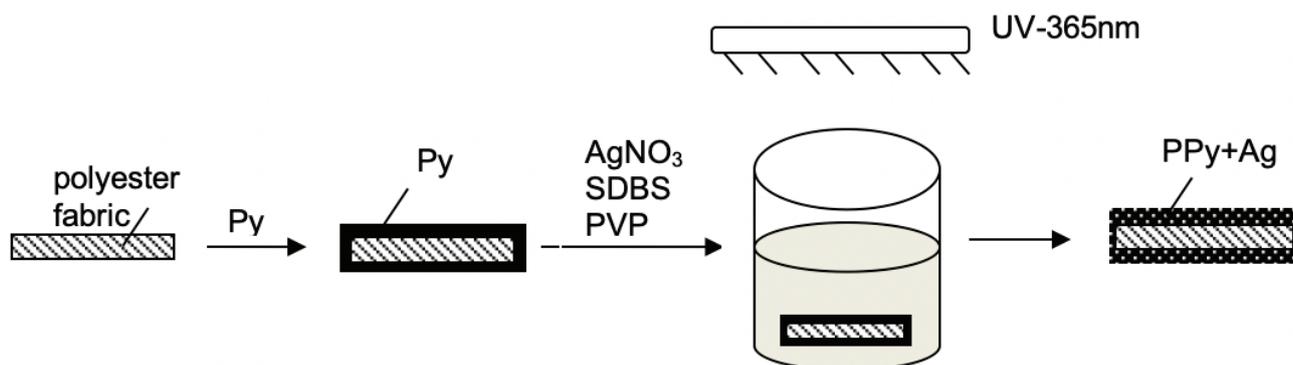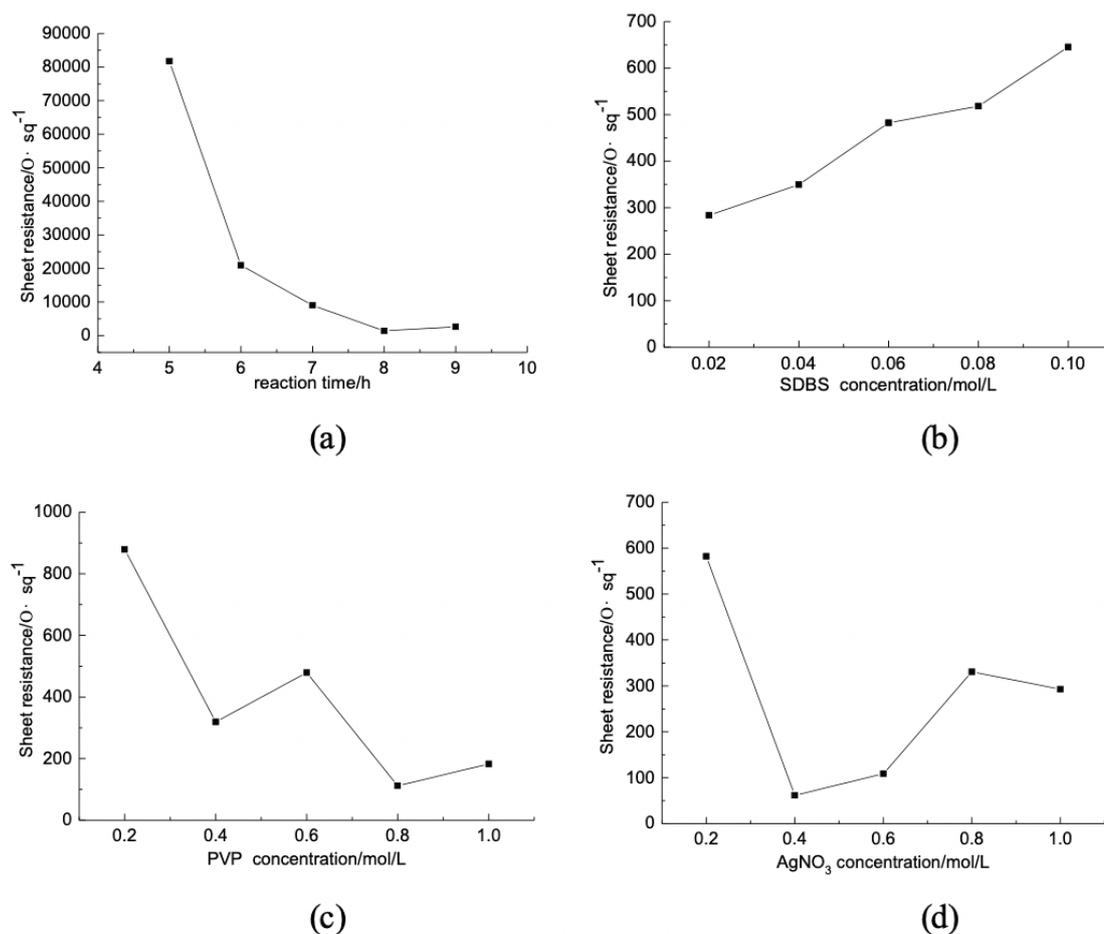

Figure 1. Preparation of PPy/Ag conductive polyester fabric.

Figure 2. Effect of preparation processes on composite fabric sheet resistance: (a) reaction time, (b) SDBS concentration, (c) PVP concentration, and (d) AgNO$_3$ concentration.

PVP has two roles in this process, namely as a capping agent for forming silver nano-rods and as a dispersing agent for the pyrrole monomer [17]. PVP can prevent the aggregation of nanoparticles efficiently. It can be seen from Figure 2c that as the concentration of PVP increased the sheet resistance of the composite fabric changed more obviously. When the PVP concentration increased, the pyrrole monomer was uniformly polymerized to form a PPy layer, while the sheet resistance of the fabric was lowered. When the PVP concentration was too high, more nano silver ions were formed which hindered the formation of the PPy film, resulting in an increase in the sheet resistance.

When the concentration of AgNO$_3$ was low, the pyrrole monomer in the solution could not be completely oxidized to form enough PPy, so the sheet resistance of the fabric was large and the conductivity was poor. As the oxidant concentration increased, the pyrrole was completely oxidized. When the concentration of the oxidant continued to increase, the pyrrole was easily over-oxidized. Some of them double-bonded in the PPy main chain which destroyed the conjugated structure of the PPy molecule and the migration and transport of the carrier, causing the molecular chain to be short-circuited and thus the sheet resistance increased.

Figure 3a shows the surface morphology of the untreated polyester fabric; Figure 3b shows a composite fabric treated for 5 h; and Figure 3c and d shows a composite fabric treated under optimum conditions for 8 h. As can be seen from Figure 3a, the untreated polyester fabric has a smooth surface. However, only a small amount of polymer adhered to the surface of the composite fabric at a reaction time of 5 h, so the sheet resistance is large. It can be observed from Figure 3c that a continuous PPy layer has been formed on the surface of the fiber and a large number of rod-like particles were formed on the surface layer.

The infrared spectrum of the sample is shown in Figure 4, where the #0 line is the infrared spectrum of the polyester fabric. The absorption peak at 1,586 cm^{-1} is a stretching vibration peak of the C=O bond. The strong and wide band at 984 and 1,090 cm^{-1} is a characteristic peak of the C–O stretching vibration. The weak absorption peak at 1,506 cm^{-1} is produced by the stretching vibration of the C=C skeleton in the benzene ring, which proves the presence of a benzene ring. At 2,343 cm^{-1} it is the stretching vibration peak of C–H bond, and 3,460 cm^{-1} is the characteristic peak of the N–H bond stretching vibration [18]. On the #1, #2, and #3 lines of the composite fabric in Figure 4, we can see the characteristic peaks of polyesters such as 984, 1,090, and 1,586 cm^{-1}. It can also be seen that the characteristic peaks at 1,506, 2,343, and 3,460 cm^{-1} are an indication that PPy has been deposited on the polyester fabric.
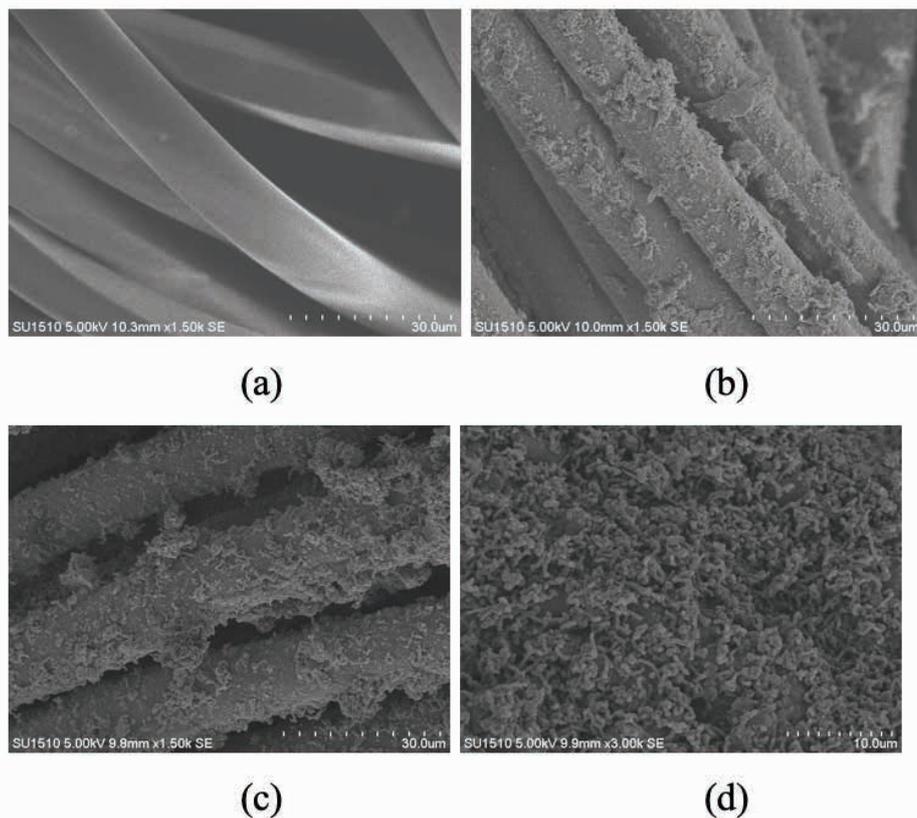
Figure 3. SEM images of specimens: (a) image of sample #0 (x1,500); (b) image of sample #1 (x1,500); (c) image of sample #2 (x1,500); and (d) image of sample #3 (x3,000).

Figure 5a and b shows the XPS survey spectra for polyester fabrics and PPy/Ag composite fabric. For polyester fabrics, there are two main peaks: C1s (282.5 eV) and O1s (530.9 eV). It is noted that the survey spectrum experienced dramatic changes due to the deposition of PPy/Ag composite film. Nitrogen is detected (unique elemental marker for PPy) by its N1s narrow region (399 eV).

The high-resolution XPS survey spectrum of PPy/Ag composite fabric displays Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ peaks at 374.2 and 368.1 eV, respectively (Figure 5c); these values are quite consistent with the values of pure silver [19]. Therefore, it is clearly evident that silver ions are reduced to silver nanoparticles in the presence of pyrrole.

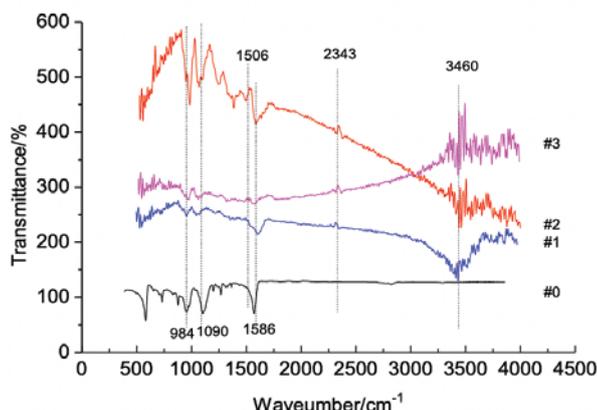**Figure 4.** Infrared spectrogram of samples.

Figure 6 shows the XRD spectrum of the fabrics. The samples under two different treatment conditions have obvious characteristic peaks around 37.6°, 43.7°, 63.9°, 76.9°, and 81.1°, which correspond to silver: (111), (200), (220), (311), and (222) crystal plane characteristic diffraction peaks. According to the results, it can be concluded that silver particles were present on the surface of the PU/Ag composite. The patterns are in agreement with JCPDS files No 00-001-1164 and confirm the metallic nature of the silver particles produced by the UV-induced reaction of PPy and AgNO$_3$ [20]. Combined with the XRD test and Figure 3d, it can be concluded that these rod-shaped particles are silver nano-rods formed by the coordination of PVP, and these continuous silver nano-rods are beneficial for improving the electrical conductivity of the fabric [17].

The silver–polymer composite materials had been reported to possess excellent antibacterial properties [21-24]. The test strains were *E. coli* and *S. aureus*. The formula for calculating the width *H* of the bacteriostatic zone is

$$H = \frac{1}{2}(D - d)$$

where *H* is the width of the bacteriostatic zone (mm), *D* is the average value of the outer diameter of the bacteriostatic zone (mm), and *d* is the diameter of the sample (mm).

Under the same conditions, the antibacterial properties of untreated polyester (sample #0) and PPy/Ag conductive polyester fabric (samples #1 and #2) were tested. The results are shown in Figure 7. Sample #0 did not have a bacteriostatic effect, whereas sample #2 had a bacteriostatic bandwidth
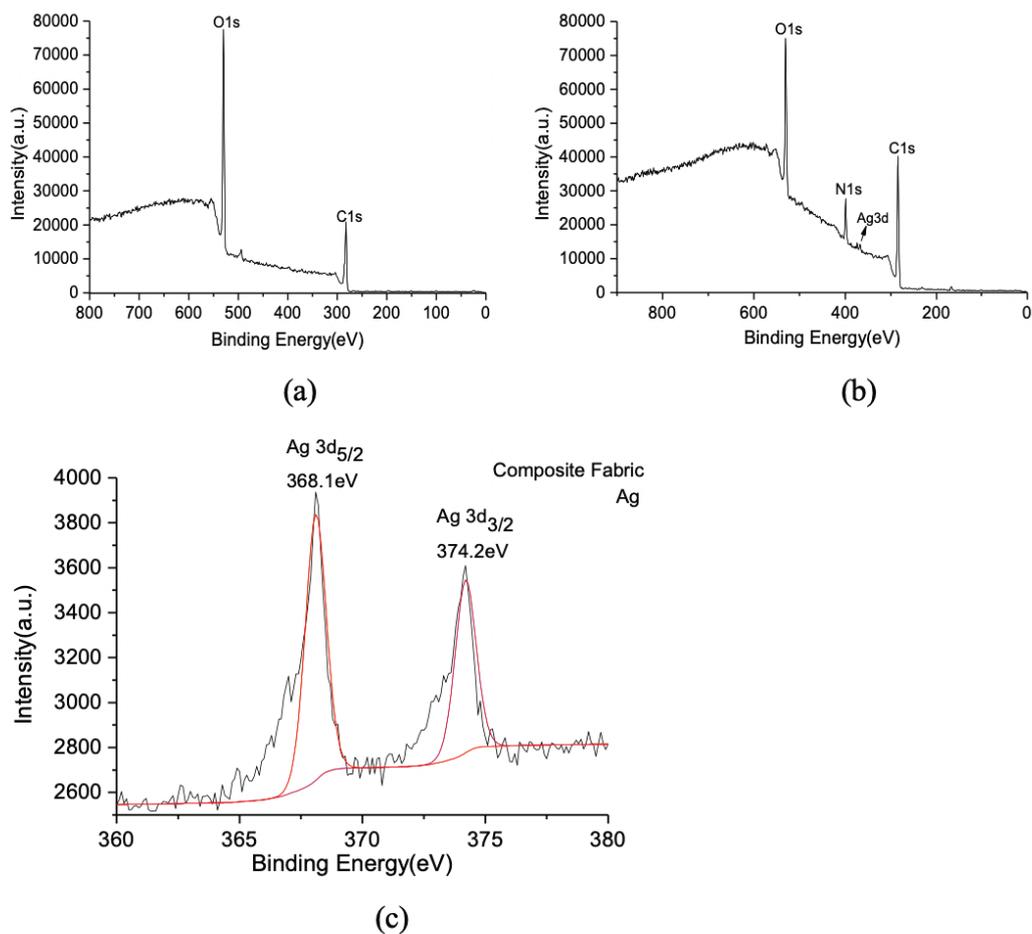
(a)

(b)

(c)

Figure 5. XPS survey spectra for (a) Polyester fabric (b) PPy/Ag conductive polyester fabric (c) XPS Ag spectra for PPy/Ag composite fabric.
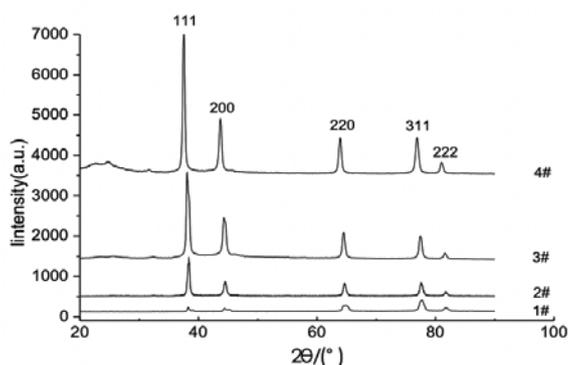

Figure 6. XRD pattern of samples.

greater than #1 which showed a better bacteriostatic effect. Table 1 shows the comparison of the antibacterial effects of the samples. It can be seen that the experimentally prepared PPy/ Ag conductive polyester fabric had a good inhibitory effect on Gram-positive *S. aureus* and Gram-negative *E. coli*.

In order to understand the extent to which the number of rubbing in practical applications impact the electrical conductivity of the fabric, the abrasion tests were carried out on the conductive fabrics and the resistance was subsequently tested. As shown in Figure 8, the variation of the sheet resistance of the three different composite fabric samples after different flat grinding times was tested. As can be seen from Figure 8, the sheet resistance of the fabric increased with the number of flat grinding times. In the process of flat grinding, the PPy films with weak adhesion on the surface of the fabric gradually fell off, and the sheet resistance gradually increased. Although this trend is relatively slow, the composite fabric retains a small sheet resistance after some friction. The ways to reduce the influence of external force or abrasion on the electrical conductivity of the composite fabric in practical application environment, and how

Table 1. Bacteriostatic effect of samples

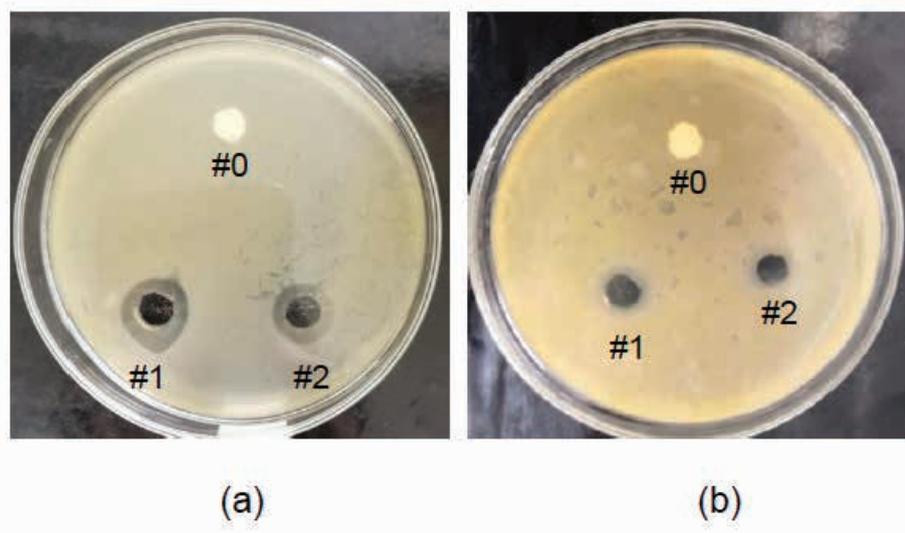| Samples	Bacterial reproduction under the sample	Inhibition zone width (mm)		Evaluate
		E. coli	*S. aureus*	
#0	Mass	0	0	No effect
#1	Slight	>1	>1	Good effect
#2	Slight	>1	>1	Good effect

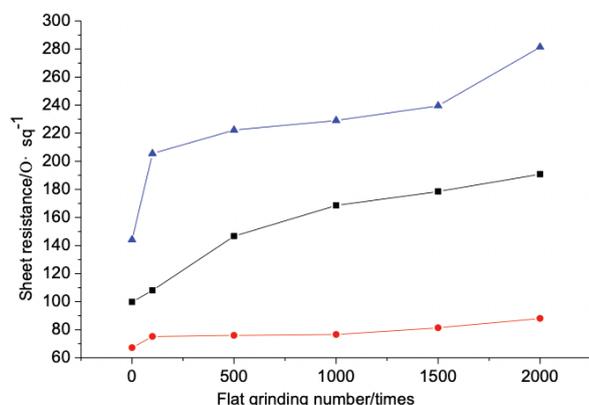**Figure 7.** Bacteriostasis test: (a) E. coli and (b) S. aureus.

Figure 8. Effect of flat grinding times on composite fabric's sheet resistance

to improve the adhesion strength and stability of the conductive film are worthy of further investigation and discussion.

4. Conclusion

This research presented a successful preparation of PPy/silver conductive polyester fabric via UV exposure. The optimized process conditions of PPy/Ag conductive polyester fabric included $AgNO_3$ concentration 0.4 mol/L, SDBS concentration 0.02 mol/L, PVP concentration 0.8 mol/L, reaction time 8 h, and the sheet resistance of the composite fabric obtained is 61.54 $\Omega \cdot sq^{-1}$. The test results showed that a continuous layer of PPy was formed on the surface of the prepared composite fabric. At the same time, the silver nano-rods formed by the coordination of PVP were beneficial to improve the electrical conductivity of the fabric. The PPy/Ag conductive polyester fabric prepared by the experiment had obvious antibacterial effect, and had good inhibitory effect on Gram-negative E. coli and Gram-positive S. aureus.

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