Electroless Silver Plating on the PET Fabrics Modified with 3-Mercaptopropyltriethoxysilane

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ABSTRACT: The feasibility of adherent silver layers onto PET fabrics by electroless plating was explored and its optimal technology for modification and electroless plating was investigated. Morphology, structure, and thermal stability of silver plating PET fabrics were characterized by scanning electric microscope (SEM), X-ray diffraction (XRD) and thermogravitric (TG) analysis. As the silver weight on the modified fabric is 25 g/m^2, the electromagnetic shielding effectiveness (SE) of silver plating PET fabric is more than 30dB at the frequency ranging from 1MHz to 5000 MHz. The results show that the silver plating PET fabric has good electrical conductivity and electromagnetic shielding property. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1912–1918, 2012

Key words: polyester fabric; 3-mercaptopropyltriethoxysilane; electroless plating; silver plating; conductive fabric

INTRODUCTION

Conductive fabrics have great application value in various fields because of their desirable properties, such as favorable electrical conductivity, electromagnetic shielding, electrostatic discharge, and the good nature of fabric. It can be used for traditional clothing, including working clothing for protecting antistatics or electromagnetic radiation and antiradiation clothing for pregnant, and innovative biomedical uses.[1–3]

For the metal plating, nickel,[4] copper,[5] silver,[6,7] gold,[8] aluminum, and their composite play an important part in recent studies. Nickel and copper display good electrical conductivity. But nickel metal layer tend to cause allergic for people. The copper layer is subject to oxidation, and these affect their stability and durability. Compared with gold, silver is cheap and provides good conductivity as well. Besides, silver has antibacterial properties. So it will be widely used in medical areas, antistatic suits, antiradiation clothes, etc.

There are some ways to obtain the silver deposition on polyester fabric. For example, ion beam assisted deposition,[9] plasma-assisted deposition,[10] magnetron sputtered coating,[11] chemical vapor deposition,[12] and physical vapor deposition.[13,14] However, they must be carried out in a vacuum. It limits the expansion of their application. Electroless plating is an effective method for silver deposition. And it has many advantages, for example, the plating layer is uniform'compact and has a low porosity. Besides, the process and equipment for electroless plating are simple and easy to be controlled.[15]

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EXPERIMENTAL

The 100% white polyester fabrics with plain weave structure (size: 7.5 cm × 5.5 cm) were used in this study.3-mercaptopropyltriethoxysilane was purchased from Jinzhou Jianghan Fine Chemical, China. Silver nitrate (AR 99.9%) was obtained from Shanghai Institute of Fine Chemical Materials, China. Other reagents were of analytical pure. In all preparations, distilled water was used.

Experimental principle

PET fabric was modified with 3-mercaptopropyltriethoxysilane through the condensation reaction of one end in 3-mercaptopropyltriethoxysilane and the hydroxyl on the PET fiber. And the other end containing mercapto group can react with silver by chelation reaction to adsorb silver firmly. Then the silver deposition on the fiber surface was conducted by the silver auto-catalytic.

The whole processes of reaction are listed in Figure 1.

Pretreatment of PET

The PET fabric was washed in the solution containing 15 g/L sodium hydroxide and 7 g/L nonionic

TABLE I
The Formula of Electroless Silver Plating

	Concentration of each solution	Application condition
Solution A	$AgNO_3$: 8.3–41.6 g/L; NaOH : 0.25 g/L; NH_4OH (28%) : some drops	20 mL solution A and 20 mL solution B; 20–60°C; 40–80 min
Solution B	$C_6H_{12}O_6$: 36–54 g/L; tartaric acid : 4 g/L; CH_3CH_2OH : 100 mL/L	

detergent fatty poly (ethylene oxide (10) ether) at 70°C for 20 min to remove oil and soil on the fabric surface. Then it was rinsed with distilled water. Alkali treatment for the cleaned PET fabric was in the solution of 200 g/L NaOH at 60°C for 30 min. Then it was rinsed with distilled water and ethanol respectively, dried at 60°C for 15 min, and weighted. The fabric was immerged in acetic ether solution of 3-mercaptopropyltriethoxysilane and washed in ethanol. Then dried at 95°C for 15 min, and weighted.

Electroless silver plating on PET fabrics

The PET fabric which had been modified with 3-mercaptopropyltriethoxysilane was immerged in silver plating solution with constant stirring for metallising reaction. The composition of solution[15] was listed in Table I. In the process of silver plating, the mix ratio of solution A and B is 1 : 1(v/v). The fabric was cleaned in distilled water. Then dried at 95°C for 20 min, and weighted.

Measurement and characterization

The thickness of silver plating PET fabric was measured by YG141*N* digital fabric thickness meter (Hongda, China).The thickness increase was calculated as follows:

$$\text{Thickness increase} = T - T_0$$

where T_0 and T are the thickness of PET fabric before and after plating respectively.

The weight of PET fabrics before and after electroless plating was measured by AL104 Electronia Balance (Mettler Toledo, Switzerland) under standard conditions. The percentage of weight increase was calculated by the following formula:

$$\text{Weight increase} = (W - W_0) \times 100/W_0$$

where W_0 and W are the weight of PET before and after plating, respectively.

The antistatic property of PET fabric was measured by fabric inductive static test instrument YG(B) 342E(Darong, Wenzhou, China) according to FZ/T01042-1996. Sample size is 50 mm × 50 mm. Test environment: temperature 20 ± 2°C, relative humidity 38 ± 2%, rotary speed 1500 R.P.M.

The tearing strength of PET fabric before and after silver plating was measured by Elmendorf Tearing Tester according to ASTMD 1424-1996.

The surface resistance of conductive fabric was measured by four point probe method using Daming R235 resistance instrument. The surface resistance is the resistance of a square sample. The units of surface resistance are commonly expressed as mΩ/□ or mΩ/sq. Scanning electric microscope (SEM, model TM-1000, Hitachi, Japan) analysis was used to observe the varying morphology of the fabric during the treatment. Crystal structure of PET fabric modified with 3-mercaptopropyltriethoxysilane and silver

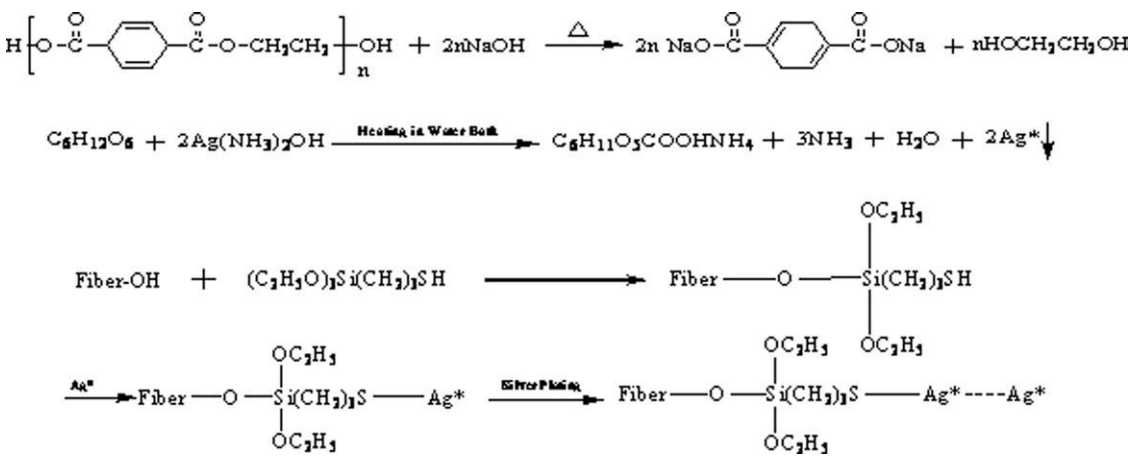

Figure 1 Schemes of PET fabric bonded silver for initiating electroless silver plating.

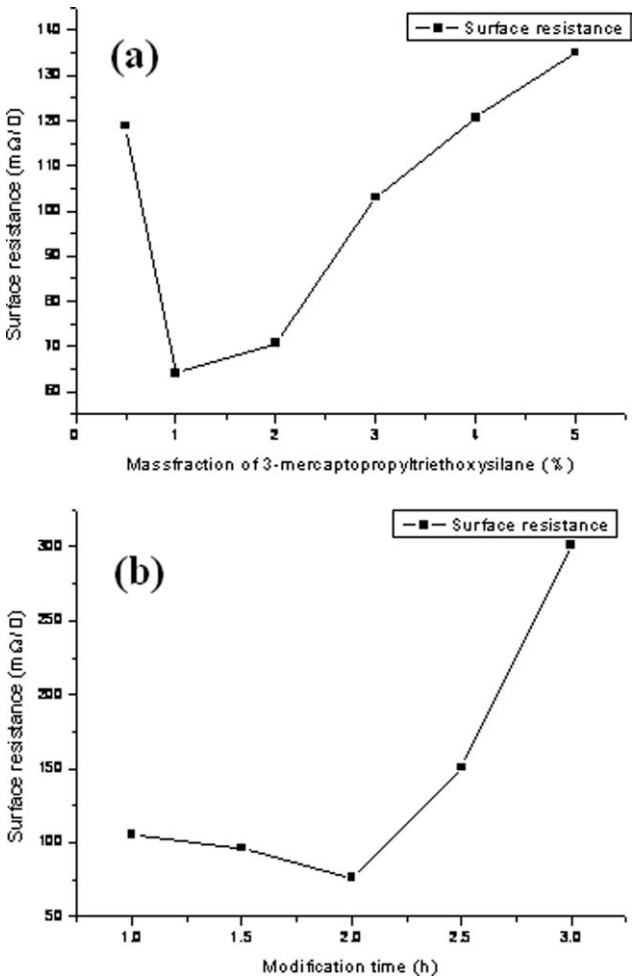

Figure 2 The effect of mass fraction of 3-mercaptopropyltriethoxysilane (a) and modification time (b) on the surface resistance.

plating PET fabric was characterized by Rigaku D/MAX-2550 PC X-ray diffraction. Thermogravimetric analysis (TG, model STA-100, Henven Beijing, China) was performed in air with heating rate of 10°C/min, from 50 to 800°C.

RESULTS AND DISCUSSION

The effects of 3-mercaptopropyitriethoxysilane mass fraction and time of modification on the conductivity of polyester fabric

The PET fabric after coarsening was modified with different mass fraction of 3-mercaptopropyltriethoxysilane for different time at room temperature. The modified PET fabric was treated by the solution as experimental section given. The factors, mass fraction of 3-mercaptopropyltriethoxysilane (a), and modification time (b), affected the conductivity of fabric. As shown in Figure 2(a), the surface resistance of silver plating PET fabric tends to decrease first and increases afterward along with the augment of the mass fraction. The optimum concentration for the highest electrical conductivity is 1%. In Figure 2(b), the surface resistance decreases at the beginning and then increases rapidly. And the turning of modification time is 2.0 h which is the best for the minimum surface resistance. From the process of formation of mercapto group on the surface of fabric, which made silver react with —SH for the silver plating. With the growth of mass fraction of 3-mercaptopropyltriethoxysilane and the modification time, the single molecule film can formed gradually and then turned into multimolecular layer on the fiber surface which built a strong hydrophobic interaction, meaning the formation of Ag—S bond through the reaction of silver and —SH became more difficult than before. Therefore, the fabric surface resistance was increasing gradually.

Electroless plating silver formulation optimization

The effects of $AgNO_3$ concentration (a), Glucose concentration (b), plating temperature (c), and time (d) on the surface resistance and rate of weight gain were listed in Figure 3. As shown in Figure 3(a), the surface resistance of fabric decreases while the rate of weight gain increases with the growth of $AgNO_3$ concentration. As the growth of $AgNO_3$ concentration above 20.8 g/L, the increasing rate of weight gain is greater than before. Such deposition makes little contribution to reducing resistance and only lead to wasting the cost of silver resulting the fastness of silver plating fabrics drops. One of the most fundamental information can draw in Figure 3(b,c) that the greater the weight gain, the smaller the surface resistance. So the optimal concentration of $C_6H_{12}O_6$ is 24.75 g/L and the best plating temperature is identified as 50°C. In Figure 3(d), the weight gain do not rise markedly when the time is 70 min which shows that the silver of plating bath have largely been reduced. And the surface resistance of PET fabric remains unchanged fundamentally at the same time.

Characterization

SEM analysis

The morphology of the original PET, coarsened PET, modification by mercapto, and silver-plated fabric was analyzed by scanning electron microscopy (SEM). In Figure 4(a), the untreated polyester shows a smooth surface. After the coarsen effect of Alkali, the fibers forms numbers of pits on the surface as shown in Figure 4(b). This will enhance the hydrophilic of fiber, as well as increase the roughness of surface, which will do good to the combination fastness of silver plating[14]. Figure 4(c) shows the fabric after modification, which is darker compared with Figure 4(b) at the same condition. It shows that mercapto modified

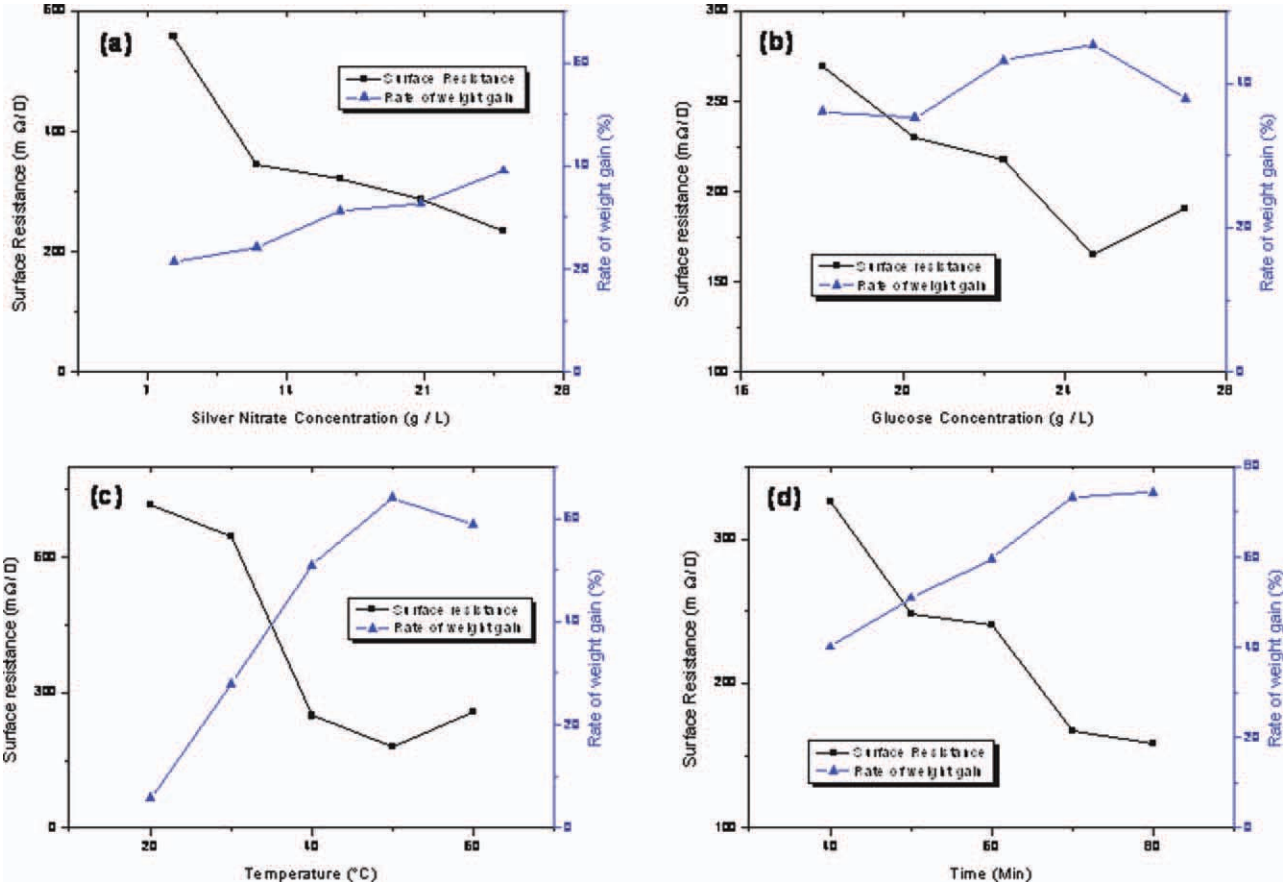

Figure 3 The effect of $AgNO_3$ concentration (a), Glucose concentration (b), plating temperature (c) and time (d) on the surface resistance and rate of weight gain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

silane is formed on the fiber surface. From Figure 4(d), a uniform and compact silver plating layer can be noticed on the surface of PET fabric.

XRD analysis

The X-ray diffraction pattern of polyester fabric after mercapto modified was shown in Figure 5(a). The characteristic diffraction peaks of it appearing in the $2\theta = 17°$, $22°$, $25°$ was strong. In Figure 5(b). The diffraction peaks appearing in the $2\theta = 38.22°$, $44.38°$, $64.6°$, $77.48°$, $81.62°$ were in behalf of silver (111), (200), (220), (311) and (222) plane.[16] The oxidation state of silver was not detected in the plating. All these showed that the silver was deposited on the surface of fabric. The characteristic diffraction peaks in Figure 5(a) decreased significantly in Figure 5(b) which showed the silver layer was uniform and density. In addition, the XRD pattern 5b shows a relatively broad diffraction peak, indicating that the size of Ag crystallites is relatively small. On the basis of the diffraction peaks of the (111) planes, the average size of the Ag crystallites in the silver plating layer calculated from XRD pattern 5b by the Scherrer formula[17] is about 30.0 nm.

TG analysis

The thermal properties of PET fabrics were detected by thermogravitric (TG) analysis. As shown in Figure 6(a), the weight loss stage is beginning at 314°C and ending at 579°C. And the last remnant is 46%. In Figure 6(b), the initial decomposition temperature of silver plating PET is 324°C and the end decomposition temperature is 564°C. The remaining of fabrics is 62%, which is more than these of the PET fabric before silver plating it shows the silver deposition on the PET surface is successful. The initial decomposition temperature of silver plating PET fabric is a little higher than the original one, which means that the silver plating have little effect on the heat-resistant property of PET fabric.

Shielding effectiveness

Combining the optimal technology, the change of thickness and surface resistance before and after silver plating was available, as shown in Table II. According to Schelkunoff theory[18], Chemical silver plating fabric shows a different electromagnetic

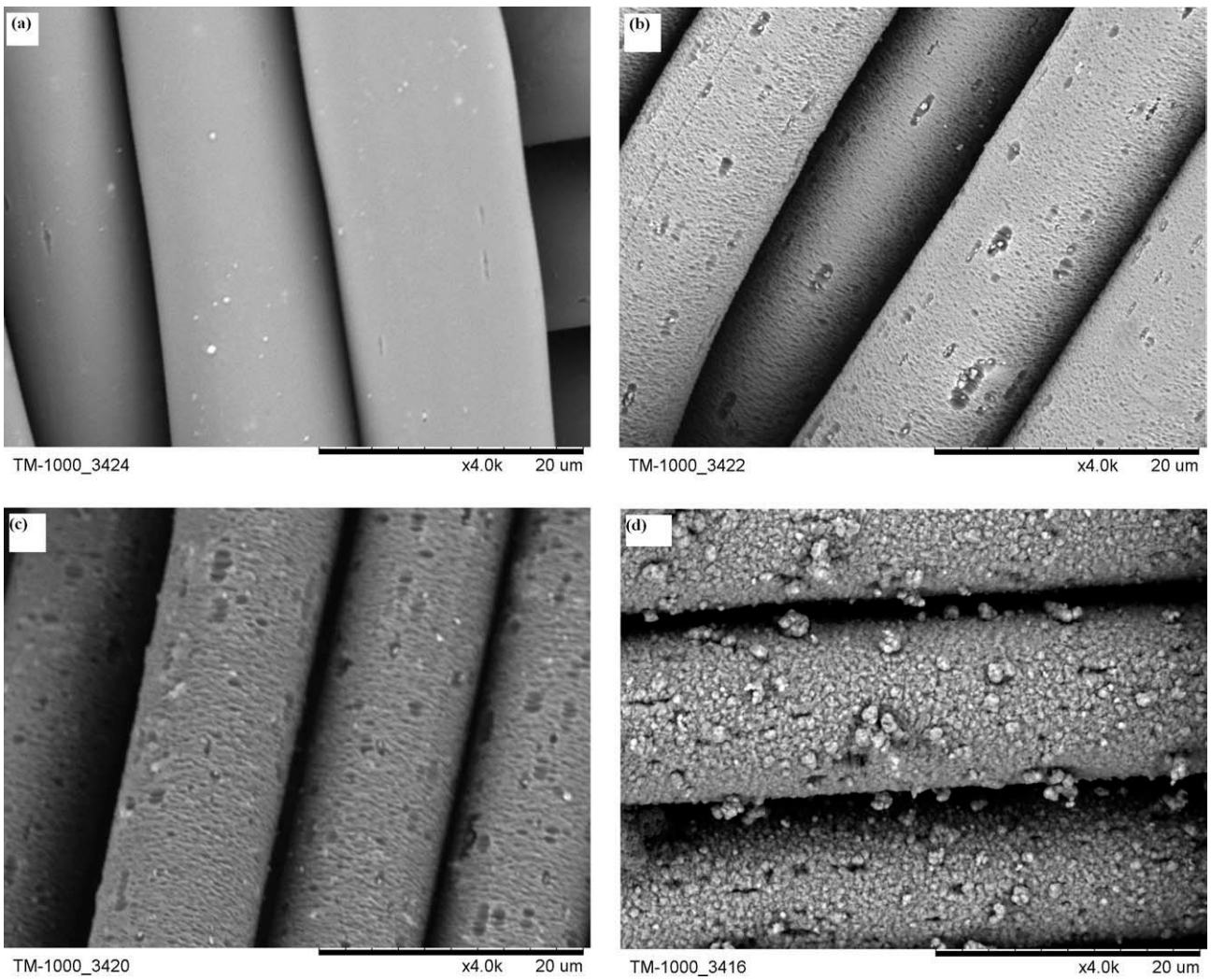

Figure 4 SEM photos of (a) PET fiber; (b) after roughening; (c) after modification with mercapto group and (d) silver plating PET fabrics.

shielding effectiveness at different frequencies, as shown in Figure 7. The electromagnetic shielding effectiveness is more than 30 dB that is equivalent to 96% of electromagnetic microwave being shielding

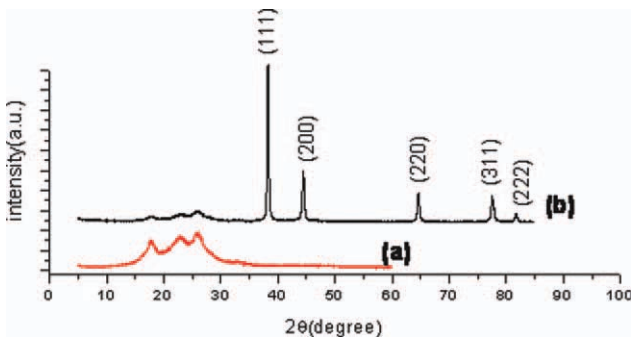

Figure 5 XRD spectra of PET fabric modified with 3-mercaptopropyltriethoxysilane (a) and after silver plating (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

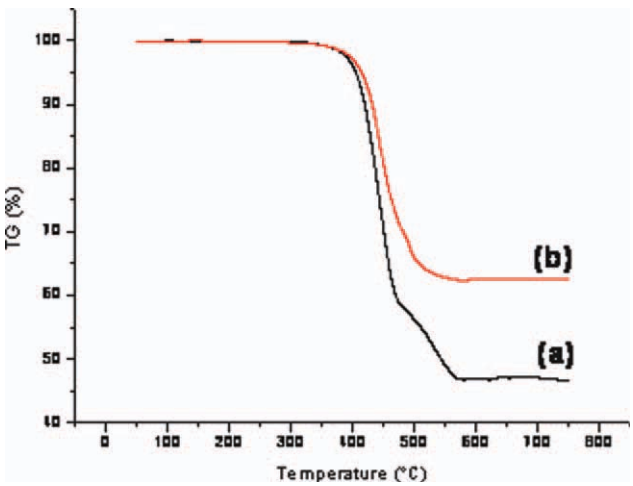

Figure 6 TG curve of PET fabric before (a) and after silver plating (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Thickness and Surface Resistance Before and After Silver Plating

	Thickness (cm)	Surface resistance (mΩ/□)
Before silver plating	0.079	nonconducting
After silver plating	0.090	0.080

off when frequencies range from 1–5000 MHz. This can meet the civil market requirements for electromagnetic protective equipment.

Antistatic performance testing

The static voltage and half-life value inductive static of PET fabrics before and after silver plating was test by inductive static instrument. As shown in Table III, the static of the silver plating PET fabric experienced a reduced value dropping from 1135 V to 139 V when compared with original fabric, which fell into about 10 times than before. Besides, the average static half-life value of the silver plating PET fabric was almost null while the half-life value of original fabric was 760S. The smaller the static voltage value and the half-life time, the better the antistatic property of the PET silver fabric. Therefore, the antistatic performance of PET fabric after electroless silver plating has been greatly improved.

Tearing strength testing

It can be seen in Table III that the tearing strength of silver plating PET fabrics was dropping from 10.18*N* to 6.37*N* when compared with the PET before plating. The tearing strength of the silver plating fabric decreased with strength of 3.81*N*, which equivalent to reduce by 37.4%. The fracture surfaces of the

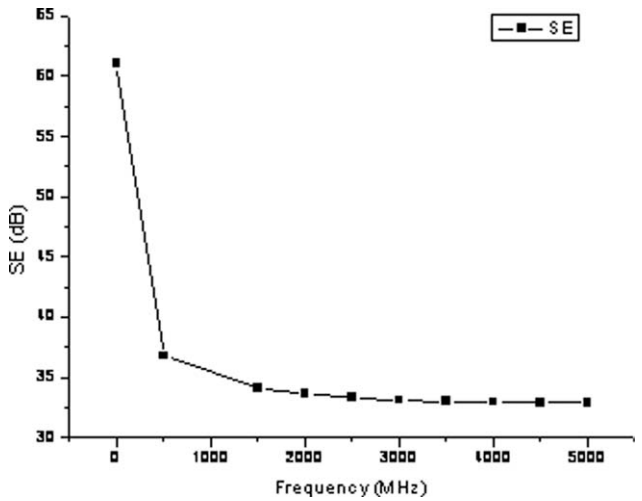

Figure 7 Electromagnetic shielding effectiveness of silver plating PET fabric.

TABLE III
Performance of the PET Fabric

	Sample	
Performance	Before silver plating	After silver plating
Static voltage (V)	1135	139
Static half-life time (s)	760	0.5
Tearing strength (N)		
Warp	12.90	8.25
Weft	10.18	6.37

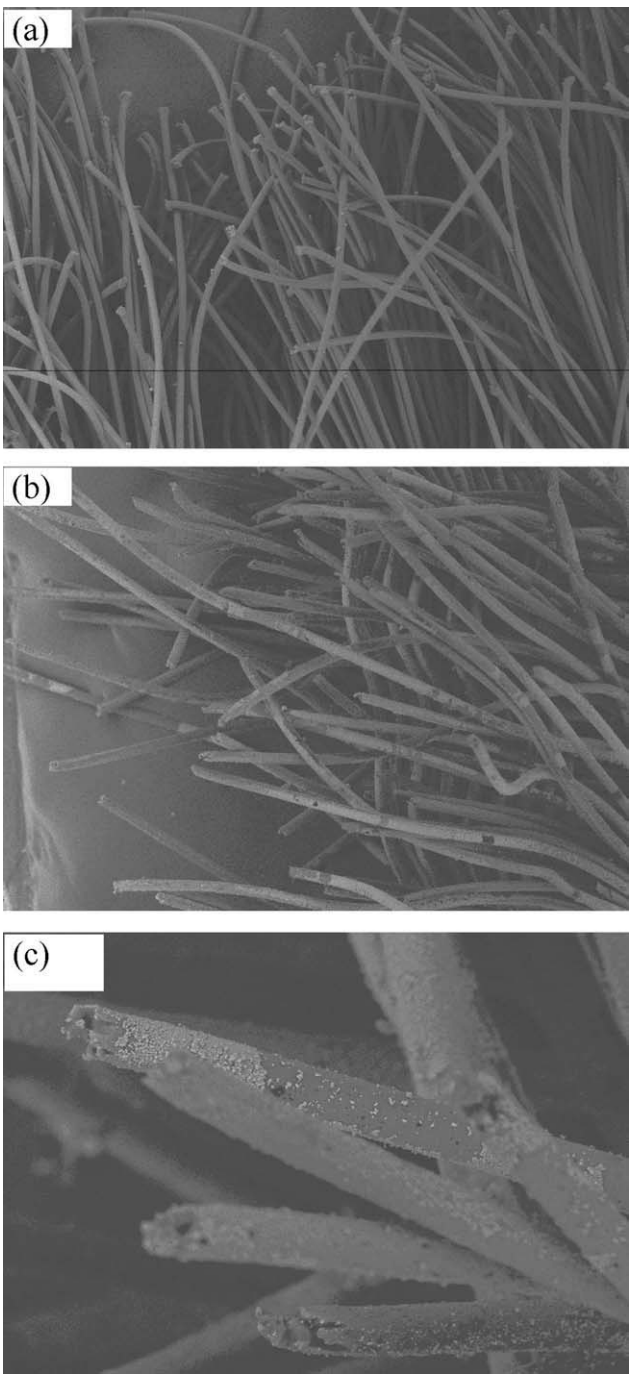

Figure 8 SEM photos of (a) PET fiber; (b) (c) silver plating PET fiber after tearing strength testing.

silver plating PET fabrics after the tearing strength testing can be analyzed by SEM images. In Figure 8(a), the fracture surfaces of origin PET after tearing are neat, which shows that the stresses of fibers are uniform. So the tearing strength is good. In Figure 8(b), the fracture surfaces of silver plating PET fibers after tearing are uneven, which mainly due to the unevenness of the stress of fibers. By further analysis, In Figure 8(c), the fiber plated by silver layer is easy to be broken; this may be due to the stress concentration caused by the silver layer. In addition, the internal fiber of yarn is easy to be broken which may caused by the unclean treatment after the coarsening with high concentrations of alkali.

CONCLUSIONS

Silver plating PET fabrics was available by electroless silver plating on the PET fabric modified with 3-mercaptopropyitriethoxysilane. Compared with the fabric before chemical silver plating, a uniform, and dense silver layer was created on the fabric surface that was shown in SEM. The results were confirmed by XRD which showed the characteristic diffraction peaks become smaller obviously and the characteristics peaks representing silver were appeared. TG curves before and after plating demonstrated that the thermal stability of PET fabric was little affected by the silver plating. As the silver weight on the modified fabrics is 25 g/m^2, the SE of silver plating fabrics is more than 30 dB at frequency ranging from 1 to 5000 MHz. Antistatic performance is preferable while its tearing strength decreased.

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