Oxidative Chemical Polymerization of 3, 4-Ethylenedioxythiophene and Its Applications in Antistatic Coatings

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ABSTRACT: The oxidative chemical polymerization of 3, 4-ethylenedioxythiophene (EDOT) was conducted at room temperature in the presence of poly(styrene sulfonate) (PSS) as the doping agent, sodium supersulphate ($Na_2S_2O_8$) and ferric sulphate($Fe_2(SO_4)_3$) as the compound oxidant and deionized water as the solvent. In order to remove sodium ion (Na^+), ferric ion (Fe^{3+}), and sulfate ion ($SO4^{2-}$), certain amount of ion exchanger was added after 24 h, the dark blue poly(3, 4-ethylenedioxythiophene) (PEDT)/PSS solution was obtained. The influence of different proportions of EDOT and PSS, different proportions of EDOT and the compound oxidant, different stirring rates on the morphology, and surface resistivity were discussed. The influence of pH value of the PEDT/PSS solution, the coating thickness, and soak time on the surface resistivity was investigated. Recipe and experimental conditions were optimized and the PEDT/PSS solution was obtained with excellent performance which has relatively low in surface resistance, good water tolerance, and light transmittance. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 109–115, 2012

Key words: oxidative chemical polymerization; 3, 4-ethylenedioxythiophene; surface resistivity; antistatic coating

INTRODUCTION

Since the discovery of polymeric organic conduct-polyacetylene by Shirakawa, Heeger and their coworkers in 1977, knowledge in this field has undergone great changes, some of these polymeric organic conductors have become industrial products, such as polypyrrole, polyaniline, polythiophene, etc.[1–6] Among the numerous conductive polymers that have been developed and studied over the past years, poly (3, 4-ethylenedioxythiophene), often abbreviated as PEDT or PEDOT, has been developed as one of the most successful material for both the fundamental and practical perspectives.[7] The polymer has many outstanding properties, such as high conductivity[8] (10 S/cm), high transparency (almost transparent in thin film), high stability, easy processing, and so on. Unfortunately, PEDT is an insoluble polymer, the drawback can be circumvented by using a water-soluble polyelectrolyte, poly(styrene sulfonate) (PSS), as a charge-balancing dopant during polymerization in water to yield a PEDT/PSS aqueous composition.[9–12]

The synthesis of PEDT can be divided into three different types of polymerization reactions: oxidative chemical polymerization,[13,14] electrochemical polymerization,[15] and transition metal-mediated coupling.[16] Chemical polymerization of EDT can be carried out with several methods and oxidants. The classical method adopts $FeCl_3$ or $Fe(OTs)_3$ [$FeIII(OTs)_3$ is commercially available as a *n*-butanolic solution from Bayer AG (trade name BAYTRON C)] as oxidizing agent. The most practically useful polymerization method for EDT is the so-called BAYTRON P synthesis that was developed by Bayer AG. This method utilizes polymerization of EDT in an aqueous polyelectrolyte (most commonly PSS) solution with $Na_2S_2O_8$ as the oxidizing agent. Carrying this reaction out at room temperature results in a dark blue, aqueous PEDT/PSS dispersion.[17–27] Another especially useful polymerization method utilizes electrochemical oxidation of the electron-rich EDT monomers. This method stands out as it requires only a few of

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monomers, short polymerization time, and can yield out both electrode-supported and free-standing films.[28–38] Many thiophene-based polymers have been prepared over the years using transition metal-catalyzed coupling of activated organometallic derivatives. Though this method yields out materials with low molecular weight, it may prove especially interesting when it is applied to the monomers with solubilizing side groups.[39–41]

In this article, $Na_2S_2O_8$ and $Fe_2(SO_4)_3$) are used as compound oxidants, PSS as a doping agent during the polymerization of EDOT. First, the influence of different proportions of EDOT and compound oxidant to the PEDT/PSS solution are studied by the FTIR spectroscopy. Second, the influence of different proportions of EDOT and PSS, different stirring rates to the micromorphology, and the surface resistivity are studied by scanning electron microscopy (SEM) and ACL-800 surface conductivity meter. Third, using microscope, we study the influence of sodium ion (Na^+), ferric ion (Fe^{3+}), and sulfate ion (SO_4^{2-}) to the macromorphology of the PEDT/PSS solution.

EXPERIMENTAL

Materials and equipment

EDOT (99.0 wt %) was purchased from Yake Chemical Agents Co. Ltd., Suzhou. PSS (20.0 wt %) was provided by Xinshou Chemical Agents Co. Ltd., Shanghai. Sodium supersulphate ($Na_2S_2O_8$) and ferric sulphate ($Fe_2(SO_4)_3$) were from aladdin reagent Co. Ltd., China. Acrylic acid (AA), isopropanol, glycol, ethanol, and benzoyl peroxide (BPO) from Lingfeng Chemical Agents Co. Ltd., Shanghai and crosslinker SC-A03 (98.0 wt %) was purchased from Shunchang Chemical Co. Ltd., Zhangjiagang.

SEM (Quanta-200 type SEM from FEI Company) and light microscopy (LM, Guangzhou LISS optical instrument Ltd, Holland) were used to study the surface morphology. FTLA 2000-104-type FTIR Spectroscopy was conducted to analyze the chemical structure of the synthesized PEDOT/PSS composite. Bar-coatings (20 μm, 9 μm, and 6 μm) from Three Permits Electronics Co. Ltd., Shenzhen were used for the surface coating. Surface resistivity was tested by a ACL-800 surface conductivity meter from Sanhe Measuring Instruments Company, Wenzhou.

Experimental process

Preparation of PEDT/PSS solution

Magnetic stirrer from Zhiwei Electrical Appliance Co. Ltd. was used for the synthesis of the composite. At room temperature(25°C), 0.8 g EDOT (99.0 wt %), 10.0 g aqueous solution of PSS (20.0 wt %) were accurately weighted and mixed in a flask, 200 mL deionized water was then added in the flask. Magnetic stirring lasted for 10 min before 2 g $Na_2S_2O_8$ and 0.015 g $Fe_2(SO_4)_3$ were added to the flask, and magnetic stirring was continued for 24 h, after which certain amount of ion exchanger was added. Being filtrated, the PEDT/PSS solution was obtained. The color of the solution changed from colorless to deepen gradually and finally into dark blue. Reaction equation is shown in Figure 1.[42]

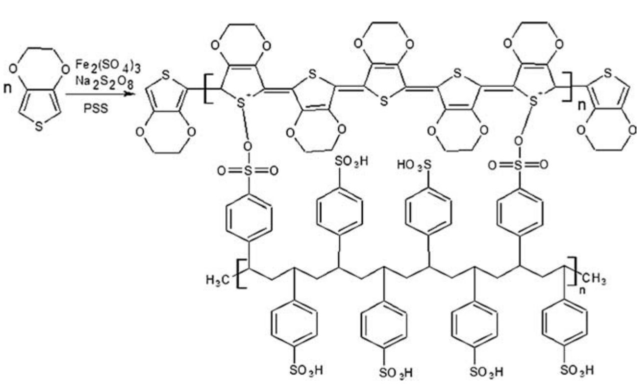


Figure 1 The preparation of PEDOT/PSS.

Preparation of the anti-static coating

The process for the preparation of the anti-static coating is as follows: First, 2 g acrylic adhesive together with 0.2 g crosslinker and 1 mL deionized water was mixed in a beaker of 50 mL, and then, 2 mL ethanol, 3 mL isopropanol, and 1 mL glycol were added to the beaker, magnetic stirring lasted for 5 min before 8 mL PEDOT/PSS solution was added, and magnetic stirring for another 5 min, the anti-static solution was obtained. The anti-static coating was conducted on PET film by bar-coating (20 μm, 9 μm, and 6 μm), then dried at 115°C for 10 min.

RESULTS AND DISCUSSION

UV spectra analysis

Figures 2 and 3 show the UV absorption of PEDT/PSS solution and the color changed during the polymerization of PEDT/PSS, respectively. Peaks at 230 nm and 260 nm corresponding to $=$C—H absorption of EDOT weakened gradually, shown in Figure 2, which proves the oxidative polymerization of EDOT.[43] And Figure 2 also shows that the weak extent of the absorption peaks are stronger at first, because the process of the polymerization is to form dimer in the first step, and then to form a higher molecular weight polymer from dimer gradually, the rate of polymerization gradually slowed down with the increasing of the molecular weight.[44] And from Figure 3, we can see the color of the solution changes from colorless to deepen gradually and

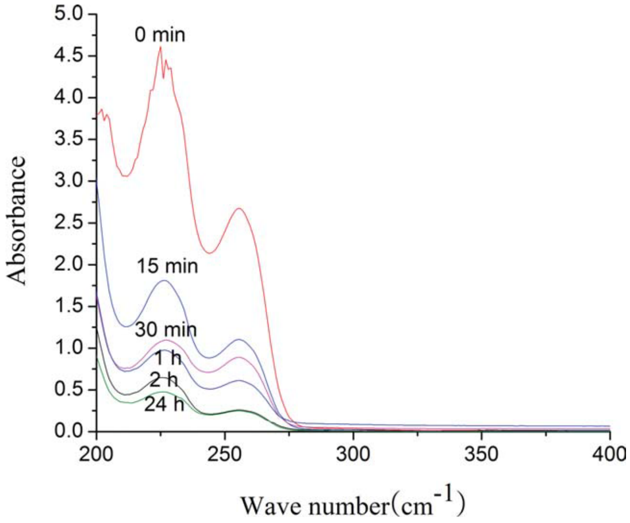


Figure 2 UV spectra of PEDT/PSS solution during the polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

finally into dark blue, which shows the oxidative polymerization of EDOT intuitively.

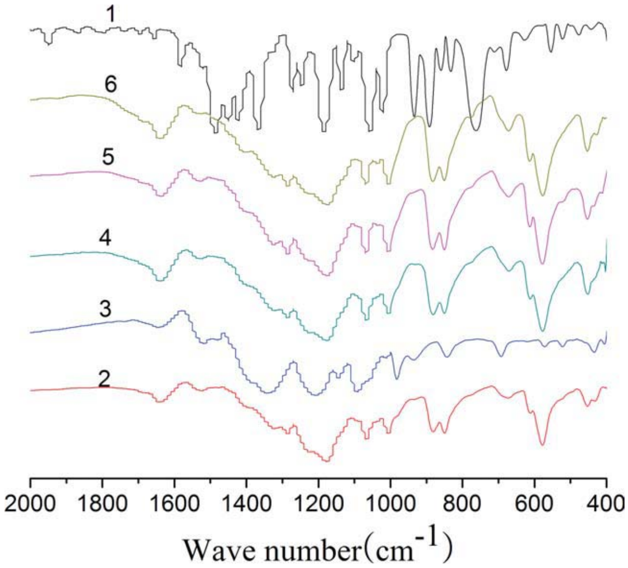


Figure 4 FT-IR spectra of EDOT (1) and PEDT/PSS solution (2-6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Infrared spectra analysis

Figures 4 and 5 show the FTIR spectra and the UV spectra of the PEDT/PSS solution, respectively, and Table I shows the recipes of the oxidative polymerization of EDOT (different proportions of EDOT and the compound oxidant). Spectrum 1 in Figure 4 corresponds to EDOT, and spectra 2, 3, 4, 5, 6 in Figure 4 correspond to recipes 2, 3, 4, 5, 6 in Table I, respectively, spectra 2, 3, 4, 5 in Figure 5 to recipes 2, 3, 4, 5 in Table I, respectively. Whether oxidative polymerization of EDOT conducted or not depends on the disappearance of the peaks at 3100 cm^{-1}(corresponding to $=$C—H bending vibration in EDOT) and 891 cm^{-1}(corresponding to $=$C—H deforming vibration in EDOT).[45] In order to show the peak at 891 cm^{-1} clearly, the region of 3100 cm^{-1} region is deleted for 3100 cm^{-1} region added to the spectrum may cause the former peak to be unclear. Peak at 891 cm^{-1} disappears in spectrum 3 in Figure 4 completely, but in spectra 2, 4, 5, 6 in Figure 4, there are still certain intensity of the absorption at peak of 891 cm^{-1} (peak at 3100 cm^{-1} is hidden by PSS absorption). Peak at 891cm^{-1} does not disappear in spectrum 2 in Figure 4 due to the less oxidant resulting in insufficient oxidation; however, the peaks do not disappear in spectra 4, 5, 6 in Figure 4 due to the more oxidant resulting in peroxidation. And Figure 5 is the weakest of the four which also shows the intensity of peaks at 230 nm and 260 nm in spectrum 3, which proves recipe 3 is more reasonable and the PEDT/PSS solution is prepared. Recipe 3 provides the right oxidant potential, which can cause neither insufficiency nor over oxidation.

Microscope analysis

Figure 6 shows microscope images of PEDT/PSS solution. PEDT/PSS solution is more homogeneous after ion-exchanging, and the large particles are

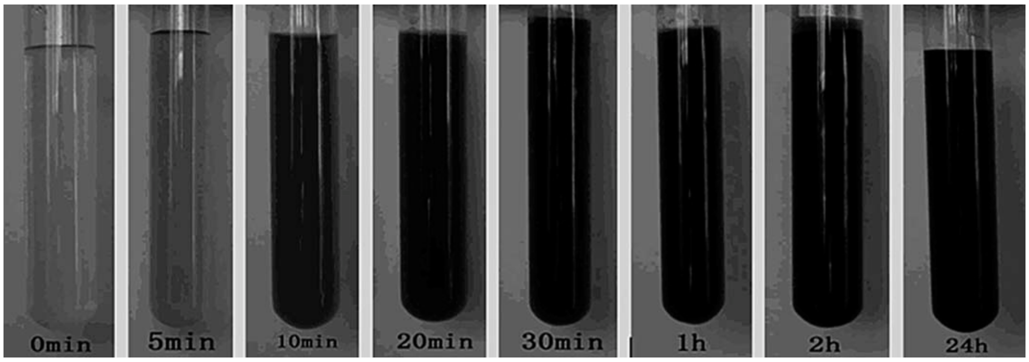


Figure 3 Color changes during the polymerization of PEDT/PSS.

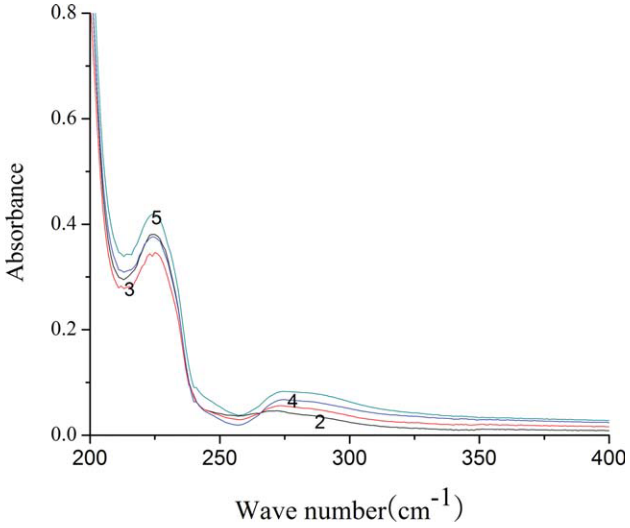


Figure 5 UV spectra of PEDT/PSS solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

disappeared, which is similar to the product of CLEVIOS^{TM} (Bayer's commercial product). That is because the chemical oxidative polymerization of EDOT is conducted based on the PSS as charge balancing counter ion that is PEDT and PSS combine through the charge balance.[46] Before ion-exchanging, there are many Na^+, Fe^{3+}, and SO_4^{2-} existing in the solution, due to these ions. On one hand, PEDT and PSS cannot combine well, and results in insoluble small particles (PEDT) in the solution. On the other hand, aggregations of PEDT/PSS are occurring in the solution. After ion-exchanging, the Na^+, Fe^{3+}, and $SO4^{2-}$ are removed, the insoluble small particles and the aggregation disappears. So the solution becomes more homogeneous.

SEM analysis

Figure 7 shows the SEM images of PEDT/PSS. The micro-structure of PEDT/PSS is granular and the sizes of the particles are decreasing with the increasing of the stirring rate as Figure 7 shows. It means that particle sizes can be varied by applying different high pressure shear rates to the PEDT/PSS dispersion when manufactured. There are hydrophilic and hydrophobic groups in the structure of PSS, as a result of the action of hydrophobic and hydrophilic groups; when PSS is dissolved in water, it will disperse into water in granular shape.[47,48] PEDT chains are tightly, electrostatically attached to PSS chains to form a higher molecular weight as shown in Figure 1, as a result of the structure, the PEDT/PSS is also in granular form in water. So, the particle size of PEDT/PSS can be controlled by adjusting the stirring rate.

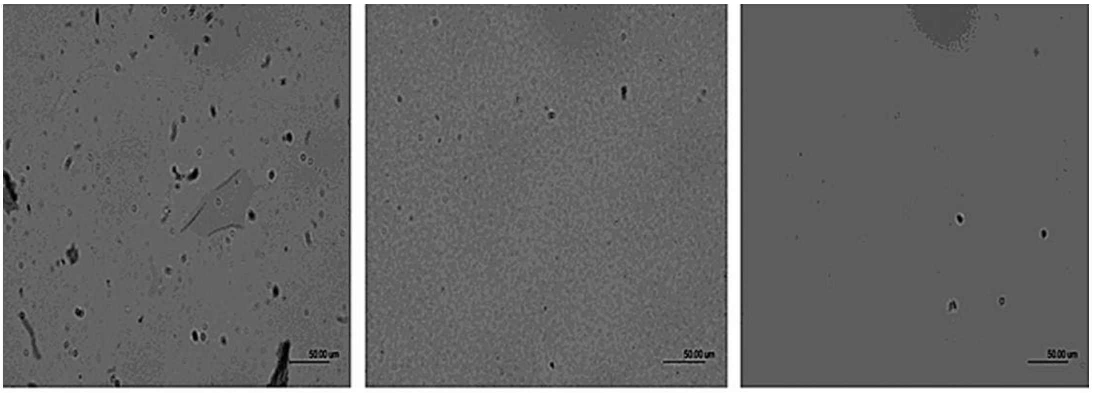
TABLE I
Recipes of the Oxidative Polymerization of 3,4-Ethylenedioxythiophene

	1	2	3	4	5	6
EDOT (g)	0.80	0.80	0.80	0.80	0.80	0.80
PSS (g)	0.00	2.00	2.00	2.00	2.00	2.00
$Na_2S_2O_8$ (g)	0.00	1.00	2.00	3.00	3.50	4.00
$Fe_2(SO_4)_3$ (g)	0.0000	0.0150	0.0150	0.0150	0.0150	0.0150

Surface resistivity analysis

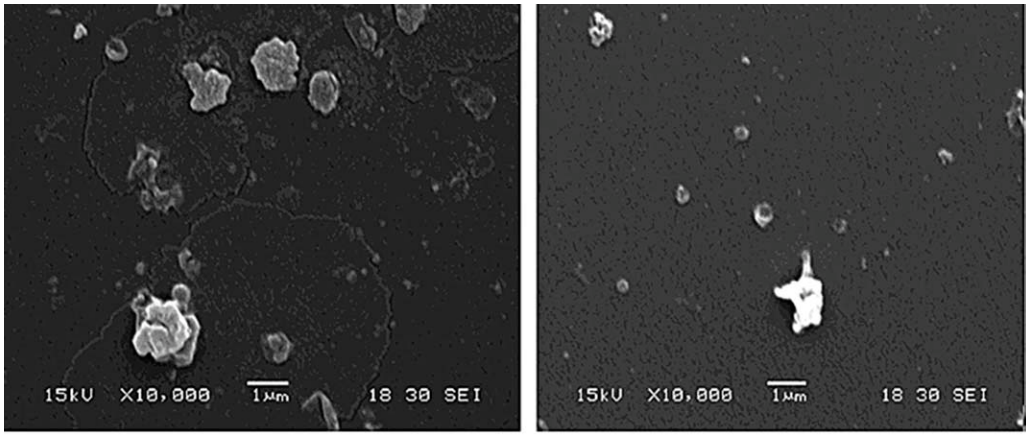
Influence of PSS content on the surface resistivity

Figure 8 shows the influence of the PSS content on the surface resistivity, Table II shows the recipes of the oxidative polymerization of EDOT. The thickness of the coating is 6 μm. The surface resistivity is decreasing with the increasing of PSS content from 4 g to 8 g, as shown in Figure 8, but when more PSS is added, the surface resistivity increases slowly. The surface resistivity reaches the lowest value when the PSS content is 10 mL. There is still sedimentation for some time when the PSS content is less than 10 mL,



Before ion-exchanging (a) After ion-exchanging (b) CLEVIOS™ (c)
(Note:enlarge 500 times)

Figure 6 Microscope images of PEDT/PSS solution.



1200 r/min **1600 r/min**

Figure 7 SEM images of PEDT/PSS.

and after more PSS is added, the sedimentation will disappear. That is because the chemical oxidative polymerization of EDOT was conducted based on the PSS as charge balancing counter ion, when the PSS content is less than 10 mL, which results in the charge balancing counter ion insufficient, so PEDT and PSS cannot combine well, it will result in sedimentation in the solution. When the PSS content reaches to a certain amount, PEDT and PSS can combine well, and the sedimentation will disappear, but PSS is non-conductive, so with the increasing of the PSS, the surface resistivity will increase slowly.[49]

Influence of pH value on the surface resistivity

Figure 9 shows the influence of pH value on the surface resistivity. The thickness of the coating is 6 μm, the pH value of the solution is adjusted by HCl (10 vol %) and NaOH (10 wt %). When the pH value was less than 9, the surface resistivity changes unobviously, as shown in Figure 9, but the surface resistivity increases significantly with the increasing of pH value above 9, which proves that the PEDT/PSS solution is stable in acidic and alkalescent circumstances. PSS has two functions in PEDT/PSS aqueous solution: the first is as the source for the charge balancing counter ion; the second function of PSS is keeping the PEDT segments dispersed in the aqueous medium. Alkaline environment can cause malfunction of PSS in PEDT/PSS aqueous solution, so surface resistance may increase in such environment. In addition, the surface resistivity reaches the lowest value when the pH value is 2. So, the pH value of PEDT/PSS solution should be adjusted around 2 when the PEDT/PSS solution is prepared.[50]

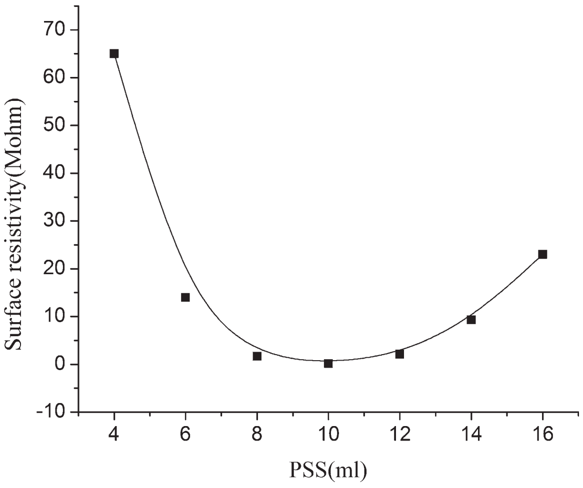


Figure 8 Influence of the PSS content on the surface resistivity.

Influence of coating thickness on the surface resistivity

Figure 10 shows the influence of coating thickness on the surface resistivity. The coatings are conducted by bar-coating of 20 μm, 9 μm, and 6 μm, respectively. The surface resistivity decreases as the coating thickness increases, as shown in Figure 10. That is because the conductive channels increase in pace with the coating thickness increasing, due to the increase of the conductive channels, the conductivity of the coating increases, and so the surface resistivity

TABLE II
Recipes of the Oxidative Polymerization of 3,4-Ethylenedioxythiophene

EDOT (g)	PSS (g)	NaPS (g)	$Fe_2(SO_4)_3$ (g)	H_2O (mL)
0.80	4.00	2.00	0.0150	200
0.80	6.00	2.00	0.0150	200
0.80	8.00	2.00	0.0150	200
0.80	10.00	2.00	0.0150	200
0.80	12.00	2.00	0.0150	200
0.80	16.00	2.00	0.0150	200

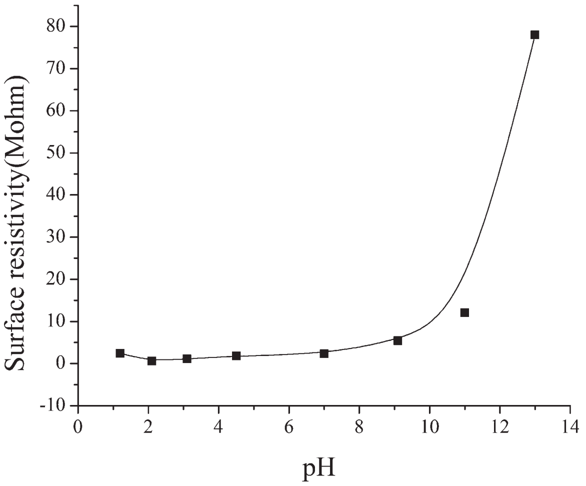


Figure 9 Influence of pH value on the surface resistivity.

decreases correspondingly. Conductivity is related to electrically conductive path. Thicker coatings bring in more electrically conductive paths, better conductivity, and lower surface resistance.

Influence of soak time to the surface resistivity

Figure 11 shows the influence of soak time on the surface resistivity. The coating thicknesses are 20 μm, 9 μm, and 6 μm, respectively. The surface resistivity increases with the extension of soak time, as show in Figure 11. That is because PEDT/PSS is water-soluble, when the coatings are soaked in water, part of PEDT/PSS dissolves into water, which decreases the conductive channels and increases the surface resistivity. But after being soaked for 5 h, the surface resistivity still within $10^7 \Omega$, the coatings are still antistatic. The reason is when the coating are conducted by bar-coating, certain amount of water-soluble and thermosetting adhesive is added in the coatings, and when the coatings are dried around 115°C, the thermosetting adhesive is crosslinked and becomes insoluble. Due to the crosslinked thermosetting adhesive, the coatings are of excellent water resistance. Resistance was evaluated by the value of surface resistance after soaking. The sample whose value of surface resistance increases is low in water tolerance or it is good in water tolerance with stable surface resistance.

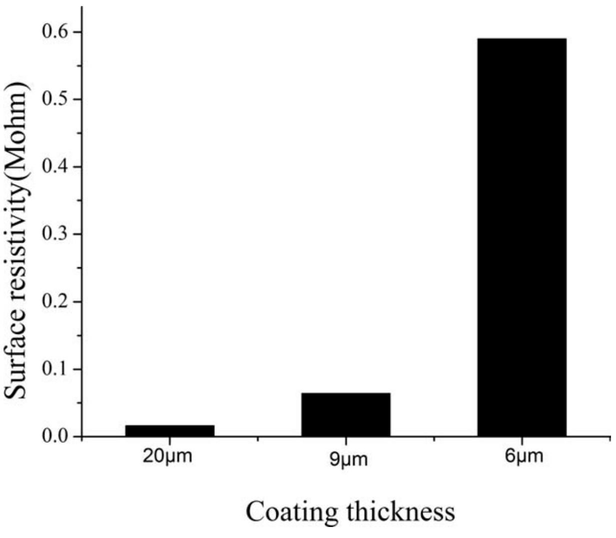


Figure 10 Influence of coating thickness on the surface resistivity.

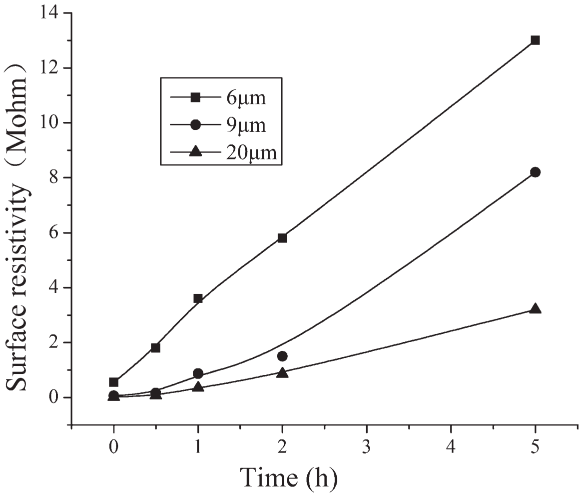


Figure 11 Influence of soak time on the surface resistivity.

CONCLUSIONS

The reasonable proportion in weight of EDOT, $Na_2S_2O_8$, and $Fe_2(SO_4)_3$) is 0.8 : 2.0 : 0.015, and the reasonable solid content is around 1.3% wt, in this case EDOT can adequately converts to PEDT and cannot be peroxidated. The reasonable proportion of EDOT and PSS is 1 : 2.5 in weight, the surface resistivity is lower and the solution is more homogeneous under this proportion. After Na^+, Fe^{3+}, and $SO4^{2-}$ being removed, the insoluble small particles disappears and the solution becomes more homogeneous. The micro-structure of the prepared PEDT/PSS solution is granular, the particle size decreases with the increasing of the stirring rate. PEDOT/PSS solution is stable in acidic and alkalescent circumstances, and the surface resistivity is lower, when the pH is around 2, the surface resistivity increases as the extension of soak time, but after being soaked for 5 h, the surface resistivity is still within $10^7 \Omega$, the coatings are still antistatic.

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