

The Copper Sulfide Coating on Polyacrylonitrile with a Chelating Agent of Ethylenediaminetetraacetic Acid by an Electroless Deposition Method and Its EMI Shielding Effectiveness

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ABSTRACT: In this study, a copper sulfide layer was instantaneously coated on the polyacrylonitrile (PAN) by an electroless plating method with the reduction agents NaHSO_3 and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and a chelating agent (ethylenediaminetetraacetic acid, EDTA). A variety of concentrations of EDTA was added to obtain the anchoring effect and chelating effect in the electroless plating bath. The mechanism of the $\text{Cu}_{x(x=1,2)}\text{S}$ growth and the electromagnetic interference shielding effectiveness (EMI SE) of the composite were studied. It was found that the vinyl acetate was residual in PAN substrate would be purged due to the swelling effect by EDTA solution. Then, the anchoring effect occurred due to the hydrogen bonding between the pits of PAN substrate and the chelating agent. Consequently, the copper sulfide layer deposited successfully by the electro-

less plating reacted upon EDTA. The swelling degree (S_d) was proposed and evaluated from the FTIR spectra. The relationship between swelling degree of the PAN composite and EDTA concentration (C) is expressed as follows: $S_d = 0.13 + 0.90 \times e^{(-15.15C)}$. On the other hand, the FESEM micrograph showed that the average thickness of copper sulfide increased from 76 to 383 nm when the concentration of EDTA increased from 0.00 to 0.20M. For this reason, the EMI SE of the composites increased from 10–12 dB to 20–23 dB. The GIA-XRD and laser Raman analysis indicated that the deposited layer consisted of CuS and Cu_2S . © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 570–578, 2010

Key words: films; nanocomposites; swelling; copper sulfide; electroless; PAN

INTRODUCTION

The coating of polymers is a fast-growing field at present. There are many alternative approaches, whereas the electroless plating technique has been the subject of research attracted a lot of interest since inception by Brenner and Riddell in 1946,¹ and in the past two decades, the study has been emphasized in its properties and applications. This valuable technique could apply to not only electrically conductive materials including graphite but also insulators like plastics, rubber, etc.²

The plating of nonconductors has been achieved for many years. The decorative articles were the

main application. However, the adhesion of the deposited layer to the substrate was usually weak. In the early 1960s, due to technological advances in chemical processing techniques and the commercial process of plating on plastics began. The industries that utilize plated plastics include the automotive, plumbing, appliance, and electronics.³ The original commercial catalyzing procedures required two processing steps. First, stannous chloride was absorbed onto the surface from a solution of SnCl_2 and HCl. Second, after rinsing, the part immersed in a solution of PdCl_2 and HCl, and palladium chloride was absorbed onto the surface. The stannous ions then reduced the palladium ions leaving discrete sites of metallic palladium for further electroless plating process.^{3,4}

Electroless plating (Autocatalytic plating) of nonconducting materials must catalytically activate the substrate surface before metal deposit onto themselves.⁵ The surface being catalyzed (sensitization

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and activation) was generally applied to make sure the metal particle could be deposited on it. In this investigation, polyacrylonitrile (PAN) was used as the plated substrate due to its excellent chemical resistance and the nitrile functional group. Originally, the nitrile group of PAN was expected to attract the cupric ion in solution to be reduced by reduction agents; therefore, the metallic layer could be plated without sensitization or activation process. However, it did not success to have a significant thickness of deposition layer. Whereas/On the contrary, it worked after the EDTA was used and the mechanism was then studied.

Electromagnetic interference (EMI) shielding was a field that plating-on-plastics technology could be utilized. EMI was an electrical "noise" generated by a piece of electrical or electronic equipment that causes some problems of the interference with the operation of another piece of electrical or electronic equipment. EMI shielding was usually used to represent the ability to absorb or reflect the unwanted "noise" or "interference" signal, typically, over a frequency range of 14 KHz to 1 GHz. It was called attenuation, a function of the electrical conductivity, measured in decibels (dB).³ Metal enclosures were used for many years as the main shielding material. This provided structural integrity as well as a shielding function. Some drawbacks of metal were weighted and designed limitations. As housings for electronic equipment has been changed from metal to polymer or polymeric composites, it became necessary to apply shielding to protect the equipment. However, their volume of resistivity is $\sim 10^{13}$ – 10^{17} ohm-cm, so they are transparent to electromagnetic waves.⁶ Several types of technical approaches have been used as an attempt to effectively solve the shielding problems of plastic housings. One method could be the electroless plating copper and/or nickel. The process used would be similar to that used to plate on plastics.³

In this study, with a chelating agent of EDTA, the copper sulfide ($\text{Cu}_{x(x=1,2)}\text{S}$) layers were electroless plated on PAN substrate without activation and sensitization procedures. It was very different from the commercial electroless plating method, especially when the substrates were noncatalytic or nonconductive. Consequently, the improvement of the EMI SE was effectively and significantly achieved. It has been well known that the adhesion of coating films and substrate is simultaneously related to the complementary effects of roughness, surface energy, surface stabilization reaction, and the possible formation of covalent bonds at the film-substrate interface. Therefore, the mechanism with respect to these complementary effects were studied and investigated by FTIR spectra determination, glancing incident angle X-ray diffraction pattern. Finally, the EMI SE of the

composites with a variety of coating films by different electroless plating procedures was measured.

EXPERIMENT

Preparation of PAN film

The PAN powder (M_w : 19,000–20,000, contained 7% vinyl acetate monomer, VAc) for preparing the PAN film as a substrate was kindly supplied by Tong-Hwa Synthetic Fiber Co. and used as a solute, whereas the *N,N*-Dimethylformamide (DMF; Nihon Shiyaku Industries, Japan.) was used as the solvent.

Weighted 14.0 g PAN powder and dissolved completely in 50 mL DMF solution to form transparent and light yellow solution. Then, poured the above solution into the shallow container slowly. After the above procedures, the PAN solution was dried out to create a thin and transparent PAN film in an oven at 45°C.

Deposition process of electroless copper sulfide layers

The composition and operational condition of electroless copper deposition solution were listed in Table I. All the reagents used in electroless copper solution were reagent graded and purchased from Wako Pure Chemical Industries. The cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was the source of cupric ion, and the sodium bisulfate (NaHSO_3) and the sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) were used as reduction agents in this study. Besides, various concentrations of ethylenediaminetetraacetic acids (EDTA) were added as not only a chelating agent but also a key factor to establish a new approach of electroless plating. The electroless plating time was 60 min.

The electroless plating bath was stirred to make sure that each chemicals mixed evenly and to remove gas released from deposition procedure. After the electroless plating process, the $\text{Cu}_{x(x=1,2)}\text{S}$ /PAN composites were dried out in a vacuum oven (SHELL LAB 1410) at room temperature to evaporate H_2O on the PAN substrate.

FT-IR spectra determination

The samples for FTIR determination were prepared by cutting them into about 2.5 cm \times 2.5 cm flakes. The spectra were recorded in absorbance with a Jasco 300E FTIR in a range of 400 to 4000 cm^{-1} at a resolution of 4.0 cm^{-1} . To evaluate the swelling degree of PAN substrate, the PAN substrate was immersed into 0.00–0.40M EDTA solution for 1 h.

TABLE I
The Composition of Electroless Deposition Solution

Reagents	Concentration
CuSO ₄ ·5H ₂ O	0.60M
NaHSO ₃	0.30M
Na ₂ S ₂ O ₃ ·5H ₂ O	0.60M
Ethylenediaminetetraacetic acid (EDTA)	0.05–0.40M
Operating conditions	
pH = 1.0–2.0	
Temperature (°C) = 75	
Deposition time = 60 min	

Glancing incident angle X-ray diffraction (GIA-XRD) pattern and laser Raman spectrum

The X-ray diffraction study of the samples were carried out by a MAC Science MXP18 X-ray diffractometer (40 kV, 150 mA) with a glancing incident angle of 0.5° and the wavelength of the GIA-XRD source was 1.54 Å (Cu K α radiation) at a scan rate of 1.0°/min.

EMI shielding effectiveness (SE) measurement

Materials for shielding applications were tested for attenuation or reduction of a signal expressed in decibels (dB). The shielding effectiveness (SE) was given by $SE = 10\log(P_{in}/P_{out}) = 20\log(E_{in}/E_{out}) = 20\log(H_{in}/H_{out})$, where P is the energy field, E is the electrical field strength, and H is the magnetic field strength. In passing through a shield, an EM wave could be separated into three components: $SE = A + R + B$, where A was the absorption, R was the reflection, and B was the multiple reflection of EM wave. The flanged circular coaxial transmission line method, ASTM Standard D 4935-99, was used to evaluate the EMI SE. The EMI SE values of composites were obtained by taking out the background shielding measurement. Since the EMI SE is voltage dependent below the range of 30 MHz,⁷ the test range of frequency in this experiment was from 30 to 1500 MHz.^{8,9}

FE-SEM micrograph observation

The surface and cross section morphologies of the Cu_x($x = 1, 2$)/PAN composites were observed by field emission scanning electron microscope (FE-SEM, JEOL-JSM 6700F). The FE-SEM image was operated at 3.0 kV.

For examination of surface morphology, the samples were coated with platinum. Nevertheless, for examination of the cross section morphology, the samples were immersed in liquid nitrogen for 10 min and were fractured, and then the fractured surfaces were coated with platinum.

Differential scanning calorimetric (DSC) analysis

DSC curves were obtained with a TA instrument, model 2910 differential scanning calorimeter, by heating from room temperature to 350°C in argon atmosphere at a heating rate of 5.0°C/min, and the temperature was maintained at 100°C for 3 min to release the water or moisture in samples. The samples (3.0 mg each) were weighted accurately and encapsulated in aluminum pans. An empty, hermetically sealed, aluminum pan was used as reference, and before the analysis of samples, the baseline was established with the reference pan.

RESULTS AND DISCUSSION

Deposition process of electroless copper plating

With adding of reduction agents (NaHSO₃, Na₂S₂O₃·5H₂O), the cupric ion was attracted by nitrile group of PAN film and was reductively to form conductive layer on the surface of PAN. The —CN functional group of PAN with one lone pair of electrons could attract the Cu²⁺ ion in solution. Therefore, the PAN film did not have to be sensitized and activated or catalyzed. It was a novel application for all the electroless plating methods.¹⁰ In this research, EDTA was used as not only a chelating agent with cupric ion but an anchor into PAN substrate. For the electroless deposition bath with EDTA, the significant thickness of copper sulfide

TABLE II
The DSC Profiles of Composites

Concentration	Exotherm range (°C)		ΔT	Onset temperature		T_{peak} (°C)	ΔH (J/g)	$\Delta H/\Delta T$ (ΔS)
	T_i	T_f		T_o (°C)				
PAN film	269.57	320.13	50.56	277.1		292.40	639.4	63.23
PAN film-CuS	0.00M	259.71	305.46	45.75	267.3	285.85	579.1	63.29
	0.05M	257.38	307.14	49.76	267.7	285.99	682.5	68.58
	0.10M	263.91	309.68	45.77	265.7	284.34	658.9	71.98
EDTA series	0.20M	259.40	313.53	54.13	263.8	279.00	627.8	57.99
	0.40M	257.64	305.98	48.34	262.6	277.25	488.0	50.48

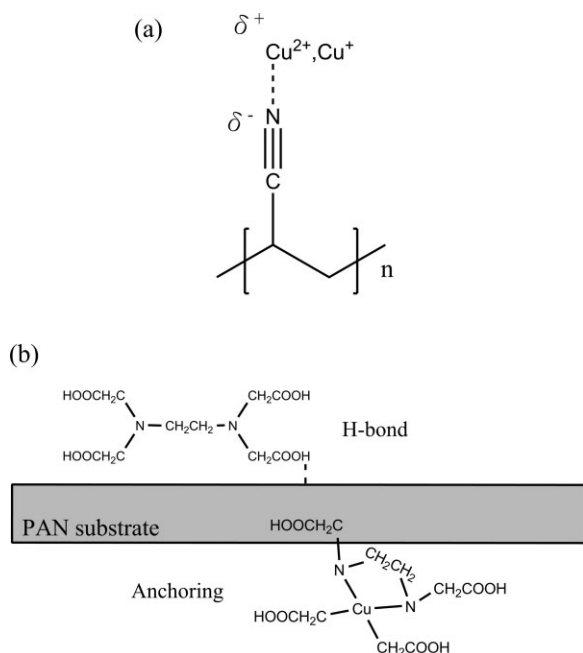


Figure 1 The illustrations of (a) The polarity of nitrile group, (b) The hydrogen bonding and anchoring of EDTA and PAN film.

(Cu_x(x = 1, 2)S) layer on PAN films was prepared. The role of EDTA was proposed in the Figure 1 and was illustrated in the followings.

In general, coating the metallic layer on nonconductive surface could be pretreated by a variety of methods. For example, Wang and Yang¹¹ fabricated Cu_xS nanowires on an oxidized copper surface. Comparing to the commercial methods, our method did not have the activation and sensitization pretreatments, but the excellent adhesion could be preserved due to the hydrogen bond and anchoring effect of EDTA shown in the Figure 1. The adhesion between PAN substrate and metallic layer was evaluated by ASTM D3359. The adhesion of our Cu_x(x = 1, 2)S/PAN films were all good enough to pass the adhesion test.

FTIR spectra of PAN films

The FTIR spectrum of PAN was shown in Figure 2(a). The major absorption bands for PAN film were CH twisting deformation at 1250 cm⁻¹, CH in-plane deformation at 1386 cm⁻¹, CH₂ bending at 1454 cm⁻¹, CN stretching at 2242 cm⁻¹, CH₃ stretching at 2869 cm⁻¹, and CH stretching at 2937 cm⁻¹. C=O carbonyl stretching at 1737 cm⁻¹ and C=C stretching vibration for VAc at 1662 cm⁻¹. The PAN films we applied contained 7% VAc, therefore, the characteristic peaks of VAc also found in the spectra of Figure 2(a). According to spectrum of the Figure 2(b), the FTIR spectra showed the characteristic peaks of PAN film was not affected by NaHSO₃ and

Na₂S₂O₃·5H₂O. However, the peak at 1662 cm⁻¹ was obviously reduced in Figure 2(c). It meant that after the PAN film was immersed in EDTA solution, the VAc was released from the swollen PAN by EDTA. Whereas only VAc have C=C in the PAN substrate.

Although the peaks at 1737 and 1662 cm⁻¹ were also the characteristic peaks of VAc in PAN film, the peak of C=O at 1737 cm⁻¹ did not reduce in Figure 2(c). It implied that the EDTA with the functional group C=O, but without C=C group took replacement of VAc. Consequently, the EDTA being anchored into the PAN substrate was proved. Therefore, the absorption strength of C=C peak (VAc) to C=O peak (EDTA) is adopted to represent the ratio of swelling degree denoted as *S_d*. The PAN films were immersed in reduction agents solution (NaHSO₃, Na₂S₂O₃·5H₂O) with a variety of concentrations of EDTA solution, and then the effects of EDTA on the swelling degree (peak area ratio of P2/P1) of PAN

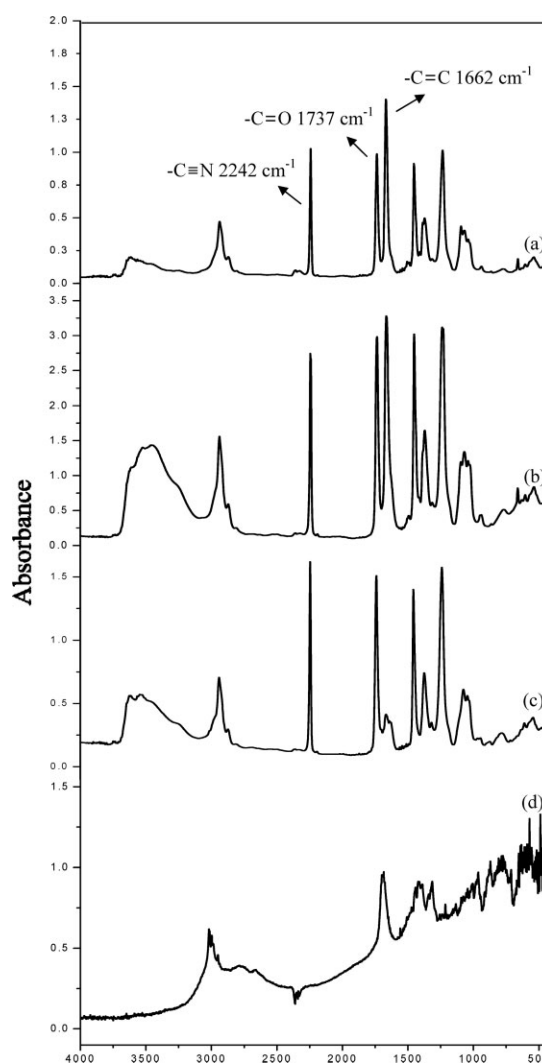


Figure 2 FT-IR spectrum of (a) Polyacrylonitrile film, (b) PAN film immersed in NaHSO₃ and Na₂S₂O₃ solution, (c) PAN film immersed in EDTA solution, (d) Pure EDTA.

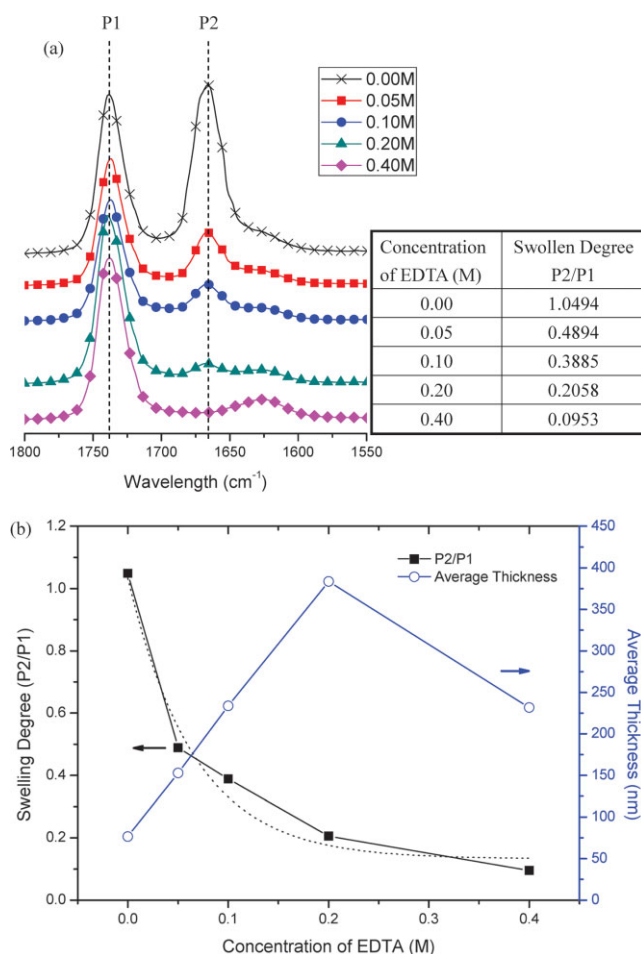


Figure 3 (a) The illustrations of peak area ratio, (b) The swelling degree and thickness of copper sulfide versus concentration of EDTA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

films were presented in Figure 3. The relationship of the swelling degree (S_d) with respect to the EDTA concentration can be fitted as the following equation and showed in the dotted curve in Figure 3(b).

$$S_d = 0.13 + 0.90 \times e^{(-15.15C)}$$

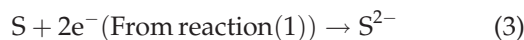
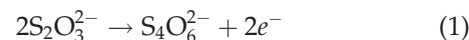
S_d : swelling degree; C : EDTA concentration.

Glancing incident angle X-ray diffraction (GIA-XRD) analysis

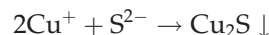
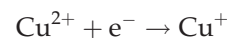
The GIA-XRD patterns of Figure 4(a–e) for a variety of EDTA concentrations were superimposed and the peaks that appeared at $2\theta = 23.37^\circ$, 31.89° , 37.99° , 46.04° , and 47.68° , respectively. After comparing with the standard JCPDS-ICDD diffraction patterns, the crystalline microstructure of β -Cu₂S (hexagonal chalcocite, JCPDS No. 31-0482, $a = 4.005$, $c = 6.806$) and CuS (hexagonal covellite, JCPDS No. 06-0464, $a = 3.792$, $c = 16.344$) were verified in the deposition layer. When EDTA was added into the electroless

deposition bath, the crystallinity of copper sulfide increased with increasing the EDTA concentration as shown in Figure 4(b–e), but Figure 4(a) did not have the significant peaks for Cu₂S and CuS.

The following equations¹⁰ can represent the formation of copper sulfide in this investigation:



The ability of these agents gradually released the sulfide ions upon hydrolytic deposition in acidic media. The formation of Cu⁺ ions could be attributed to the reduction of Cu²⁺ ions by the sulfide ions present in the bath.¹² Anuar et al.¹³ applied an electrodeposition method to manufacture Cu₂S thin film and deposited on Ti substrate. Cu(II) reduction process suggesting deposition at the electrode was written as follows:



At room temperature, copper sulfide could form five stable phases¹⁴: covellite CuS, anilite Cu_{1.75}S, digenite Cu_{1.8}S, djurleite Cu_{1.95}S, and chalcocite

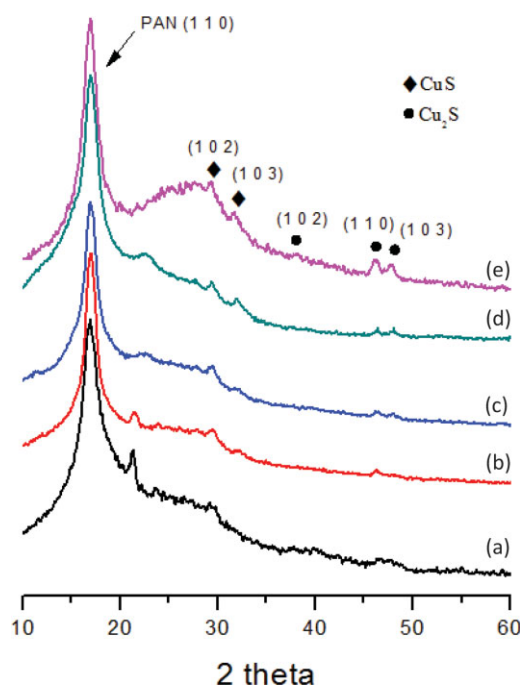


Figure 4 The GIA-XRD patterns of the copper sulfide coatings prepared with (a) 0.00M, (b) 0.05M, (c) 0.10M, (d) 0.20M, (e) 0.40M EDTA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

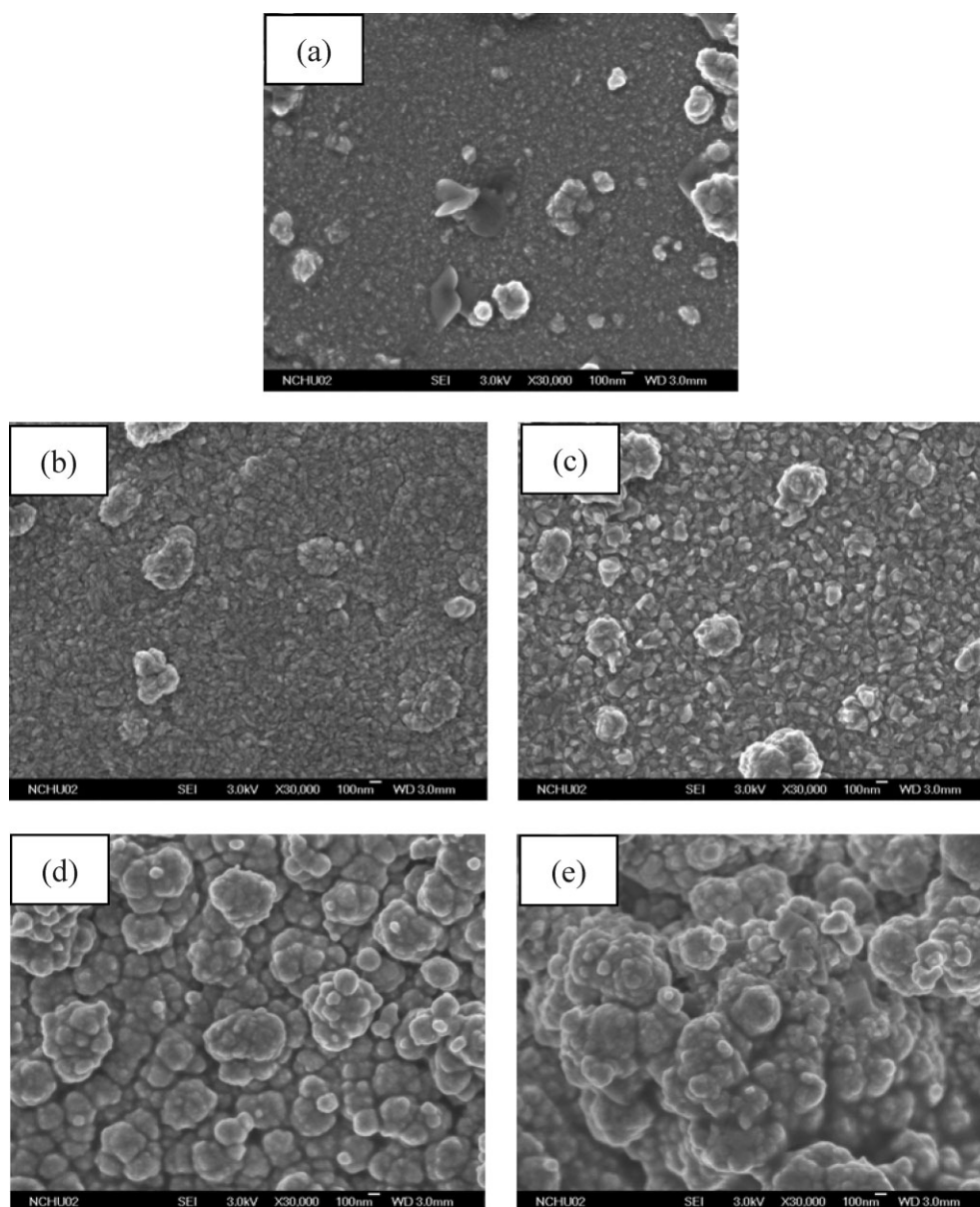


Figure 5 The morphology of the copper sulfide coatings prepared with (a) 0.00M, (b) 0.05M, (c) 0.10M, (d) 0.20M, (e) 0.40M EDTA.

Cu_2S . In this research, NaHSO_3 and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ were used as reduction agents, and the analyses of GIA-XRD showed the Cu_2S and CuS were deposited on PAN films. However, Shu et al.¹⁵ and Shukla et al.¹⁶ applied the formaldehyde (HCHO) in electroless copper plating, the results revealed the Cu (1 1 0), Cu (2 0 0), Cu and (2 2 0) plated on the substrates. On the other hand, the Fe (II) also used as a reduction agent (Sone et al.¹⁷) and Cu (1 1 0), Cu (2 0 0), and Cu (2 2 0) plated on substrate. Haram et al.¹² prepared copper sulfide by Cu^{2+} ions reacted with S^{2-} ions which generated by hydrolysis of thiourea. S^{2-} ions in solution reacted with Cu^{2+} ions to form the precipitation of $\text{Cu}_{x(x=1,2)}\text{S}$, it resembled in this work.

Morphology of PAN-plated copper sulfide

The FE-SEM morphologies of $\text{Cu}_{x(x=1,2)}\text{S}/\text{PAN}$ composites prepared in this study were categorized in Figure 5. The deposition bath without adding chelating agent would make the $\text{Cu}_{x(x=1,2)}\text{S}$ precipitate in the solution and do not give effective deposition onto PAN films. On the other hand, those with the anchor and chelating effects of EDTA proposed and illustrated in Figure 1 can significantly improve to give effective deposition. It was obvious that there were different surface structures of $\text{Cu}_{x(x=1,2)}\text{S}$. In Figure 5(a), the PAN electroless plated copper without adding EDTA, the $\text{Cu}_{x(x=1,2)}\text{S}$ deposited onto PAN showed a roundness structure and irregular $\text{Cu}_{x(x=1,2)}\text{S}$ surface. However, the $\text{Cu}_{x(x=1,2)}\text{S}$ grains

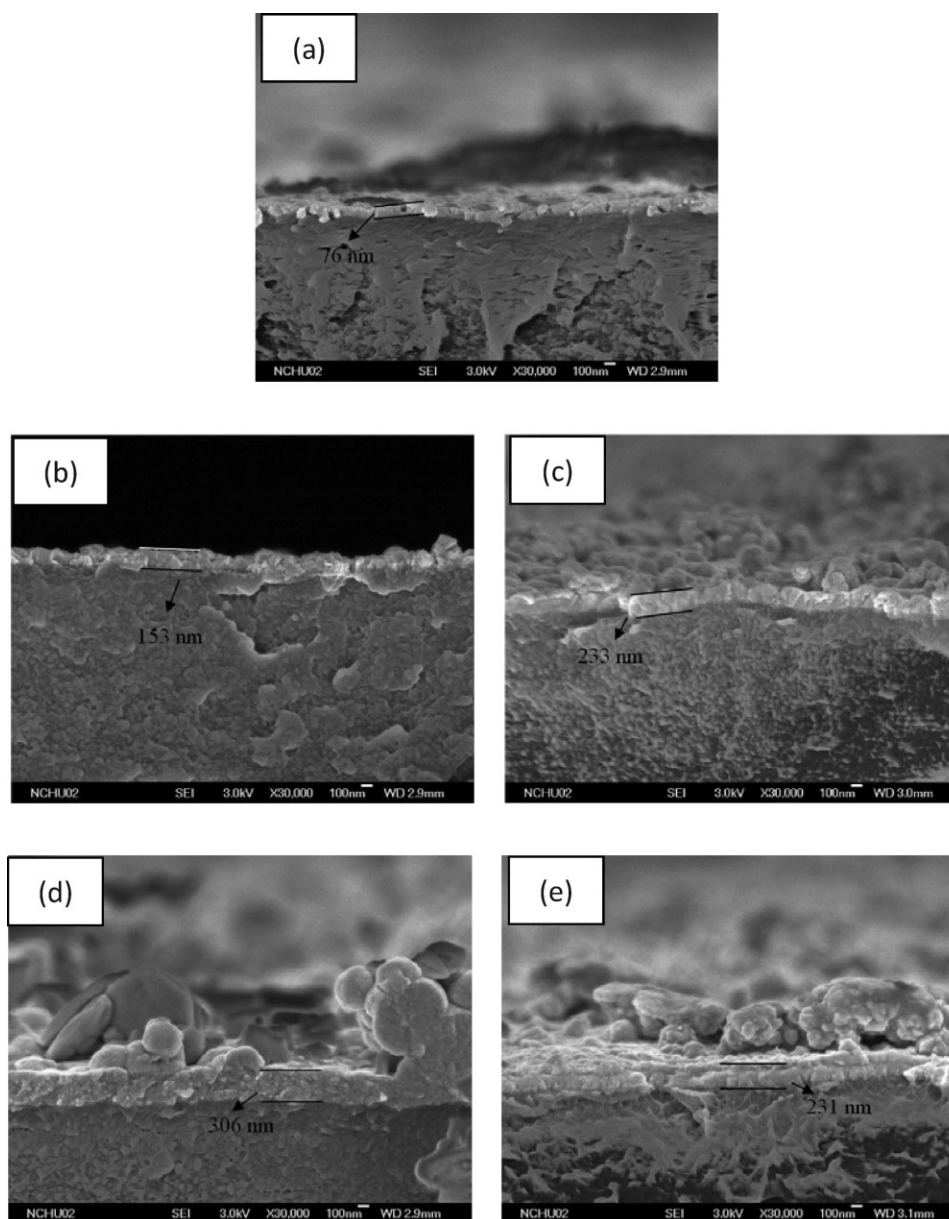


Figure 6 The cross section micrograph of the copper sulfide coatings prepared with (a) 0.00M, (b) 0.05M, (c) 0.10M, (d) 0.20M, (e) 0.40M EDTA.

with adding 0.05–0.40M EDTA in electroless deposition bath *in situ* should aggregate and the diameter of $\text{Cu}_x(x=1,2)\text{S}$ roundness particles were about 50–400 nm as shown by Figure 5(b–e), and became a compact deposition layers as indicated by cross section morphology.

$\text{Cu}_x(x=1,2)\text{S}$ was deposited when the cupric ion chelated with EDTA and attracted near PAN surface and reduced by reduction agents. The significant deposition layer was obtained when 0.05M EDTA was used in Figure 5(b) with comparison to that without EDTA as shown in Figure 5(a). The more uniform and even deposition surface was observed by the comparison of Figure 5(b–e). The primary particle size of $\text{Cu}_x(x=1,2)\text{S}$ grains was about 50 nm

in Figure 5(b) and about 100 nm in Figure 5(c). The primary particles and grains will grow larger as increasing the concentration of EDTA. The higher concentration of EDTA (0.20–0.40M) resulted in a round and large structure as shown in Figure 5(d), (e). Kondo et al.¹⁸ had indicated that the electroless copper deposition had lower deposition rate and the acceleration of copper sulfide deposition would occur in the presence of chelating agents. Anuar et al.¹³ prepared the Cu_2S film and used EDTA to obtained Cu-EDTA solution and the presence of EDTA in aqueous solution was found to improve the lifetime of the deposition bath was found by Zainal et al.¹⁹ However, the mechanism of deposition thickness increasing with EDTA was not clearly

discussed. In this investigation, we found that the PAN molecular chains were swollen by EDTA solution. The VAc monomers existed originally in the PAN film would be purged and the EDTA anchored into PAN substrate. It is illustrated in previous section of FTIR spectra of PAN films. Therefore, it resulted in that the cupric ion chelated with the EDTA on the PAN film. Consequently, the copper sulfide was almost deposited on the PAN film, not precipitated in the solution. The advantage of EDTA agent was not only to provide the reaction sites but also to accelerate the growth of the copper sulfide layer as indicated by Figure 3(b) and observed by the FE-SEM pictures in Figure 6. Figure 3(b) shows that the swelling degree which related to the anchoring effect was completely governing by the amount of EDTA and had a saturation value. Nevertheless, the average thickness of copper sulfide coating increased with the increasing of EDTA concentration upto 0.20M and then decreased.

In our electroless deposition bath, the NaHSO_3 and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ were used as the reduction agents, and the EDTA played an important role that it chelated cupric ion and anchored into PAN substrate, so that the cupric ion closed near PAN film enough to increase the efficiency of plating onto PAN films. Therefore, the copper sulfide deposited uniformly.

Figure 6(a–e) were the cross section views of the $\text{Cu}_{x(x=1,2)}\text{S}/\text{PAN}$ composites. According to the illustrations of Figure 6(a), the average thickness of copper sulfide layer was 76 nm. The roughness and irregular surface without the presence of EDTA was also evidenced by the cross section view of Figure 6(a) as well as the morphology of Figure 5(a). At the plating process, the cupric ion was attracted onto the PAN film due to the polarity of EDTA. Consequently, the location of EDTA can play a role of seed of reduction site. The different stages of film growth: incubation/nucleation, growth, and terminal phases in the chemical bath deposition have been described by Nair et al. and Lokhande et al.^{20–22} The micrograph of Figure 6(b–e) showed the average thickness of copper sulfide layer plated on PAN films increased from 153 to 383 nm by adjusting the concentration of EDTA as plotted in Figure 3(b). It is noticed that when the swelling degree (S_d) approached saturation, the thickness of copper sulfide layer decreased and a maximum thickness appeared at 0.20M EDTA, which can be explained as shown in Figure 6(e). For high concentration of EDTA, the extra EDTA would increase the rate of copper sulfide deposition into solution and should not benefit the formation of compact layer. Consequently, the flaking would take place and the thickness of copper sulfide layer on the surface of PAN film decreased as illustrated in Figure 6(e).

Grozdanov and Najdoski²³ showed that the copper sulfide could be precipitated instantaneously

from aqueous solutions of corresponding salts by addition of Na_2S . A variety of Cu_2S , $\text{Cu}_{1.8}\text{S}$, $\text{Cu}_{1.4}\text{S}$, and CuS films were obtained by a variety of the different bath composition. It was similar to our study for the application of EMI shielding. In this investigation, the $\text{Cu}_{x(x=1,2)}\text{S}/\text{PAN}$ composites were fabricated and the EMI SE was increased from 10–12 dB to 20–23 dB because of thickness increasing.

EMI shielding effectiveness measurement

The copper sulfide layer had mobile charge carriers which interacted with the electromagnetic fields in the electromagnetic radiation. The EMI SE of the $\text{Cu}_{x(x=1,2)}\text{S}/\text{PAN}$ composites manufactured in this study were measured between 30 and 1500 MHz and plotted in Figure 7. The EMI effect is obviously controlled by the thickness of copper sulfide layer. The thickness of copper sulfide affected the EMI SE due to the incident EMI wave reflected by copper sulfide layer. Jana and Mallick²⁴ studied the effect of the thickness of conductive layer of composites on EMI SE and found that the EMI SE increased and return loss decreased with increasing thickness of composites. The EMI SE effect was significantly improved for the $\text{Cu}_{x(x=1,2)}\text{S}/\text{PAN}$ composites by comparing the curves of 0.05M and 0.00M EDTA in Figure 7 because the thickness of copper sulfide with 0.05M EDTA is doubled (153 nm/76 nm). The thickness of the copper sulfide layer reached to a maximum at 0.20M EDTA and then decreased, therefore, the best electroless plating condition for EMI SE was 0.20M EDTA.

DSC analysis of $\text{Cu}_{x(x=1,2)}\text{S}/\text{PAN}$ composites

The DSC results of $\text{Cu}_{x(x=1,2)}\text{S}/\text{PAN}$ composites were summarized in Figure 8 and Table II. It was

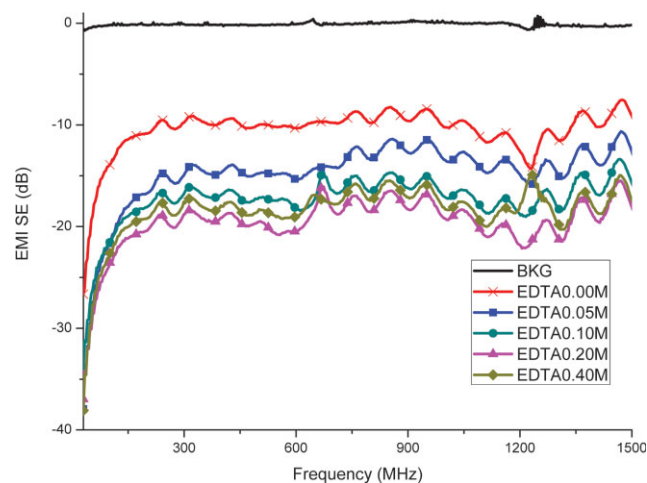


Figure 7 The EMI shielding effectiveness of $\text{Cu}_{x(x=1,2)}\text{S}/\text{PAN}$ composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

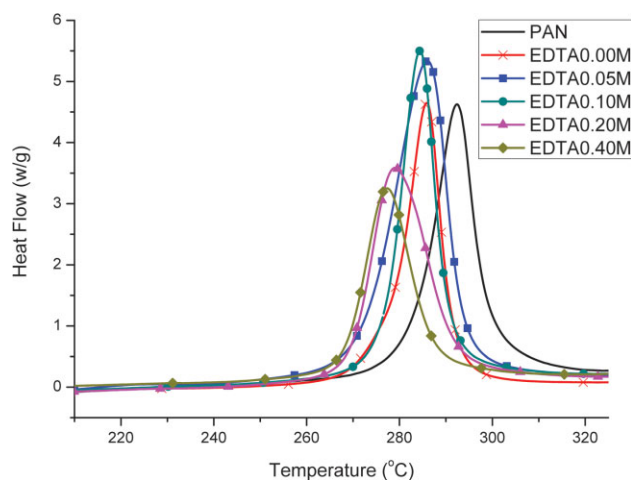


Figure 8 The DSC curves of $\text{Cu}_x(x = 1, 2)\text{S}/\text{PAN}$ composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed that the peak temperatures, T_{peak} and onset temperature, T_0 , of the composites were less than that of PAN and decreased with increasing the EDTA concentration. It meant that the crystal region of PAN was affected by the rigid copper sulfide grain and the chain mobility of PAN was restrained.

CONCLUSIONS

The principle in achieving the significant EMI SE of the composite is always the same: thickness of the metal layer and good adhesion of the interface between the coating films and the plastic substrate. In this research, the composites were prepared by applying electroless plating method. The GIA-XRD and laser Raman spectrum identified the composition of deposited layer was $\text{Cu}_x(x = 1, 2)\text{S}$. The chelating agent EDTA provided the anchor effect. It was demonstrated by FTIR spectra and played a critical role to successfully give the effective deposition. The swelling degree (S_d) was proposed and evaluated by the equation: $S_d = 0.13 + 0.90 \times e^{(-15.15C)}$, where C is the concentration of EDTA. The average thickness of copper sulfide layer increased from 76 to 383 nm as the EDTA concentration increased from 0.00 to

0.20M. Consequently, the EMI SE of the composites increased from 10–12 dB to 20–23 dB.

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