

Electrochemical Synthesis of Polyacrylonitrile (PAN)–Copper Composite Conductive Film

JIANGUO TANG,^{1,*} XIANFENG CHU,² XIA GAO,³ and WENYUAN ZHAO¹

¹Department of Applied Chemistry, College of Textile and Fashion, Qingdao University, Qingdao, 266071, People's Republic of China; ²Crystal Material Laboratory, Zhejiang University, Hangzhou, People's Republic of China; ³Department of Polymer Material, Dalian Polytechnic University, Dalian, People's Republic of China

SYNOPSIS

Polyacrylonitrile–copper composite film was synthesized by electrochemical reduction of a swollen film made by blend solution of a polyacrylonitrile–copper(II) ion which was coated on a electrode surface. The morphological structure of this composite film in the cross section was measured by a scanning electronic microscope and it showed three composite layers: a densely deposited layer, a transition layer, and an undeposited layer. The deposited layer consisted of the copper element and gave a high conductivity (10^0 S-cm^{-1}). In the transition layer, there was a great amount of a tree-shaped copper deposit, but no such deposit can be found in the undeposited layer. The experiment data showed that the conductivity of the film increases with increase of electrochemical reduction time and decreases with increase of ratio of nitrile group to the copper(II) ion. The viscosity of polyacrylonitrile–copper(II) ion solution is enhanced by a decrease of the ratio of the nitrile group to the copper(II) ion. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Organic conductive polymers have attracted great attention not only for scientific reasons, but also for their huge potentialities of applications,^{1–3} such as in rechargeable batteries, electronic switching elements, microwave transmission, reflection, absorption, and shielding,⁴ radiation detectors, and sensors. Whether intrinsically conductive or in the composite form,^{5,6} conductive polymers have been a popular area of research and numerous articles about chemical, electrical, and mechanical properties of the conductive polymers have appeared recently.^{7–10} On the other hand, the synthesis approaches were largely developed, especially in electrochemical syntheses.^{11,12}

Recently, polymer–metal complexes as conductive polymers have attracted much interest in the world. El-Sobati and co-workers¹³ studied 2,2'-azobisisobutyronitrile (AIBN)-initiated polymerization of an acrylonitrile–metal complex salt in *N,N*-di-

methylformamide (DMF) with transition metals (as a catalyst) and obtained a polyacrylonitrile (PAN)–metal complex salt. Wu and co-workers¹⁴ heated PAN containing the copper(I) ion and confirmed the complex structure between PAN and the copper(I) ion. All research mentioned above concerned the complex of copper ions with PAN, but composite film of the copper element and PAN by an electrochemical reaction has not been reported.

The purpose of this study was to make PAN–copper(0) electrically conductive composite film (ECCF) by an electrochemical reaction, to confirm the morphological structure of ECCF, and to determine the electrochemical reaction conditions.

EXPERIMENTAL

Materials

Commercial PAN (93% acrylonitrile, 6% methyl acrylate, and 1% itaconic acid, made by Zibo Synthetic Fiber Factory, China) was used without any purification; reagent-grade *N,N*-dimethylformamide (DMF, Guangzhou Xinjing No. 2 Chemical Factory,

* To whom correspondence should be addressed.

China) was used as a solvent without any purification; and reagent-grade copper chloride (Tianjin No. 2 Chemical Factory) was dried at 105°C overnight to eliminating absorbed and crystal water before use.

Syntheses of Samples

PAN and copper chloride were dissolved in DMF in a glass vessel which was equipped with a reflux exchanger. The glass vessel was heated to $90 \pm 5^\circ\text{C}$ and kept for 14 h. During the period of the heating process, the color of the mixture gradually changed from green to dark brown. After the PAN was gradually dissolved in DMF completely, the so-called PAN-copper(II) blend solution (PCBS) was obtained.

The PCBSs were coated on the surface of a rectangular carbon electrode (only on the front and three lateral surfaces). The films were dried in air at ambient temperature for 10–16 h. The films made by this method are semi-solidified films (SSF), whose thickness was limited to 700 μm .

The electrochemical reactions were carried out in a single-compartment electroreactor (Fig. 1). The

anode was a copper plate which has 4 cm length, 2.5 cm width, and 0.5 cm thickness, and the cathode was the same-sized carbon plate with the SSF. Distilled water was used as the medium in the reactor. A adjustable dc power supply unit was used to provide the required direct current. The electrochemical reactions were started at 25°C and continued for a designated time. After the reactions were finished, the films were stripped from the cathode plate carefully and then rinsed with water and dried at 105°C for 4 h. The final films were defined as being electrically conductive composite film (ECCF).

Measurements

The rheological property of PCBS was determined by an NXS-11 rotating viscometer (Chengdu, China). The viscosity of the solutions was calculated according to the formula

$$\eta = k\alpha$$

where η is the apparent viscosity (Poise); K , the instrumental constant; and α , the value of the reading on the instrumental gauge at a certain shear rate D (s^{-1}).

The volumetric conductivity of ECCFs was measured by a dc technique. The samples were trimmed into rectangular pieces (5×10 mm). The 5 mm-width copper probes were used as electrodes. The conductivity was calculated by the following formula:

$$\sigma = \frac{i}{V} \cdot \frac{l}{wb} \text{ S cm}^{-1}$$

where b is the thickness of ECCFs; w , the width of the probe; l , the distance between two probes; i , the electrical current; and V , the voltage of the dc power.

The morphological structure of ECCFs was measured by a scanning electronic microscope, Cambridge Instrument S250MK IV. The films used in the test were broken into thin and long pieces and adhered to the sample frame. After coating with silver, the films were observed.

The complex structures of SSF and ECCF were measured by a Fourier transform infrared spectrometer, Nicolet 750, U.S. The SSF and ECCF were dried at 105°C for 4 h and then ground into powder; both the samples were measured in KBr pellets.

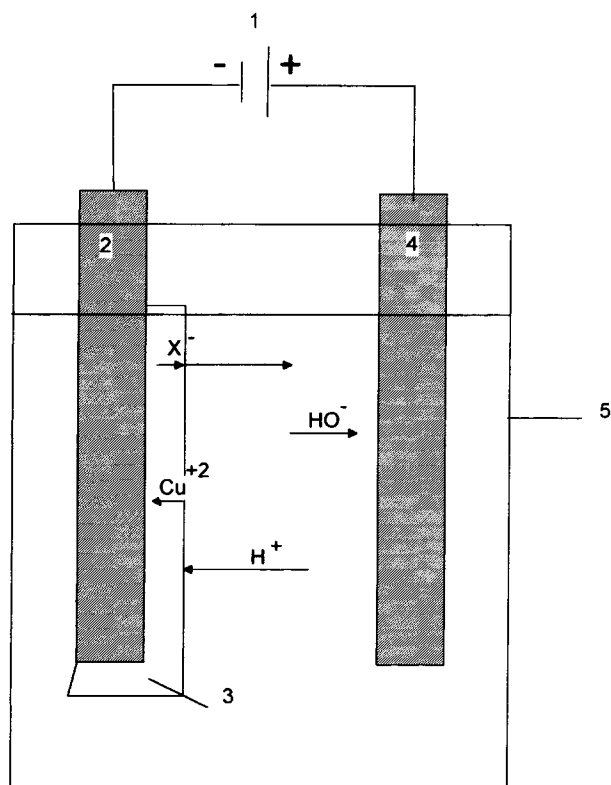


Figure 1 Electrochemical reactor: (1) dc power (voltage from 0 to 100 V); (2) carbon electrode (cathode); (3) SSF; (4) copper electrode (anode); (5) electrochemical reactor.

RESULTS AND DISCUSSION

Influential Factors in Preparation of SSFs

Preliminary experiment data showed that the rheological property of PCBSs had a great influence in obtaining the smooth SSF on the cathode plate. Figure 2 shows that the viscosity of the solutions decreases with increase of the shear rates and that the characteristic of shearing thinning is present. The viscosity of the blend solutions decreases with increases of the ratios of the nitrile group to the copper(II) ion. A higher proportion of the copper(II) ion to PAN in the blend solution causes a worse rheological property of the solution. No difficulty was present when the ratio was from 3 : 1 to 1 : 1 in making SSFs in our experiment conditions.

It should be noticed that to prepare SSF successfully enough drying time of SSF in ambient temperature is very important to prevent the copper(II) ion to diffuse into the water in the initial insertion into the electroreactor. The morphological structural images of the ECCFs were confirmed by their scanning electronic micrographs (Fig. 3 and Table I). We can divide the cross section of the ECCFs into three parts: a densely deposited layer, a transition layer, and an undeposited layer. The thickness of the transition layer of ECCF B is 461 μm (64.8%) and that of ECCF A is 350 μm (50.2%). The thickness of the undeposited layer of ECCF B is 231 μm (32.4%) and that of ECCF A is 325 μm (46.9%). These results clearly show that drying time largely affects the ratio of thickness of transition layer to that of the undeposited layer.

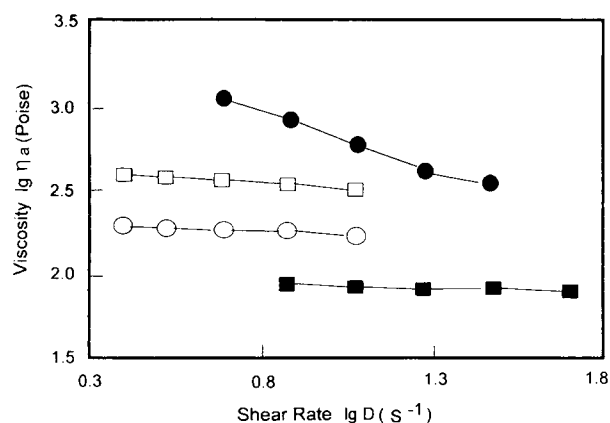
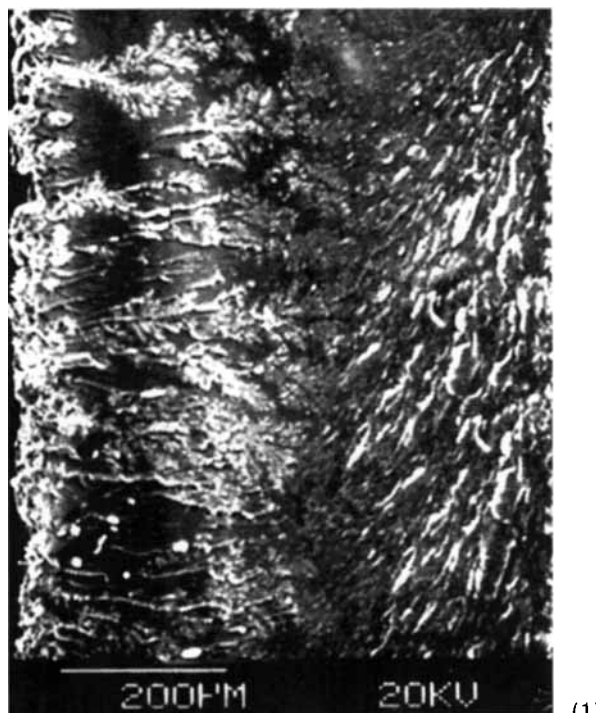
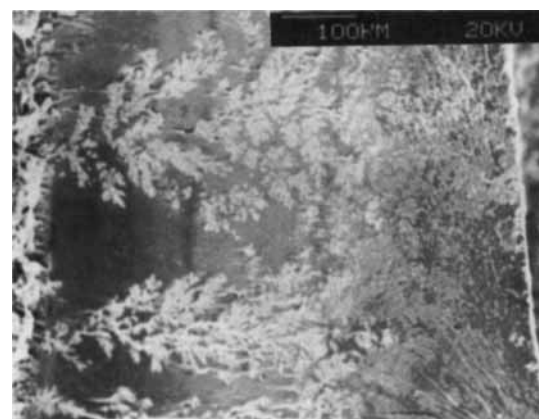


Figure 2 Relationship between shear rate and viscosity of PAN-copper(II) blend solution. Concentration of PAN to DMF in PCBS: 17% (wt); (●) nitrile : Cu(II) = 1 : 1 (mole/mole); (□) nitrile : Cu(II) = 2 : 1 (mole/mole); (○) nitrile : Cu(II) = 3 : 1 (mole/mole); (■) no copper(II) ion in solution (concentration 17% wt) of PAN in DMF.



(1)



(2)

Figure 3 SEM photographs of ECCFs. (1) ECCF A—concentration of PAN to DMF in PCBS: 17% (wt); ratio (mole/mole) of nitrile to copper(II) in PCBS: 2 : 1; drying time of SSF: 16 h; current: 0.8 A; reaction time: 2 h. (2) ECCF B—concentration of PAN to DMF in PCBS: 17% (wt); ratio of nitrile to copper(II) in PCBS: 2 : 1; drying time of SSF: 10 h; current: 0.8 A; reaction time: 2 h.

Influences of Electrochemical Reaction Conditions on Conductivity of ECCFs

The conductivity of ECCFs obtained by this electrochemical method was influenced by various factors such as current strength, ratio of nitrile groups to the copper(II) ion, and time of the electrochemical reaction. The effect of the ratio of nitrile groups in

Table I Data of Morphological Structure of Composite Conductive Film

Sample	PCBS			ECCF					
	Concn of PAN to DMF (% wt)	Ratio of Nitrile to Cu(II)	SSF	Deposited Layer		Transition Layer		Undeposited Layer	
			Drying Time at Ambient Temp (h)	Thickness (μm)	Proportion %	Thickness (μm)	Proportion %	Thickness (μm)	Proportion %
A	17	2 : 1	16	20	2.9	350	50.2	325	46.9
B	17	2 : 1	10	20	2.8	461	64.8	231	32.4

PAN to the copper(II) ion on the conductivity of ECCFs is shown in Figure 4. The conductivity decreases with increase of the ratios of the nitrile group to the copper(II) ion. When the ratio is more than 3 : 1, conductivity is reduced to 10^{-4} S cm^{-1} . This means that only when the ratio of the nitrile group to the copper(II) ion is less than 3 : 1 does the SSF have enough copper(II) ion and the ECCF excellent conductivity.

The effect of current strength on conductivity of ECCFs was studied at seven different current strengths and the result is shown in Figure 5. It was found that the values of the conductivity of the ECCFs first increases with increase of the electrical current when the current was relatively low, and it reaches maximum at 0.5 A, and then it decreases until to 0.7 A, finally attaining the constant value of 2 S cm^{-1} . Before the maximum, the higher current strength causes easier dispersion of the copper(II) ion to the cathode (carbon electrode) and makes the

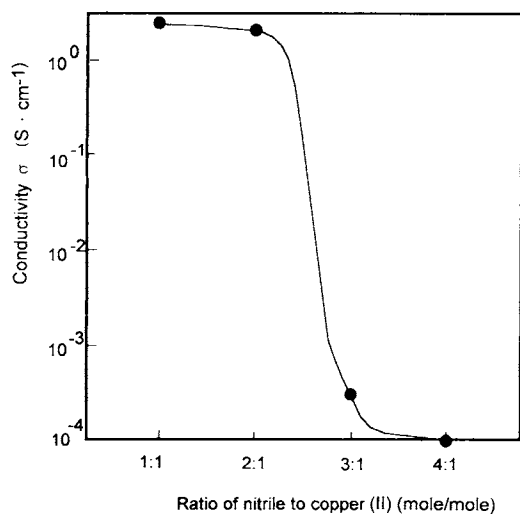


Figure 4 Effect of ratio of nitrile group to copper(II) ion on conductivity of ECCF. Concentration of PAN to DMF in PCBS: 17%; drying time of SSF: 16 h; current: 0.8 A; reaction time: 2 h.

ECCFs have higher conductivity. After the maximum, the higher current causes the temperature in the electroreactor to increase, and the phase separation (resulted in both the solvent of DMF in SSF to penetrate from the inner layer to the outer and finally into the bath and the water in the bath to penetrate into SSF from its outer layer to the inner one) is enhanced, so that the viscosity in the surfacial skin in SSF is increased. The higher viscosity inhibited the dispersion of the copper(II) ion. But it should be noticed that the difference of conductivity of ECCFs is only 5 S cm^{-1} , therefore, it was not largely affected if the temperature was limited below 72°C.

The conductivity of ECCFs as a function of the electrochemical reaction time in this experiment is depicted in Figure 6. The results show that the conductivity of the film increases with increase of the reaction time. This is easily understood because the process of the dispersion of the copper ion(II) needs time to penetrate toward the cathode.

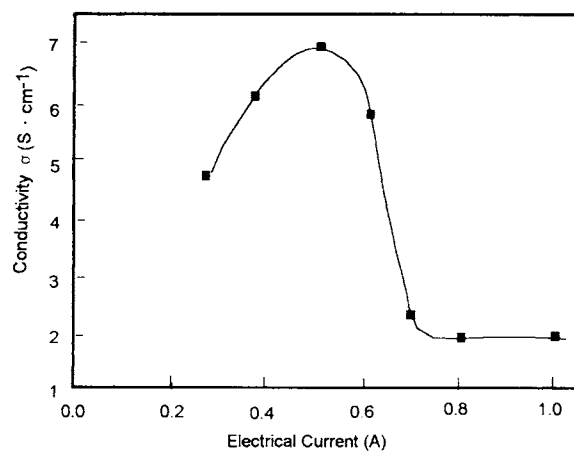


Figure 5 Effect of electrical current on conductivity of ECCF. Concentration of PAN to DMF in PCBS: 17%; drying time of SSF: 16 h; ratio of nitrile group to copper(II) ion: 2 : 1; reaction time: 2 h.

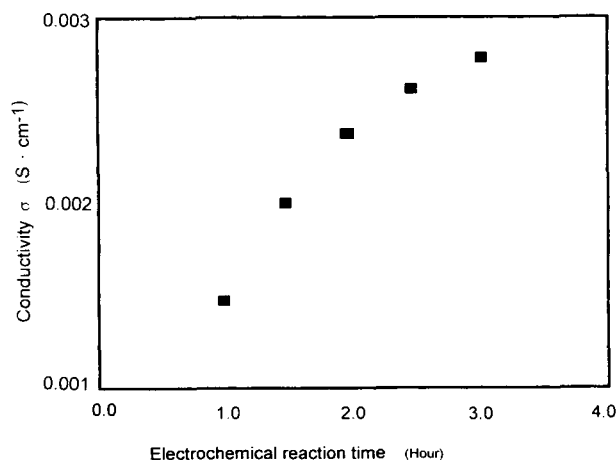


Figure 6 Effect of electrochemical reaction time on conductivity. Concentration of PAN to DMF in SSF: 15%; drying time of SSF: 16 h; ratio (mole/mole) of nitrile to copper(II): 2 : 1; current: 0.8 A.

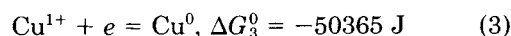
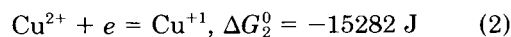
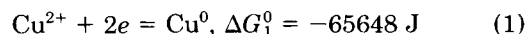
Comparing Figure 6 with Figure 5, we can notice that the difference of conductivity between the two figures is of $10^3 S \cdot cm^{-1}$ order. This indicates that the lower concentration (15% in Fig. 5) of PAN to DMF causes the SSF to have a higher swollen degree, so that the bulk viscosity in it is lower. After the cathode with SSF was inserted into the electro-reactor, the copper(II) ion on the surface of SSF cannot be held and so diffuses into the bath. This reduces the copper(II) concentration in SSF to a lower level. In our experiments, the green color of Cu^{2+} was found in the beginning of electrochemical reaction when SSF was prepared by the solution.

Analysis of Morphological Structure of ECCFs

From all considerations mentioned above, the details of the morphological structure can be analyzed further and the explanations can be given clearly. As shown in Figure 3(1), the picture of SEM has indicated that the ECCF includes three layers: a densely deposited layer, a transition layer, and an undeposited layer. The thickness of the densely deposited layer is $20 \mu m$; the transition layer, $350 \mu m$; and the undeposited layer, $325 \mu m$. Their dimensional proportion is 2.9 : 50.3 : 46.9. On the other hand, after ECCF was rinsed, dried, and cleaned, the side which had attached to the carbon electrode shows a brown copper color, but other side does not. This exhibits that the deposited layer is composed of the copper element.

This can be explained according to the following electrochemical reactions: Under the electrical field (Fig. 1), the positive ion Cu^{2+} in SSF tends to get

through the film and reaches the cathode. The thermodynamic principle of these reactions on the cathode can be given as the following formulas:



Because of the $|\Delta G_1^0| > |\Delta G_3^0| > |\Delta G_2^0|$ in eqs. (1)–(3), it is difficult for the first reduced product Cu^{1+} to be attained in the film and the main reactions on the cathode should be that Cu^{2+} is reduced to Cu^0 .

In the transition layer (Fig. 7), we can see the growing image of the deposition. It is just like many “trees,” whose “trunks” were grown out of the densely deposited layer and “branches” out of the “trunks.” From the view of the deposited copper growth, it can be confirmed that in the process of the electrochemical reaction the closest copper ion Cu^{2+} can obtain electrons first, change to copper Cu^0 , and then initiate the deposited sites (“tree root”) corresponding to the possibility principle. The depositing growth of these sites (“tree root”) along the thickness direction is equivalent to the extension of the electrode, and the grown electrodes (“tree trunk”) further accept the penetrating copper(II) ion and reduce the ion into Cu^0 . With the developing of deposition (the extension of the electrode), the thickness of the transition layer increases. When this extension reaches the critical skin layer, the penetrating process cannot continue and the growth of the electrode (“tree trunk growth”) ceased.



Figure 7 Morphological structure of transition layer of ECCF from SEM. Concentration of PAN to DMF in PCBS: 17% (wt); ratio (mole/mole) of nitrile group to copper(II) ion: 2 : 1; drying time of SSF: 16 h; current: 0.8 A; reaction time: 2 h.

The undeposited layer (Fig. 8) is the skin layer which was left due to the drying of SSF in ambient temperature and the phase separation caused by the dispersion processes of DMF out of SSF and water into SSF during the period of electroreaction.

Chemical Linkages Among the Components in SSF and ECCF

The chemical linking situations among the nitrile groups, copper ion, and DMF were characterized by FTIR. The infrared spectra of the dried SSF and ECCF are shown in Figure 9. It can be seen from the graphs that 2339.5 and 2191.0 cm^{-1} in Figure 9(A) confirmed the presence of the complex between the $\text{—C}\equiv\text{N}$ and the copper(II) ion in SSF.^{13,14} But the two bands become extremely weak in ECCFs [Fig. 9(B)], indicating decreases of the complex in the electrochemical process. The changes of the 2339.5 and 2191.0 cm^{-1} bands before and after the electrochemical process indirectly imply that there is a copper element in ECCFs.

But the new band obtained at 621 cm^{-1} is the result of very complicated reduction byproducts in SSF under the high voltage drop (20–50 V). It may be converted from the reduction byproducts of $\text{—C}\equiv\text{N}$ and other groups, e.g., $\text{R—CH}_2\text{—NH}_2\cdot\text{HCl}$.¹⁵ The decrease of both 3446.6 and 3357.9 cm^{-1} bands, the stretching vibration of carboxylic hydroxy (—OH),^{15,16} may result from the electrolysis of —OH . The exact information of band 621 cm^{-1} needs further research because of the complication of electroreduction in SSF.

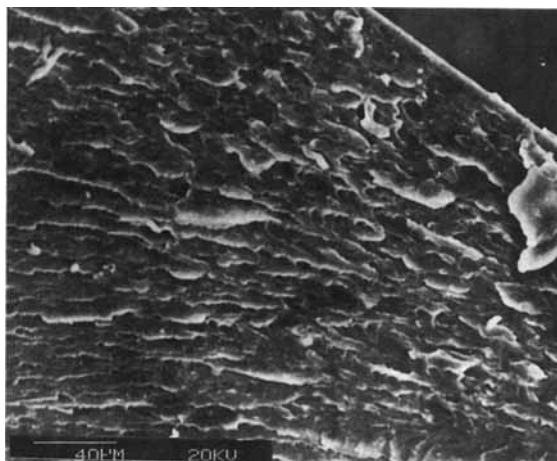


Figure 8 Morphological structure of undeposited layer of ECCF. Concentration of PAN to DMF in PCBS: 17% (wt); ratio (mole/mole) of nitrile group to copper(II) ion: 2 : 1; drying time of SSF: 16 h; current: 0.8 A; reaction time: 2 h.

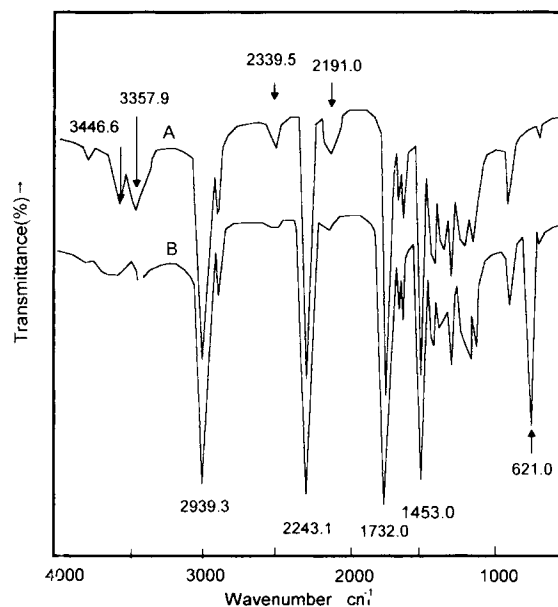


Figure 9 FTIR spectra: (A) dried SSF—concentration of PAN to DMF: 17%; ratio (mole/mole) of nitrile to copper(II) ion: 2 : 1; drying time of SSF: 16 h; dried at 105°C for 4 h. (B) ECCF—concentration of PAN to DMF: 17%; ratio (mole/mole) of nitrile to copper(II) ion: 2 : 1; drying time of SSF: 16 h; current: 0.8 A; reaction time: 2 h; dried at 105°C for 4 h.

CONCLUSION

To obtain the polyacrylonitrile–copper(0) composite film, the electrochemical reactions used in this research provide a proper method. The morphological structure of ECCF includes three layers, of which the densely deposited layer is made up of the copper element and the part of transition layer consists of the copper element also. The conductivity of the final film is gained from the copper layer and the transition layer. The proper electrical current and electrochemical reaction time can enhance the conductivity of the final film while the ratio of nitrile to the copper(II) ion should be lower than a critical value so as to give the final film the high conductivity. The preparing conditions of the blend solution of the polyacrylonitrile–copper(II) ion and the manufacturing conditions of SSFs affect the conductivity and the morphological structure of the electrically conductive composite film.

REFERENCES

1. Y. H. Park, S. H. Choi, S. K. Song, and S. Miyata, *J. Appl. Polym. Sci.*, **45**, 843–851 (1992).

2. M. Inagaki and E. I. Toh, *Syn. Met.*, **35**, 383-385 (1990).
3. A. K. Kalkar, S. Kundagol, S. Chand, and S. Chandra, *J. Appl. Polym. Sci.*, **51**, 1213-1220 (1994).
4. A. Kaynak, J. Unsworth, R. Clout, A. S. Mohan, and G. E. Beard, *J. Appl. Polym. Sci.*, **54**, 269-278 (1994).
5. H. Tang, Z. Y. Liu, J. H. Piao, X. F. Chen, Y. X. Lou, and S. H. Li, *J. Appl. Polym. Sci.*, **51**, 1159-1164 (1994).
6. E. Ruckenstein and L. Hong, *J. Appl. Polym. Sci.*, **53**, 923-932 (1994).
7. D. S. Kelkar and N. V. Bhat, *J. Appl. Polym. Sci.*, **43**, 191-195 (1991).
8. D. S. Kelker and N. V. Bhat, *J. Appl. Polym. Sci.*, **43**, 197-200 (1991).
9. P. Mitra and M. Biswas, *J. Appl. Polym. Sci.*, **45**, 1685-1692 (1992).
10. M. N. Vijayashree, S. V. Subraanyam, and A. G. Samuelson, *J. Appl. Polym. Sci.*, **49**, 2171-2177 (1993).
11. K. M. Choi and K. H. Kim, *J. Appl. Polym. Sci.*, **44**, 751-763 (1992).
12. J. Tang, Z. Li, and H. Yu, *Shandong Fang Zhi Gong Xue Yuan Xue Bao (P.R. China)*, **8**, 70-76 (1993).
13. A. Z. El-Sobati, M. A. Diab, A. S. Hilal, and M. N. Moussa, *Acta Polym.*, **40**(4), 236-237 (1989).
14. C. R. Wu, B. Liedberg, and S. Akbar, *Syn. Met.*, **26**(1), 121-132 (1988).
15. G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley, Chichester, New York, Brisbane, Toronto, 1980, pp. 57-66.
16. L. J. Bellemy, *The Infrared Spectra of Complex Molecules*, Halsted Press, New York, 1975, pp. 107-125.

Received September 1, 1995

Accepted February 6, 1996