Micromorphological Structure and Its Forming Mechanisms of Polyacrylonitrile-Based Copper Gradient Composite Film

JIANGUO TANG,[1,2] KEAO HU,[1] DONG GUO,[2] HAIYAN LIU,[2] ZHAOKUN ZHENG,[2] WENYING GUO,[2] SHAO DU,[2] YIQIN ZHOU,[3] RENJIE WU[1]

[1] Institute of composite materials, Shanghai Jiao Tong University, Shanghai, 200030, People's Republic of China

[2] Department of Chemical Engineering, Qingdao University, Qingdao, 266071, People's Republic of China

[3] Department of Applied Chemistry, Qingdao University, Qingdao, 266071, People's Republic of China

ABSTRACT: In this article, the micromorphological structure of polyacrylonitrile-copper gradient composite film obtained from the electrochemical reduction of a swelling cathode film was investigated with a scanning electronic microscope and a transmittance electronic microscope. It was found that the micromorphological structure in deposited phase is constructed with copper particles and sheaves of polyacrylonitrile chains. The diameters of both the copper particles and the sheaves of macromolecules are about 50 nm. Thus the idea of the interpenetration between polymeric matrix and deposited metal is suggested. Under the enhanced power voltage and the reactor temperature, the maximums of current in the loop of reaction system shift to lower electrochemical reaction time. That means the higher value of them makes the higher activity in the two aspects of ion move and ion reduction in swelling cathode film. The dissolving experiment of gradient composite film showed that it does not dissolve in *N,N*-dimethylformamide, and this further confirmed the interpenetration between the polymer matrix and the deposited copper. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1927–1932, 1999

Key words: polyacrylonitrile; copper; interpenetration; electrochemical; composite

INTRODUCTION

Metal-filled polymers or polymer-based metal composites have attracted much scientific attention in the world because of their wide applications to conductive, electronic, and optical materials,[1,2] such as layered or multilayer composites which can take on the good behavior of the

Schottky effect in electronic and optical fields.[3] In general, these composites, which not only have the flexibility of polymers but also the functional properties of metals and/or metal compounds, are widely needed in many fields.

Research largely developed in recent years,[4–8] and it focused on the understanding and control of the morphological structures to obtain the desired properties. In contrast to conventional simple mixing between polymer matrices and metal powders, researchers have focused on two routes: one is the morphological structure of gradient distribution of metal component(s), and the other is the nanoscale morphology of metal and/or metal compound phase in polymer matrices.

Our group has developed an electrochemical method by which a swelling cathode film (SCF) was reduced into a gradient composite film (GCF).[9,10] The effects of electrochemical conditions on the electric conductivity and morphological structures have been investigated in our previous work.[9,10]

In this article, we report our findings on micromorphological structure of GCF, and discuss the relationship between micromorphology and electrochemical conditions. These results will help us to understand the principles for preparing GCF.

EXPERIMENTAL

Materials

A commercial polyacrylonitrile (PAN) copolymer (93% acrylonitrile, 6% methyl acrylate, and 1% itaconic acid, made by Zibo Synthetic Fiber Factory, Zibo, China) was used as the polymer matrix, reagent-grade N,N-dimethylformamide (DMF) (Guangzhou Xinjing No. 2 Chemical Factory, Guangzhou, China) was used as the solvent for PAN, and reagent-grade copper chloride (Tianjin No. 2 Chemical Factory, Tianjin, China) was used as a copper ion resource. No reagents and materials were pretreated before use.

Synthesis of the Samples

All samples were synthesized by the electrochemical methods which were established in our previous articles.[9,10] However, we have largely ameliorated the experimental plan and the major electrochemical conditions.

The synthesis of the samples included three steps. First, PAN and copper ions (Cu^{++}) were dissolved in DMF in the same vessel at $80 \pm 2°C$ for at least 24 h. Second, the solution was coated on a copperized column cathode and was predried at ambient temperature for 24 h. The films obtained were still swollen by DMF and allowed copper ions to disperse under the proper potential. The films were called swelling cathode films (SCF). Third, SCFs were reduced electrochemically under the proper electrochemical conditions. The electrochemical reactions were started at the designated temperature, $30 \sim 60°C$. The reaction time was 3 h. In this study, the power voltage was considerably decreased to less than 3.6 V which is in the region of the voltage in common solution electrochemical reactions.

Measurements

The morphological structure of GCF was measured by a scanning electronic microscope (SEM), Cambridge Instrument S250MK III (Cambridge Co., UK). The samples in the test were broken into thin and long pieces, adhered to the sample frame, and gilded. The photograph of the electronic energy spectrum of the components in the cross-section of GCF was taken on the same SEM.

The constituent distribution of deposited copper in the cross-section was confirmed by the electronic energy spectrum with the SEM. The samples were treated by the same method with SEM tests. The benchmark is the vaporized gold. The calculation of the copper content in different layer was

$$C = \frac{A}{B} \times 100\% \qquad (1)$$

where C is a relative percentage of deposited copper relating to a location in the cross-section of GCF, A the content of deposited metal (copper), and B the content of gold.

The micromorphological structure (MPS) in the cross-section of GCF was tested by a transmittance electronic microscope (TEM) of JEM-2000 EX (Jeol Ltd., Tokyo, Japan). The samples were observed and pictures were taken under TEM after they were prepared by cutting GCF into extremely thin chips on a microtome of Dupont MT-6000 (Sorvall Instruments, Delaware, USA). The electronic diffraction patterns were taken at the same time on the TEM mentioned above.

Dissolving GCFs and SCFs

The dissolving experiments were performed as follows. The weighed, ground, and mixed GCF was added into 10 cuvettes which were put into a bath at constant temperature $80 \pm 5°C$. The bath was heated at daytime, about 8 h. Every other day (about 48 h) we took a cuvette out from the bath, filtered the dissolved (or swollen) mass, and dried the residues at 85°C in vacuum. After complete drying, the residues were weighed separately. The percentage of lost weight was calculated according to the following equation:

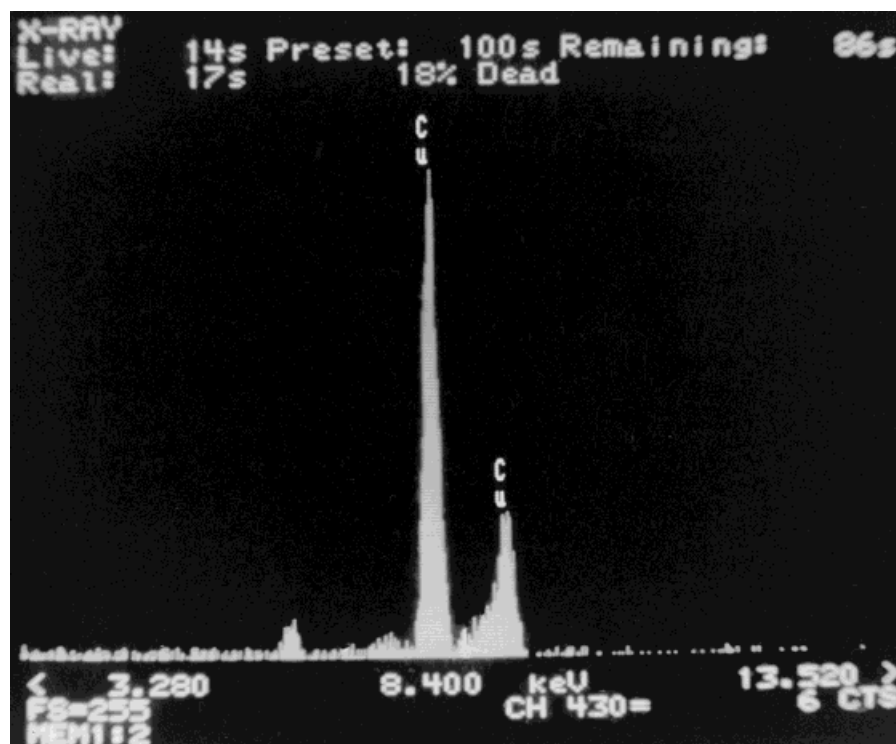$$W\% = \frac{W_0 - W}{W_0} \times 100\% \qquad (2)$$

Figure 1 Photograph of an electronic energy spectrum on SEM. Conditions: predrying time of SCF: 24 h; voltage of power: 2.4 V; temperature in electrochemical reactor: 30°C.

where $W\%$ is the lost weight of GCF due to dissolving in DMF, W_0 the initial weight of GCF before dissolving, and W the weight after dissolving for the designated time.

Unelectrolyzed samples were prepared with SCFs. The SCFs were not electrolyzed but immersed in the electrochemical reactor for 3 h at the same temperature. The parallel dissolving experiments of unelectrolyzed SCFs were performed under the same conditions for dissolving GCFs.

RESULTS AND DISCUSSION

MPS of GCF

In previous articles,[9,10] we have presented our research results on morphological structures of GCFs made up of a polymer matrix and a deposited copper phase. The basic construction form of GCF is the three-layer morphology: the metal deposited layer, the transition layer, and the metal-undeposited layer. We have suggested that deposited phase, which is constructed of deposited layer and transit layer.

In this article, we further investigate the distribution of metallic constituent in the cross-section of GCF by electronic energy spectrum on SEM. In the range of electronic scanning, the copper peaks are clearly present (Fig. 1). This confirms the presence of copper in the deposited phase instrumentally. Corresponding to the deposited layer, transit layer, and undeposited layer, the quantity of deposited copper relative to that of gold which was vaporized in the pretreatment was recorded by the same means (Table I). The data confirm the decrease of deposited copper from deposited layer to undeposited layer. This gradient distribution accords with the results of the SEM in our previous work.

In the experiment of TEM (Fig. 2), the dark dendriform domains in the cross-section of GCF were clearly seen. According to phase-contrast (bright-field) and Z-contrast (dark-field) (Z is atomic number) rules, the dark field is the deposited phase. This confirmed that the constituent of the deposited phase is an agglomeration of very small particles that have diameters of only about 50 nm. On a black dot, an electronic diffraction

Table I The Percentage of Deposited Copper Distribution Along the Cross-Section of GCF

	Percentage of Elements (%)			Content of Copper, C (%)[a]
	Au	Cu	Cl	
In deposited layer	63.375	33.898	2.276	53.49
In transit layer	71.847	26.312	1.841	36.62
In undeposited layer	93.036	5.987	0.978	6.44

[a] The percentage of Cl is relatively low and it is neglected in the calculation according to Eq. (1).

test was done and the diffraction pattern of multicrystals was obtained (Fig. 3). These data showed that the deposited phase was constructed of nano copper particles. On the other hand, the PAN matrix showed as the bright field which consists of about 50-nm sheaves of macromolecular chains, and obviously they were embedded with deposited metallic particles. About 100 macromolecular chains were comprised in the sheaves of macromolecular chains, according to the diameter of helix structures of PAN molecules.[11]

We deduce from the micromorphological structure above, that the PAN matrix should be welded by the deposited phase; and thus GCF should take on the properties of a thermosetting plastic that does not dissolve in its solvents. The result of dissolving experiments of GCF depicted in Figure
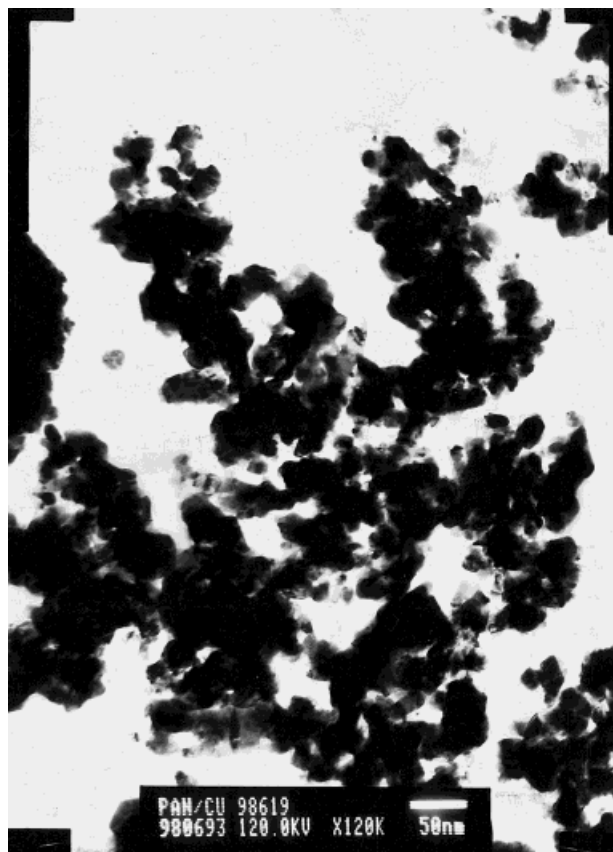

Figure 2 Photograph of GCF on TEM. Conditions: predrying time of SCF: 24 h; voltage of power: 2.4 V; temperature in electrochemical reactor: 30°C.
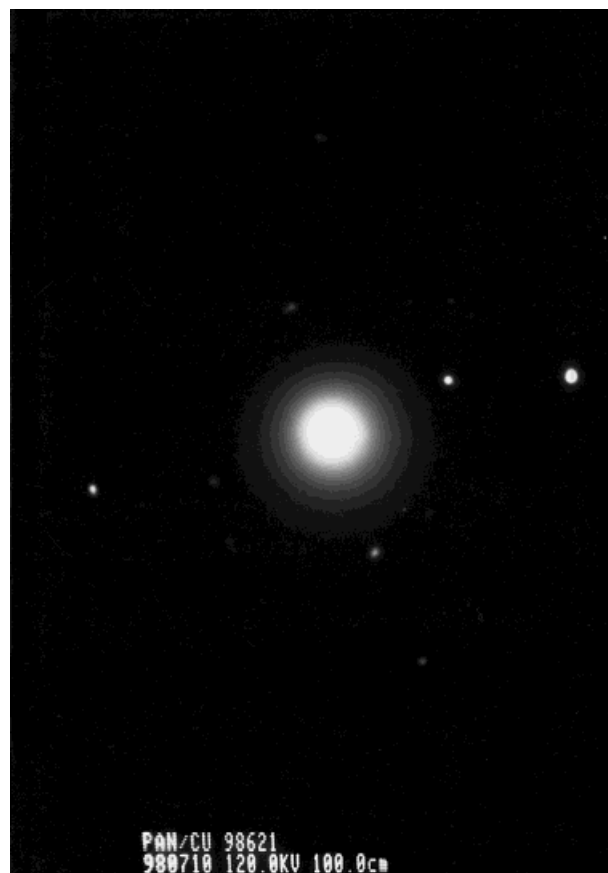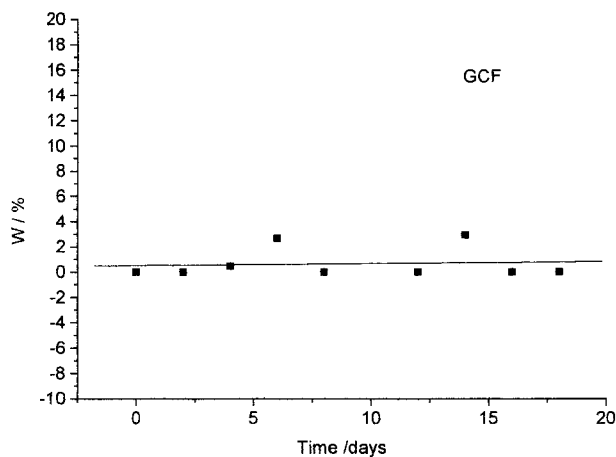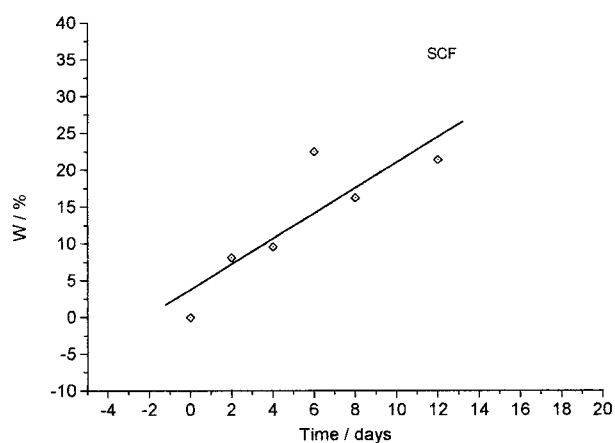

Figure 3 Electronic diffraction pattern (the sample is the same as in Figure 2).

(a)

(b)

Figure 4 The dissolving curves of GCF, (a) for GCF and (b) for SCF.

4 demonstrates that Figure 4(a) is the dissolving curve of GCF, in which the percentage of lost weight of GCF is nearly zero through the whole period of dissolving time, 18 days. However, in Figure 4(b), the lost weight curve increases linearly with the increase of dissolving time of SCF. In 12 days, the lost weight of SCF reaches 23.5% wt. This showed that SCFs can still dissolved in solvent DMF but GCF cannot.

Electrochemical Mechanism for Forming MPS of GCF

Figures 5 and 6 depict the relationship between electrochemical conditions, such as power voltage and temperature in the electroreactor, and electrochemical reaction time.

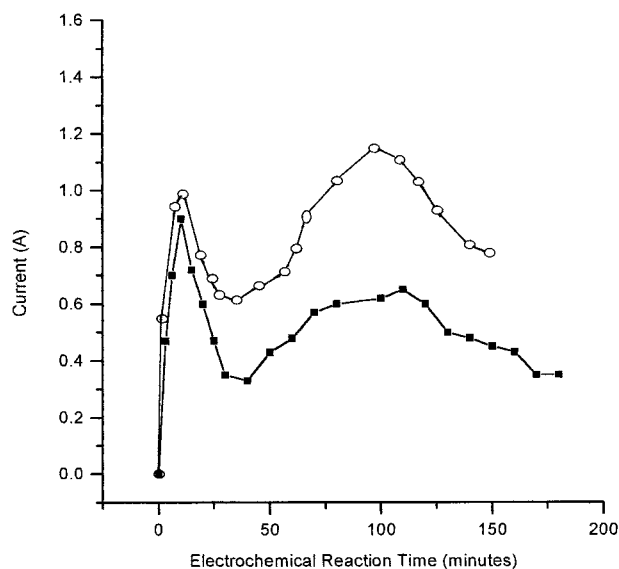Under constant electrical voltage, the change of current with electrochemical reaction time in

Figure 5 The effect of different power voltages on current. Conditions: predrying time of SCF: 24 h; temperatures in electrochemical reactor: 30°C. ■, 2.0 V; ○, 2.4 V.

the loop shows that there are two active periods of ion dispersion (Fig. 5). The first one is near in the 15–20 min range and the second one is in the 100–120 min range. From the locations of the peaks we find the tendency, that under higher voltage, the peaks shift to the left.
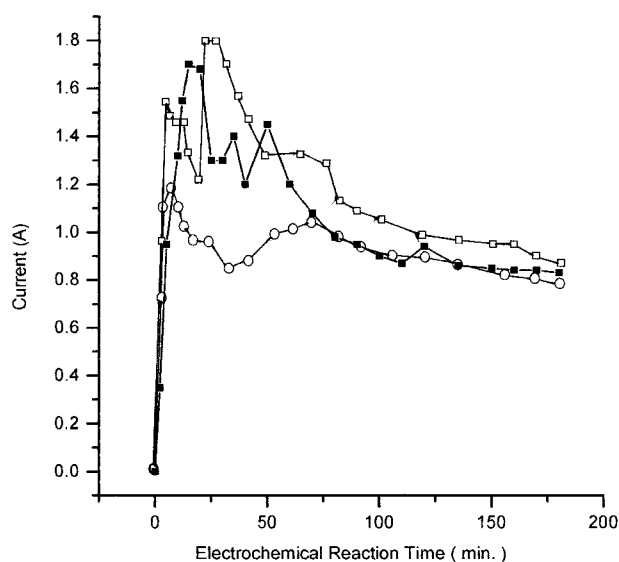

Figure 6 The effect of different temperature in electrochemical reactor on current. Conditions: predrying time of SCF: 24 h; power voltage: 2.4 V. ○, 40°C; □, 50°C; ■, 60°C.

Under higher temperature in the electrochemical reactor, we found higher current curves and the tendency that, under higher temperature, both peaks clearly shifted to the left. From 30°C [Fig. 5 (○, 30°C)] to 50°C [Fig. 6 (○, 40°C; □, 50°C)], the first peak moved from 20 min to 5 min, and the second peak from 100 min to 30 min. This showed that the higher temperature gives higher activity of ion dispersion in SCF, but at 60°C, only the lower peak value was present. This result is similar to that of a previous study on the change of the deposited phase area.[9] It is a very complex process because of the effects of temperature, function of water in electrolyte, solubility of copper ion(II) at different temperatures, etc. Thus, the details need further investigation.

As we pointed out in our previous article,[9,10] ion movement in SCF is the premise of obtaining the gradient deposition phase. In general, it should have two basic cases: one is that the free movement of ions occurred in the interspace of macromolecules and the relative ions were not limited by the interaction between ions and macromolecules; and the other is that the movement of coalescent ions occurred only by the change of conformation of macromolecules.[12] In the latter case, these ions attached on the chains by complex, hydrogen bonds, polar force, ion bonds, and/or other intermolecular interactions. In SCF, the degree of swelling by solvent is very low and the major mode of ion movement should be the latter one. Therefore, when we boosted the electrochemical conditions such as power voltage and temperature in the reactor, the ion move could be enhanced. This shift effect of maximum in Figures 5 and 6 under the boosted electrochemical conditions can be enough to show this.

Reduction of ions into metal comprises nucleation and growth. The formation of undeposited layer (Table I) indicates that nucleation is a slower process than that of crystal growth. This provides the opportunity for ions to come to the cathode side and nucleate nearly in the interval of about 50 nm, and the formed crystals in the scale of 50 nm closely agglomerated in SCF (Fig. 2). In the processes of nucleation and growth of the nanoparticles the deposited phase is embedded through the sheaves of macromolecules. There-fore, the polymer-metal interpenetrated composite (PMIC) was formed.

CONCLUSIONS

On the basis of the previous work by our group, we have investigated the MPS of GCF by TEM, electronic energy spectrum on SEM, electronic diffraction on TEM, etc. Evidence for a PMIC idea was obtained. According to the relationship between the MPS and the changes of electrochemical conditions including power voltage and reactor temperature, a possible forming mechanism of PMIC is suggested. Because the preparation of GCF was performed in the range of conventional electrochemical conditions (the voltage is 2–3 V), the data and the analyses have wide significance.

REFERENCES

1. Im, S. S.; Lee, J. S.; Kang, E. Y. J Appl Polym Sci 1995, 57, 431.
2. Fermandez, A. M.; Nair, P. K. Polym Films, 1992, 35, 459.
3. Lei, J.; Liang, W.; Marin, R. Synth Met 1992, 47, 351.
4. Rothon, R. Polymer Science and Technology Series: Particulate-Filled Polymer Composite; Addison Wesley Longman Limited: London, 1995; p. 235, 279, 317.
5. Bhattacharya, S. K. Metal-Filled Polymers: Properties and Applications; Marcel Dekker: New York, Basel, 1986.
6. Lei, J.; Liang, W.; Martin, R. Synth Met 1992, 47, 351.
7. Freeman, R. G.; Grabar, K. C.; Allison, K. J. Science 1995, 267, 1629.
8. Golden, J. H.; Disalvo, F. J.; Frechet, J. M. J. Science 1996, 273, 782.
9. Tang, J.; Hu, K.; Fu, S.; Qi, H.; Cui, W.; Jia, Z.; Li, K.; Pang, H.; Wang, F. J Appl Polym Sci 1998, 69, 1159.
10. Tang, J.; Chu, X.; Gao, X.; Zhao, W. J Appl Polym Sci 1996, 61, 1773.
11. Tang, J. GAO FEN ZI TONG BAO, 1995, 4, 227.
12. Ciardelli, F.; Tsuchida, E.; and Wohrle, D. Macromolecule–Metal Complexes (Ch.); Beijing University Press: Beijing, 1999; p. 165.