

# Relationship Between Structures of Polyacrylonitrile (PAN)–Copper Gradient Composite Film and Electrochemical-Reaction Conditions

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**ABSTRACT:** In this article, the relationship between the morphological structure and electrochemical conditions, the crystal structure in the electrochemical deposited phase, and the thermal properties of polyacrylonitrile (PAN)–copper gradient composite films (GCF) were studied. The results showed that the morphology of the GCF depended very much on the electrochemical conditions used in the reactions. The percent area of the deposited phase on the cross section of the GCF decreases with increases of the predrying time of the solution coated on the cathode, the power voltage, and the temperature in the electrochemical reactor. According to the data of a differential scanning calorimeter and a scanning electronic microscope, PAN chains are physically crosslinked by a deposited phase. Under the electrochemical conditions used in this article, the components of PAN are not affected by the electrochemical reactions. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1159–1165, 1998

**Key words:** polyacrylonitrile; electrochemical reaction; composite; morphology

## INTRODUCTION

In recent years, some scientists have combined polymers with metals together and obtained many useful composite materials.<sup>1</sup> In addition to being used as microwave absorptions and shieldings of instruments and computers,<sup>2</sup> new applications were found, such as radiation initiation of polymerization<sup>3</sup> and sheath–core powders.<sup>4</sup>

However, the majority of these composite materials were made only by mixing various metal powders with polymers. Their morphology cannot

be controlled by manufacturing conditions. Therefore, many important applications were limited due to processing means and some properties needed in many special fields cannot be obtained.

According to the reasons analyzed above, our group synthesized a PAN–copper gradient composite film by electrochemical means.<sup>5</sup> This implied that the principles of electrochemical synthesis of organic conductive polymers<sup>6,7</sup> can be applied to prepare composite materials having good conductivity. With the electrochemical methods, we can control the morphological structures of the composite films by variations of the electrochemical conditions and impart many properties to composite films. In this article, we analyzed the effects of electrochemical conditions on the structures, chemical components, and thermal properties of gradient composite films (GCF).

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## 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 a solvent for PAN, and reagent-grade copper chloride (Tianjin No. 2 Chemical Factory, Tianjin, China) was used as a copper ion resource. All reagents and materials were not pretreated before use.

### Preparations of Samples

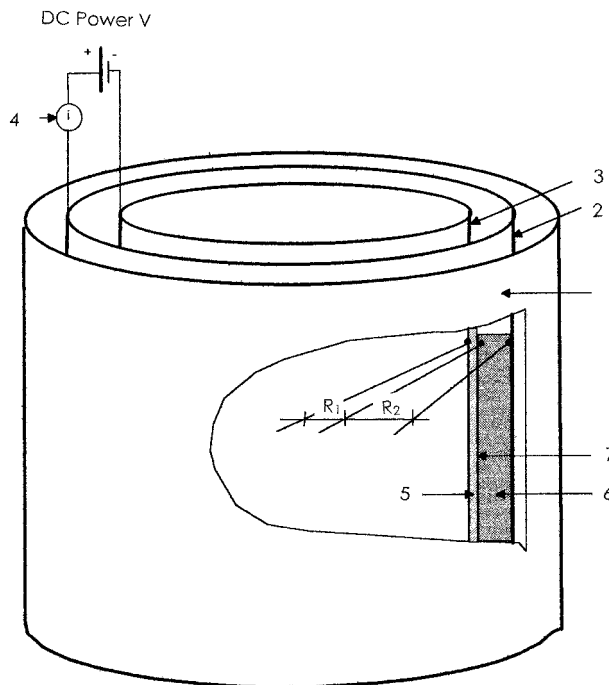
The synthesis methods of the GCF were similar to those of the previous articles,<sup>5</sup> but there are some differences in the consideration of the reactor and electrochemical conditions. PAN was dissolved in DMF in glass vessels which were equipped with reflux exchangers. The glass vessels containing the mixture were heated to  $75 \pm 2^\circ\text{C}$  for the mixture and then copper(II) chloride was added into it according to the calculation of the designated receipt. After PAN dissolved, the vessels were kept at a constant temperature for more than 12 h to obtain homogeneous solutions. The solutions from this method were coated on the outer surface of the inner cylindrical electrodes used as cathodes (Fig. 1). The coated solution films were dried at ambient for 10–38 h. They are called DCSF.

The reactor is a single-compartment cylindrical electrochemical type (Fig. 1). The initial electrochemical medium is distilled water which was added between two cylindrical electrodes. The electrode cylinders are metallic materials which cannot take part in the electrochemical reactions in the system.

The electrochemical reactions were started at the designated temperature:  $30\text{--}45^\circ\text{C}$ . The reaction time, voltage, and current were set according to the formation condition of the desired morphological structure of the GCF. After reaction, the films were stripped from the cathode carefully and then rinsed with water and dried at  $75\text{--}85^\circ\text{C}$  for 8–16 h. The final films are defined as polymer–metal gradient composite films (GCF).

### Measurements

The morphological structure of the GCF was measured by a scanning electronic microscope: a Cam-



**Figure 1** Electrochemical reactor: (1) electrochemical reactor; (2) anode; (3) cathode; (4) current meter; (5) DCSF; (6) medium; (7) interface between DCSF and medium.

bridge Instrument S250MK IV. The GCF used in the test was broken into thin and long pieces, adhered to the sample frame, and coated with gold.

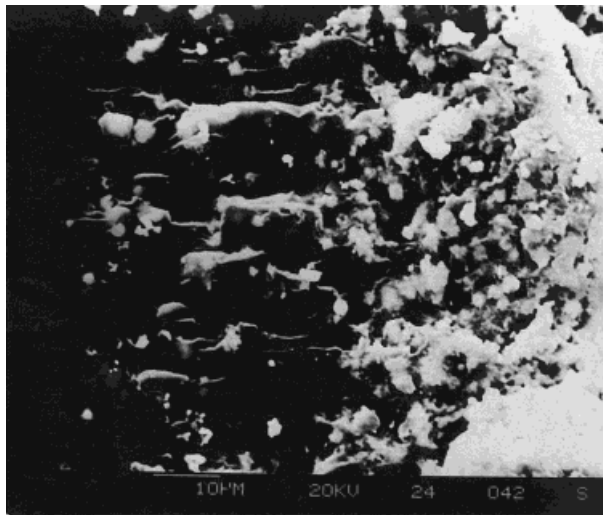
The deposited metal, copper, in the GCF was measured by a wide-angle X-ray spectrometer, D/max-rB (Japan), and the samples were used after they were dried at  $85^\circ\text{C}$  for 16 h.

The Fourier transform infrared (FTIR) spectrometer used in measuring the components of electrolyzed and unelectrolyzed PAN film was a Nicolet 750 (USA). The unelectrolyzed PAN film was prepared by casting a DMF solution of PAN, and the electrolyzed film, by electrolyzing the dried unelectrolyzed PAN film under the same electrochemical conditions as those used in preparing the GCF. All samples were dried at  $85^\circ\text{C}$  for 16 h before being cut into thin pieces for KBr pellets. The thermal properties of the GCF were measured by a differential scanning calorimeter, a Perkin–Elmer 7 Series thermal analysis system (USA).

## RESULTS AND DISCUSSION

### Relationship Between Morphological Structure of GCF and Electrochemical Reaction Conditions

As in a previous report,<sup>5</sup> the morphological structure of the PAN–copper composite films is a com-



**Figure 2** Morphological structure of GCF obtained by SEM. Conditions: predrying time of DCSF, 38 h; power voltage, 20V; temperature in reactor, 30°C.

posite cross section: a metal-deposited layer, transition layer, and undeposited layer. This conclusion is further confirmed in Figure 2, although the synthesis conditions were changed, and which shows that the GCF including metal and a polymer matrix can be obtained by electrochemical means.

The morphological structure of the deposited-metal layer and the transition layer depends very much on the electrochemical conditions, such as the predrying time of the DCSF, power voltage, and temperature in the reactor bath. Under these electrochemical conditions, a series of related processes will occur as follows: (1) Copper ion(II) must penetrate through the DCSF to the cathode, receive the electron, and then become  $\text{Cu}^0$ ; (2) the penetrating rate of copper ion(II) in the DCSF is controlled by the bulk viscosity of the DCSF; (3) the bulk viscosity of the DCSF is determined by the bulk temperature of the DCSF and the degree of phase separation between the solvent and the PAN copolymer; (4) the higher temperature gives a lower viscosity DCSF but causes faster phase separation; and (5) the phase separation further enhances the viscosity of the DCSF. Obviously, the electrochemical conditions affect the processes above and thus determine the morphological structure of the deposited phase in the GCF. In the following discussion, this relationship between the electrochemical conditions and morphological structure is represented by the percent area of the deposited phase including the depos-

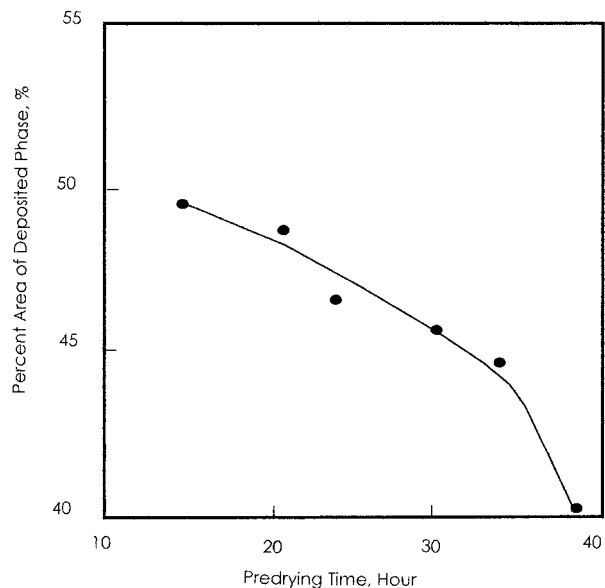
ited layer and the transition layer in the cross section of the GCF.

#### *Effect of Predrying Time of DCSF on Morphology of GCF*

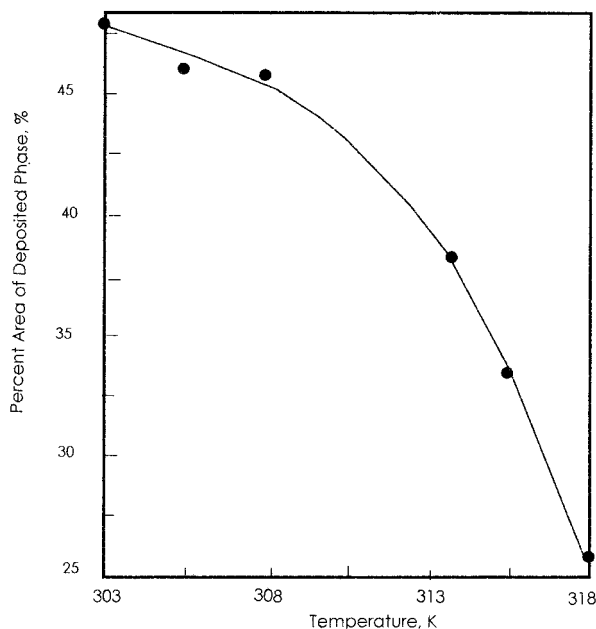
The result of the morphological changes of the GCF with predrying time of the DCSF is shown in Figure 3. It is seen that, with increase of the predrying time of the DCSF, the percent area of the deposited phase decreases. This shows that the longer predrying time can result in a lower deposited phase. The reason is that a longer predrying time causes a higher viscosity in the DCSF and impedes copper(II) penetration. Obviously, a shorter predrying time should be used to obtain a higher yield of the deposited phase, but too short of a predrying time may let copper ion(II) disperse into the medium and thus the loss of the ion. The optimized predrying time should not be shorter than 10 h at ambient temperature.

#### *Effect of Temperature in the Reactor on Morphological Structure of GCF*

The change of the morphological structure of the GCF with the reactor temperature is shown in Figure 4. The percent area of the deposited phase is shown to decrease with increase of the reactor temperature. It is natural that higher tempera-



**Figure 3** Effect of predrying time of DCSF on morphological structure. Conditions: power voltage, 20 V; temperature in reactor, 30°C.



**Figure 4** Effect of temperature in the reactor on morphological structure of GCF. Conditions: predrying time of DCSF, 24 h; power voltage, 20 V.

ture causes faster phase separation and thus higher viscosity.

#### **Effect of Power Voltage on Morphological Structure of GCF**

Figure 5 shows the decrease of percent area of the deposited phase with increase of the power voltage. This result is contrary to the principles of electrochemistry<sup>7</sup> in that higher power voltage should initiate a faster dispersion rate of ions in the DCSF and give a higher quantity of the deposited metal. This is because, in this experiment, the increased penetrating rate of the ion caused increase of the temperature in the DCSF. Once it occurs, the phase separation of the polymer from the solvent should increase, getting the same temperature effect result.

#### **Morphological Mechanism of GCF Corresponding to Voltage and Current in the Electrochemical Reaction**

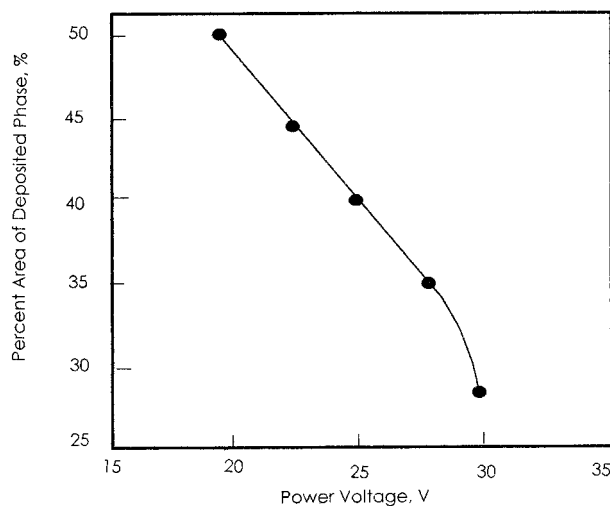
In this electrochemical system (Fig. 1), the electrochemical reaction is different from the common solution reaction. The voltage drop between two electrodes results from the DCSF and the medium used in these experiments. The DCSF and the medium are like two linking resistances, but their resistance values are changeable with the reac-

tion process. The morphology is determined by the voltage drop on the DCSF.

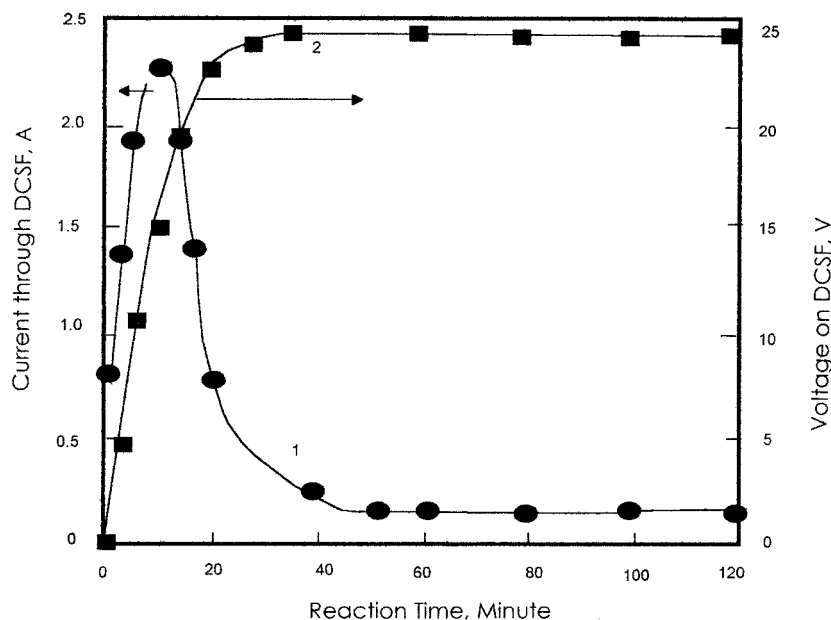
The change in the voltage drop on the DCSF and the current through it are shown in Figure 6. The current through the DCSF [Fig. 6(1)] shows a maximum at 10 min and becomes a constant after 40 min. Comparing the change of current with that of the voltage, the voltage drop on the DCSF with the electrochemical time [Fig. 6(2)] shows a decrease of the slope of this curve from 10 min and a constant of the voltage drop after 40 min. These voltage drop changes on the DCSF and current, however, can be explicated by the principle of how ion disperses. Ion penetrations were accelerated under the electric field in the period from 0 to 10 min and reached the most active state. The data in Figure 6 also confirm that active reduction of copper ion(II) should occur in 40 min. Corresponding to Figure 2, this period should be the major one for the formation of the morphological structure of the GCF. After 40 min, the ion penetrations become slower because the intrapotential produced in the DCSF decreases the effective voltage on the DCSF.

#### **Components in Metal-Deposited Phase of GCF**

The copper components in the metal-deposited phase of the GCF were confirmed by X-ray diffraction (Fig. 7). It is clear that the GCF show strong diffraction peaks of copper crystals at  $2\theta = 43.24$  and  $2\theta = 50.36$ , which correspond to diffractions of 2.09 and 1.81 Å lateral repeat distances.<sup>8</sup> This



**Figure 5** Effect of power voltage on morphological structure. Conditions: predrying time of DCSF, 24 h, temperature in reactor, 30°C.



**Figure 6** Change of current through DCSF and voltage on DCSF with reaction time. Conditions: predrying time of DCSF, 24 h; power voltage, 20 V; temperature in reactor, 30°C.

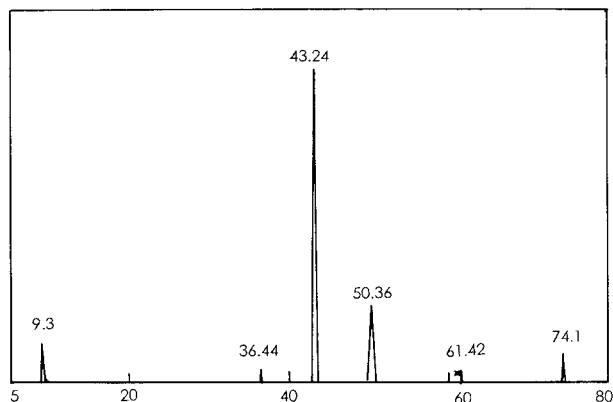
confirms that this electrochemical process can provide copper(0) crystal and accords with the observation that a brown copper color is seen on the side surface and the cross section of the GCF. From the consideration of the dimension of the molecular conformation of PAN and the scale of copper crystal cells in the deposited phase, the diameter of the molecular chain spiral rod of PAN is 0.6 nm,<sup>9</sup> while the lateral repeat distance of the copper crystals is about 0.2 nm. Thus, the formation of copper crystal cells among PAN molecules should be possible. But small peaks at

$2\theta = 9.3, 36.44, 61.42,$  and  $74.1$  show that there is a small amount of  $\text{Cu}^{1+}$  and  $\text{Cu}^{2+}$  remaining in the GCF.

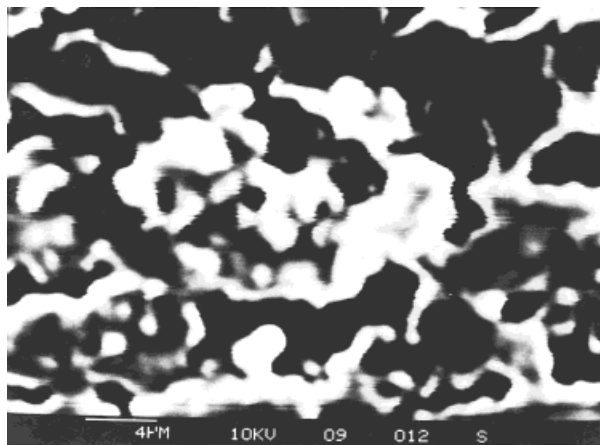
#### Congregating Structure Between Copper and PAN in Deposited Phase of GCF

The morphological structure of the deposited phase on the side surface of the GCF was observed by SEM and the result is shown in Figure 8. A linked bright spot network is clearly seen. Since the deposited phase has a lower thermal contraction than that of the PAN copolymer matrix in the drying process, the bright spot network must be the deposited metal in the electrochemical reaction. This gives the conclusion that a network of deposited metal is formed in the electrochemical reaction process in the copper-deposited layer, and the conductivity of the GCF is imparted by the network.

The DSC curves of the PAN copolymer film and the GCF showed, on the other hand, that there are some differences (Fig. 9). First, in comparing curve 1 for the PAN copolymer with curve 2 for the GCF, the glass transition temperature decreases from 120 to 77°C. The decrease of the glass transition temperature is possibly due to the higher thermal conduction of the copper network than that of the pure PAN copolymer which activates



**Figure 7** Diffraction result of GCF by WAXD. Conditions: predrying time of DCSF, 24 h; power voltage, 20 V; temperature in reactor, 30°C.



**Figure 8** Morphology of deposited phase on the side surface of GCF obtained by SEM. Conditions: predrying time of DCSF, 24 h; power voltage, 20 V; temperature in reactor, 30°C.

some macromolecular segment movement at a lower temperature. Second, in curve 2, there is a strong thermal absorption peak at 111°C after the glass transition temperature of 77°C and its onset temperature is very close to the glass transition temperature in curve 1. It should be the movement of the PAN chain segments.<sup>9</sup> Because the peak shape is not the “S” of the glass transition but “an inverse bell,” the suggestion can be made that the segment movement at 111°C must be impeded.<sup>9</sup> In the GCF, the impedance should be due to the physical crosslinking of the crystallization of the deposited phase which corresponds to the network of copper in Figure 8. Combining the results of Figures 8 and 9, it is evident that PAN molecules either are involved in the deposited phase in the reduction process of copper(II) or that the deposited phase in the GCF is penetrated by the PAN molecules.

#### Effect of Composite Between PAN Copolymer and Copper on Thermal Properties of PAN Matrix

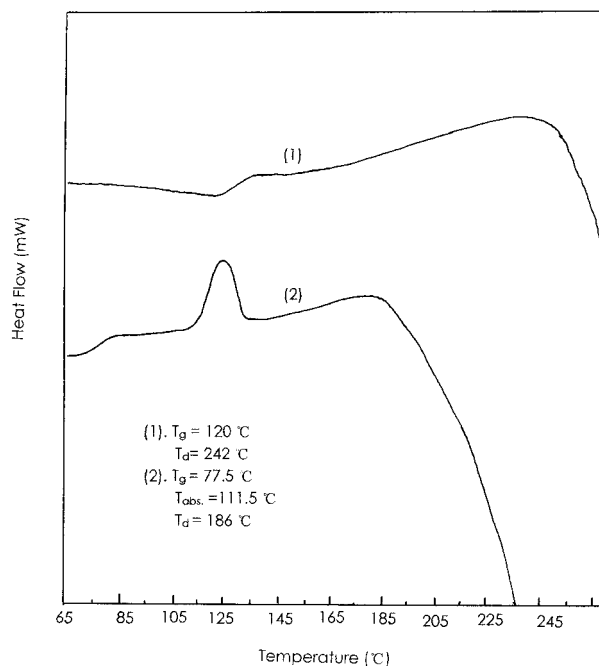
In comparing curve 1 with curve 2 in Figure 9, there are two major differences: (1) The glass transition temperature of PAN in the GCF was decreased to 77°C from 120°C. Its cause was considered in the above section; and (2) the thermal degradation temperature of PAN is decreased to 182°C from 242°C. Concerning the decrease of the thermal degradation temperature of the PAN copolymer, the process of degradation of the PAN copolymer may be catalyzed by the remaining copper(II).<sup>10</sup>

#### Effect of Electrochemical Process on Chemical Components of PAN

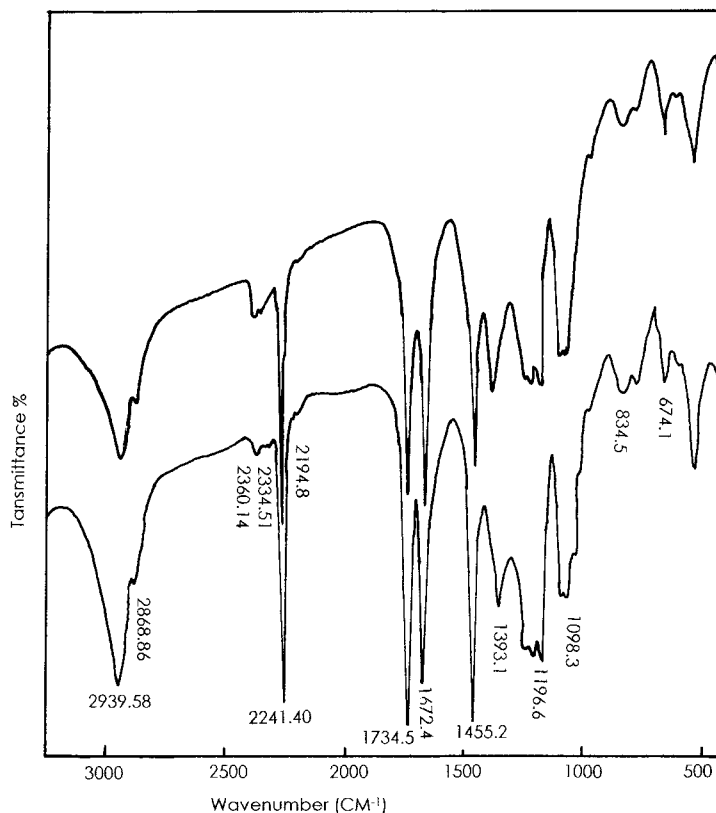
Figure 10 shows the results of the FTIR on the PAN film (curve 1) and the electrolyzed PAN film (curve 2) under the electrochemical conditions used for preparing the GCF. In comparing 1 with 2, the peaks of all the major groups<sup>11</sup> do not change. We conclude that the components of the PAN copolymer are not affected by the electrochemical conditions.

#### CONCLUSIONS

Polyacrylonitrile–copper gradient composite films (GCF) can be obtained under proper electrochemical conditions. The morphological structures of the GCF are comprehensively affected by the electrochemical conditions in the system. The principles of changes of a voltage drop on the DCSF and the current through them confirm that the morphology of the GCF is mainly formed in the initial period of the electrochemical reaction. In the deposited phase of the GCF, macromolecules interpenetrate with copper crystals, and because of the penetrations between the PAN chain and



**Figure 9** DSC curves of (1) PAN film and (2) GCF. Conditions: PAN film: the unelectrolyzed one; GCF: predrying time of DCSF, 24 h; power voltage, 20 V; temperature in reactor, 30°C.



**Figure 10** Components of electrolyzed PAN copolymer film and unelectrolyzed film by FTIR. Electrochemical conditions for electrolyzed PAN copolymer film: power voltage, 30 V; temperature in reactor, 45°C; electrolyzing time, 3 h.

the copper crystals, the thermal movement of the PAN chain segments is impeded and, thus, a strong thermal absorption peak is observed. The glass transition temperature and degradation temperature of PAN decrease due to the presence of a deposited phase and copper(II) remaining in the GCF. Under the electrochemical conditions used in these experiments, the chemical components of PAN cannot be changed.

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