The Preparation and Electrical Conductivity of Polyacrylamide/Graphite Conducting Hydrogel

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ABSTRACT: Polyacrylamide/graphite superabsorbent composite was synthesized by free radical polymerization of acrylamide monomer using N, N'-methylene-bis-acrylamide as crosslinker, potassium persulfate as initiator, and graphite as functional filler. On the basis of the superabsorbent composite, a hydrogel with a conductivity of 0.86 mS cm^{-1} was obtained. The preparation conditions were optimized. The influence of crosslinker, initiator, monomer, graphite, water absorbency, and temperature on the conductivity of the hydrogel was investigated, an adsorbed network structure model for polyacrylamide/graphite conducting hydrogel was purposed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1490–1495, 2008

Key words: adsorption; conducting polymer; hydrogels; hydrophilic polymers; polyacrylamide; graphite

INTRODUCTION

Superabsorbent polymer has a network structure with a suitable crosslinking degree. It is not only able to absorb hundred to thousand times its own mass of water to form a stable hydrogel, but also the absorbed water is hardly removed under some pressure. Because of good solloid stability, superabsorbent polymer is potentially used in fuel cells, supercapacitors, dye sensitive solar cells, and rechargeable lithium batteries.[1–4]

On the basis of the superabsorbent hydrogel, a protonic hydrogel from polyacrylamide and strong inorganic salt was reported by Wieczorek et al.[5] Recently, a hydrogel composite with semi-interpenetrating networks made of a polyelectrolyte and polyaniline nanoparticles was also reported by Dispenza and Siddhantaa.[6,7] Here, a superabsorbent hydrogel consisting of polyacrylamide and graphite was prepared. Graphite is a conducting material, the conductivity of graphite comes from the electron mobility on delocalized π orbital, which is different from the conductivity of inorganic salts and polyaniline

nanoparticles hydrogels due to ionic mobility.[6] Combining the conducting property of graphite and the colloid stability of superabsorbent polymer, such as polyacrylamide to form a conducting hydrogel is significant for developing new conducting materials. Polyacrylamide/graphite superabsorbent composite was synthesized by free radical polymerization reaction. The influence of preparation conditions on the conductivity of hydrogel and an adsorbed network structure model for polyacrylamide/graphite conducting hydrogel is discussed in this article.

EXPERIMENTAL

Materials

Acrylamide monomer (analytical grade, 99.5%) supplied by Shanghai Chemical Factory, Shanghai, China was used as received. Graphite micropowder having a specific surface area larger than 80 m^2 g^{-1} and an average particle size smaller than 1.6×10^{-6} m was commercially purchased from Shanghai Colloid Chemical Industry, China, and was dried at 105°C for 4 h before use. N, N'-(Dimethylene)acrylamide as a crosslinker was obtained from Shanghai Chemical Reagent, China. Radical initiator potassium persulfate was supplied by Xilong Chemicals, China, and purified by recrystallization from 66 wt % ethanol/water solution before using.

Preparation of polyacrylamide/graphite superabsorbent composite

A predetermined amount of acrylamide monomer and graphite micropowder was dissolved and
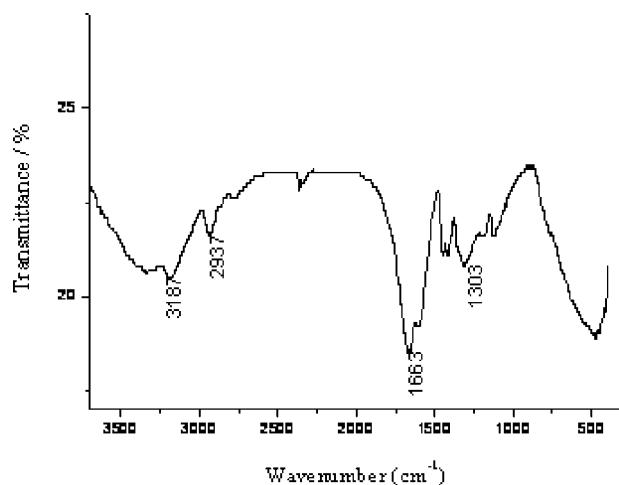
Figure 1 FT-IR spectrum of superabsorbent composite (10 wt % graphite, 0.08 wt % crosslinker, 0.9 wt % initiator, 50 wt % monomer concentration, and at 80°C).

dispersed in distilled water thoroughly to form a mixed solution. A given amount of crosslinker N, N'-(dimethylene)acrylamide was dissolved in the monomer/graphite mixed solution. Then the system was degassed under vacuum for about 30 min. Radical initiator potassium persulfate was added to the solution consisting of monomer, graphite, and crosslinker. Under a nitrogen atmosphere, a polymerization reaction took place under stirring and heating at 80°C in a water bath for 20 min. After completion of the polymerization reaction, the resultant mixture was immersed in excess distilled water and then filtered through Whatman filter paper No. 54 to remove any impurities. The product, a typically black jell, was dried under vacuum at 80°C for more than 3 h to constant weight, and ground and screened using a 40-mesh screen. Thus a powdered polyacrylamide/graphite superabsorbent composite was obtained.

The swelling of polyacrylamide/graphite composite in distilled water

The powdered composite of 3 g was immersed in distilled water of 500 mL at room temperature for at least 3 h to reach swelling equilibrium [water absorbency about 160 water (g)/sample (g)], which resulted in the absorption of water into the network of the composite and the formation of a swollen (conducting) hydrogel. The unadsorbed water was removed by filtration over a 40-mesh stainless steel screen and hanging up for 25 min.

Measurement of conductivity and water absorbency

The conductivity of hydrogel was measured by inserting a Pocket Conductivity Meter (HANNA8733)

into a cylinder containing swollen hydrogel of 30 g. The water absorbency (Q_{H_2O}) of the superabsorbent composite was determined by weighing the swollen and dried sample according to Eq. (1).[8]

$$Q_{H_2O} = \frac{M(\text{swollen sample}) - M(\text{dry sample})}{M(\text{dry sample})} \quad (1)$$

FTIR spectrum of the superabsorbent composite in KBr was recorded using a Nicolet Impact 410 spectrometer. In Figure 1, the absorption peak at 3187 cm^{-1} is for the N—H bending, 2937 cm^{-1} is for the —CH$_2$— stretching, 1663 cm^{-1} is for the C=O bending, 1303 cm^{-1} is for the C—H bending, respectively. The C=C double bond stretching vibration for acrylamide monomer at 1613 cm^{-1} disappeared. The results indicate the formation of polyacrylamide in the superabsorbent composite.

RESULTS AND DISCUSSION

Influence of crosslinker concentration on the conductivity of hydrogel

As shown in Figure 2, the conductivity of hydrogel increases with the increase in the amount of crosslinker from 0 to 0.04 wt %. Beyond a crosslinker amount of 0.04 wt %, the conductivity of hydrogel decreases.

The conductivity of hydrogel depends on the size of polymeric space network.[9,10] Clearly, a lower concentration of crosslinker does not produce enough crosslink points to construct a polymeric three-dimensional network to absorb graphite particles. Especially, when the crosslinker concentration is smaller, the polymeric network does not form effectively. As a consequence, the graphite micropowders
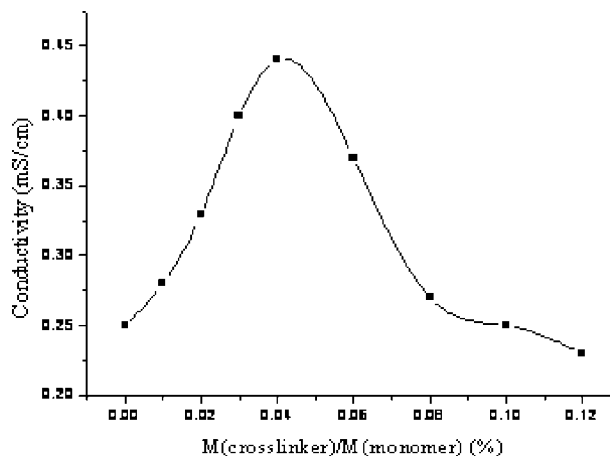

Figure 2 The conductivity of hydrogel versus the crosslinker amount in the composite (10 wt % graphite, 1.0 wt % initiator, 50 wt % monomer concentration. and at 80°C).
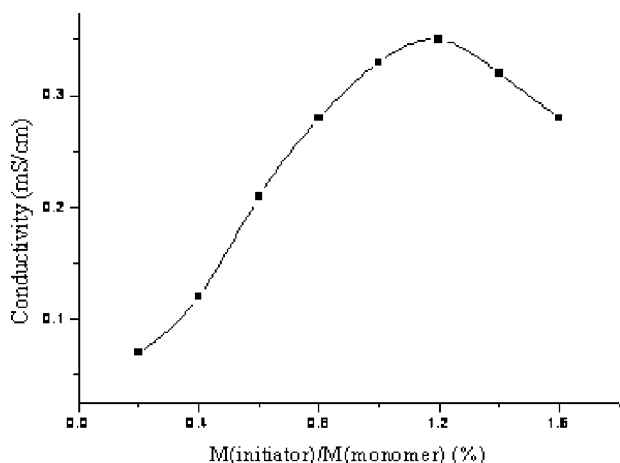
Figure 3 The conductivity of hydrogel versus the initiator amount in the composite (10 wt % graphite, 0.04 wt % crosslinker, 50 wt % monomer concentration, and at 80°C).

are dispersed in solution and washed out in the preparation process of superabsorbent composite. On the other hand, higher crosslinker concentration produces the tighter crosslinking density and the smaller network space of polymer, which is not enough to hold graphite particles. The connection between graphite particles weakens, and the conductivity of hydrogel declines.
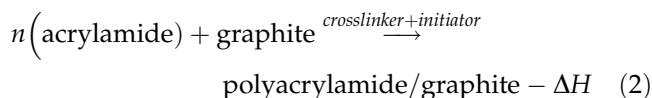
Influence of initiator concentration on the conductivity of hydrogel

From Figure 3, it can be seen that the conductivity of hydrogel increases with the increase of the initiator amount from 0.3 to 1.2 wt %, but decreases when the initiator amount changes from 1.2 to 1.6 wt %. The reason is that when the initiator concentration is lower, the polymerization reaction takes place slowly, produces a polymer network with fewer and larger space volume, which is not enough to hold graphite particles. On the contrary, higher initiator concentration produces a polymer network with more and smaller space size, which also decrease graphite content in the polymer network. Under above two cases, the hydrogel can not contain enough graphite particles to form conducting channels, therefore, the conductivity of hydrogel declines. In our experiment conditions, the initiator amount of 1.2 wt % is better.

Influence of monomer concentration on the conductivity of hydrogel

The concentration of acrylamide monomer is another factor affecting the conductivity of hydrogel. Figure 4 shows that the conductivity of hydrogel increases in the range of 35–46 wt % monomer concentration, and declines in the concentration of 46–60 wt %. The

behavior can be explained according to the polymerization reaction shown as follows:

$$n\left(\text{acrylamide}\right) + \text{graphite} \xrightarrow{crosslinker+initiator}$$

$$\text{polyacrylamide/graphite} - \Delta H \quad (2)$$

The polymerization of acrylamide monomer is an exothermic reaction (enthalpy decrease, $-\Delta H$). According to the rate law, under a higher concentration of acrylamide monomer, the reaction takes place faster, which causes the uneven dispersion of the network of polymer and graphite particles, and the connections between graphite particles are interdicted. Thus lower conductivity occurs. On the other hand, under a lower concentration of acrylamide monomer, the reaction becomes slower, and can not polymerize effectively, the monomer exists in small molecule or oligomer instead of polymer, a three-dimensional polymer network can not be formed effectively, and graphite particle can not be held in the polymer network, which leads to the lower conductivity. In our experimental conditions with a monomer concentration of 46 wt %, the reaction can take place effectively and evenly, the hydrogel possesses the highest conductivity.

Influence of reaction temperature on the conductivity of hydrogel

As shown in Figure 5, the conductivity of hydrogel increases with the increase of reaction temperature from 60 to 80°C in the preparation process of the composite, but declines in the range of 80 to 90°C.

As we know that the polymerization reaction takes place slowly under lower temperature, and does not
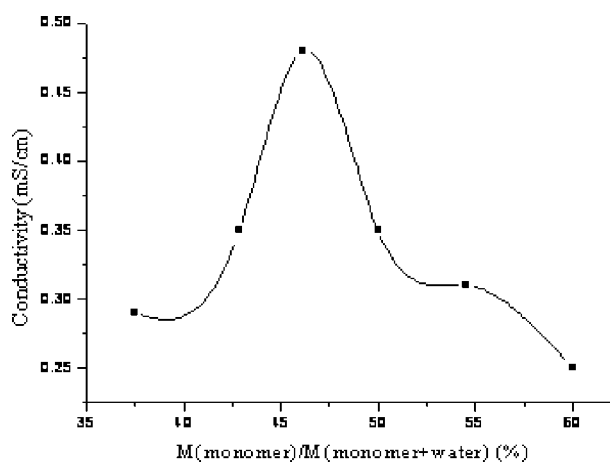

Figure 4 The conductivity of hydrogel versus the monomer concentration in the composite (10 wt % graphite, 1.2 wt % initiator, 0.04 wt % crosslinker, monomer concentration 46 wt %, and at 80°C).
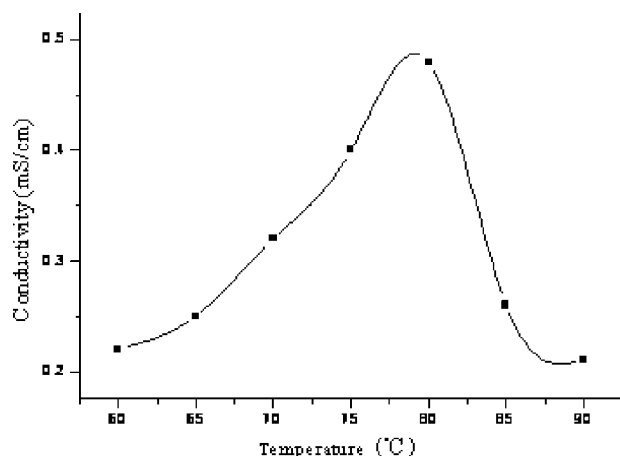
Figure 5 The conductivity of hydrogel versus the reaction temperature in the preparation of the composite (10 wt % graphite, 0.04 wt % crosslinker, 1.2 wt % initiator, and 46 wt % monomer concentration).

occur at the temperature below 60°C, the polymer network to hold graphite particles does not form effectively, the conductivity of hydrogel declines. When the reaction temperature is beyond 60°C, the reaction rate increases with the increase in temperature, but the molecular weight decreases. In case of crosslinked polymer, the molecular weight between crosslinking points (Mc) decreases. This decrease in Mc leads to an increase in the amount of graphite retained in the composite, and consequently the conductivity increases with the increase in temperature up to 80°C. However, the polymerization is an exothermic reaction [shown in Eq. (2)], a higher temperature is unfavorable for the reaction taking place to the right. The acrylamide and graphite disperse in the solution in the state of monomer, oligomer, or micropowder, instead of composite. The connection
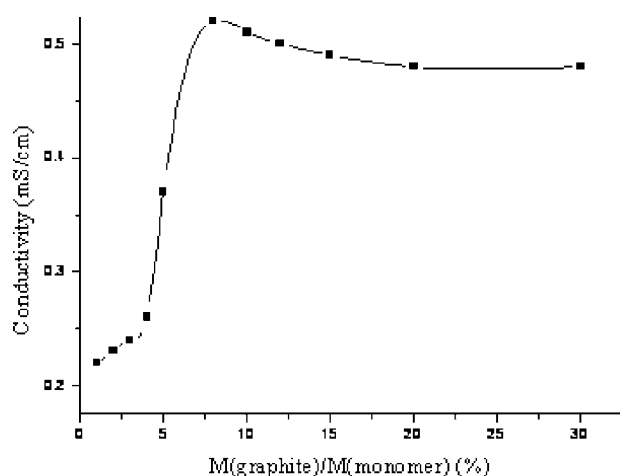
between graphite particles is fewer, which leads to the decline of the conductivity of hydrogel.

Influence of graphite amount on the conductivity of hydrogel

From Figure 6, it can be seen that the conductivity of hydrogel increases slowly with the increase of graphite amount in the range of 0–3 wt %, and sharp increase in the amount of 3–8 wt %. When graphite content is 8 wt % and water absorbency is 160 times, the conductivity of hydrogel reaches 0.52 mS cm^{-1}. Beyond an amount of 8 wt %, the conductivity of hydrogel decreases.

Clearly, when graphite content is lower, the connections between graphite particles are fewer, the electron transmission channels can not run through effectively, and the conductivity is lower. With the increase of graphite amount, the connections between graphite particles increase, which leads to the enhancement of the conductivity. According to experimental results shown in Figure 6, graphite content of 3 wt % is a critical value, higher than 3 wt %, a conducting network can be formed.

On the other hand, when the graphite amount exceeds 8 wt %, the graphite particles aggregate gradually, or partly disperse in solution instead of absorbing on the network of polymer, which results in the little decline of the conductivity.

Influence of water absorbency of composite on the conductivity of hydrogel

As shown in Figure 7, the conductivities of hydrogels decrease with the increase of the water absorbency of superabsorbent composite when the (Q_{H_2O}) is larger than 10 times. When the water absorbency

Figure 6 The conductivity of hydrogel versus the graphite amount in the composite (0.04 wt % crosslinker, 1.2 wt % initiator, 46 wt % monomer concentration, and at 80°C).
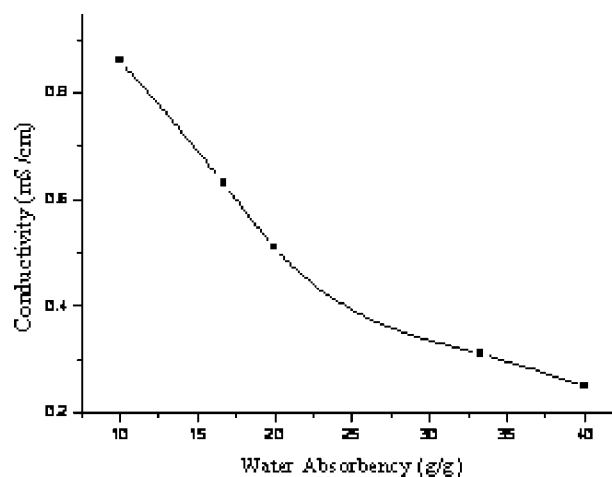

Figure 7 The conductivity of hydrogel versus the water absorbency of the composite (10 wt % graphite, 0.04 wt % crosslinker, 1.2 wt % initiator, 46 wt % monomer concentration, and at 80°C).
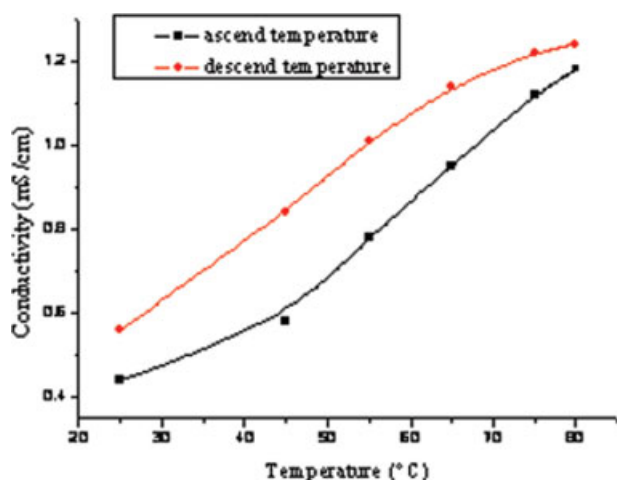
Figure 8 Influence of measurement temperature on the conductivity of hydrogel (10 wt % graphite, 0.12 wt % initiator, 0.04 wt % crosslinker, 46 wt % monomer concentration, and at 80°C). *The conductivity of sample was measured after keeping it at the determined temperature for 5 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

is 10 times, the conductivity of hydrogel reaches 0.86 mS cm^{-1}. It is believed that the conductivity of the hydrogel is based on the connections between graphite particles. With the increase of the water absorbency, more solvent enters the network of polymer, and the connections between graphite particles are diluted, which leads to the interdiction of electron transmission channels and the decline of the conductivity of hydrogel.

Influence of temperature on the conductivity of hydrogel

Figure 8 shows that the conductivity of hydrogel increases with the increase of temperature. Obvi-
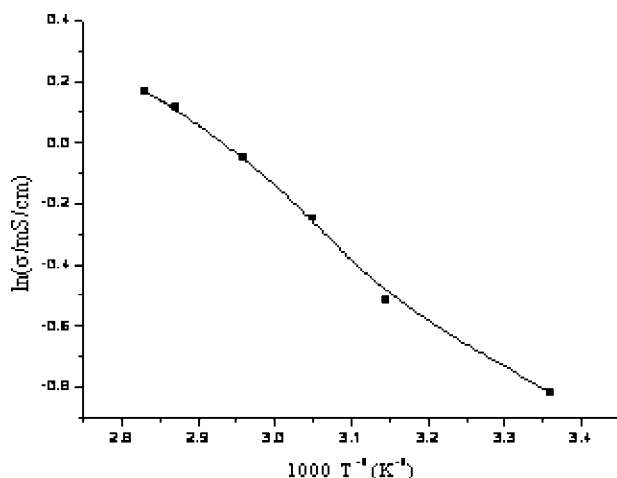
ously, this is due to the fact that the electrons move faster under higher temperature than under lower temperature.

It is noticeable that the composite has different conductivities at ascend-temperature curve and descend-temperature curve, and the conductivity on descend-temperature curve is higher than that on ascend-temperature curve at the same temperature. On the basis of the fact that the conductivity of sample was measured after keeping it at the determined temperature for 5 min, the conductivity–temperature behavior of the hydrogel can be interpreted that the structure and conductivity of the hydrogel have temperature-hysteresis effect. Once the time for keeping temperature to measure the conductivity of sample is prolonged, the ascend-temperature curve and descend-temperature curve will tend to superposition.

The conductivity–temperature behavior of the conducting hydrogel can be described by Arrhenius equation.

$$\sigma(T) = A \exp\left[\frac{-E_a}{RT}\right] \tag{3}$$

where E_a is the activation energy, R is the molar gas constant, A is a constant, and T is absolute temperature. From Figure 9, $\ln\sigma - 1/T$ shows linearity relationship. The E_a is calculated as 233.34 J mol^{-1} and the A is 290.03.

Adsorbed network structure model

According to above discussion, an adsorbed network structure model of polyacrylamide/graphite conducting hydrogel is proposed, which is shown in Figure 10. It is known that a polyacrylamide network is formed during polymerization reaction. Since there are active groups on graphite (—OH) and polymer (—CONH$_2$), the graphite particles can

Figure 9 Influence of temperature on the conductivity of hydrogel (10 wt % graphite, 0.12 wt % initiator, 0.04 wt % crosslinker, 46 wt % monomer concentration, and at 80°C).
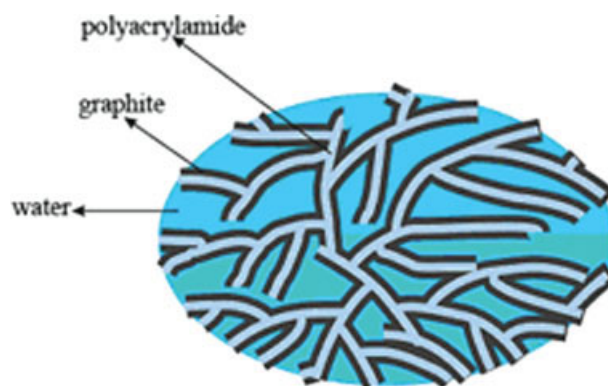

Figure 10 Adsorbed network structure model of polyacrylamide/graphite conductive hydrogel. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
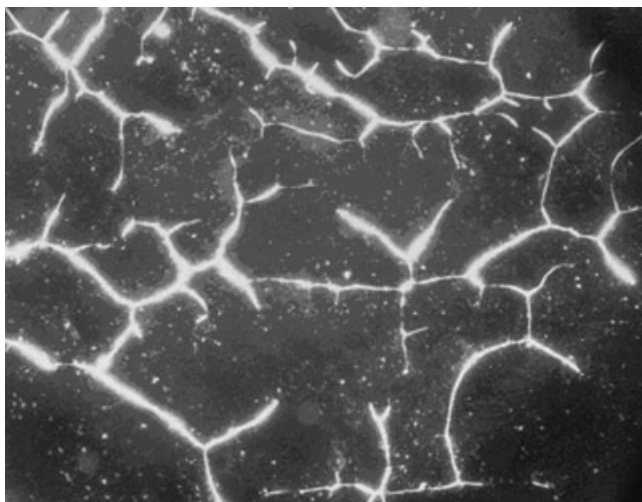
Figure 11 Polarizing microscopic photograph of polyacrylamide/sericite hydrogel.

be absorbed on the polymer network by physical or chemical combination to form another appended network due to hydrogen bondings between the —OH groups on graphite and —CONH$_2$ groups on polyacrylamide. In this case, whole system becomes a polymer network adsorbed graphite particle structure, the graphite particles can contact each other, and the conducting channel is formed. On the basis of the adsorbed network structure, the influence of crosslinker, initiator, monomer concentration, graphite amount, and water absorbency on the conductivity of hydrogel can be explained, which further proves the rationality of the structure model.

To prove the rationality of adsorbed network structure model of polyacrylamide/graphite conducting hydrogel, a polyacrylamide/sericite hydrogel was prepared under the same preparation conditions as polyacrylamide/graphite was made, and its polarizing microscopic photograph was recorded and shown in Figure 11. Because of the polarized light property of sericite particles (graphite particles do not have polarized light property), bright network structure belongs to the sericite network in Figure 11. Under the polymerization reaction conditions, polyacrylamide can form a network structure, and sericite particles can not by themselves. Therefore, the bright network structure is believed that

sericite particles are absorbed on the network of polymer to form another appended network. In this case, whole system becomes a polymer network adsorbed sericite particle structure.

CONCLUSIONS

1. A polyacrylamide/graphite superabsorbent composite was prepared by solution polymerization method. The preparation conditions were optimized as 0.04 wt % crosslinker, 1.2 wt % initiator, 8 wt % graphite, 46 wt % monomer concentrations, and a reaction temperature of 80°C. The highest conductivity of hydrogel was up to 0.86 mS cm^{-1} when the superabsorbent composite absorbed distilled water of 10 times.
2. The conductivity of hydrogel increases with the decrease of water absorbency of the superabsorbent composite, and with the increase of temperature. The structure and conductivity of hydrogel have hysteresis phenomenon to temperature.
3. On the basis of the investigation of the influence of crosslinker, initiator, monomer, graphite, water absorbency, and temperature on the conductivity of hydrogel, an adsorbed network structure model of polyacrylamide/graphite conducting hydrogel is proposed.

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