

Investigation of the Properties of Conductive Hydrogel Composite Containing Zn Particles

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ABSTRACT: In this work, the conductive hydrogel composites containing Zn particle synthesized and their electrical and thermal properties were investigated. Polyacrylamide/Zn composites were synthesized by free radical polymerization in aqueous solution. The effect of preparation conditions such as the influence of crosslinker amount, initiator amount, Zn amount, and water absorbency on electrical conductivity of hydrogel was investigated. The effect of preparation conditions on thermal properties has been characterized using thermogravimetric

analysis (TGA) method. The structures of metal-composites were evaluated by FTIR and scanning electron microscopy (SEM) methods. SEM revealed a more uniform pore size when Zn particles were used when compared with pure polyacrylamide. TGA curves showed that both hydrogels were stable up to 600°C. The Zn/polyacrylamide hydrogels have a good conductivity of 4.30 mS cm⁻¹. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: hydrogel; composite; conductivity

INTRODUCTION

Hydrogels, which are tridimensional structures formed by the cross-linking of hydrophilic polymeric chains, present their swelling degree in solution dependent on the chemical nature of the media, pH, ionic strength, and temperature.¹ Not only it is able to absorb hundreds to thousands times mass of water to form a stable hydrogel, but also the absorbed water is hardly removed under some pressure. About three decades ago, superabsorbent polymers were introduced into the agriculture and diaper industries and then their applications were extended to other industries where an excellent water holding property was prime importance.^{2–4} Hydrogels and conducting polymers are two of the most promising types of polymers being used for new material development. Both hydrogels and conducting polymers are stimuli-responsive materials whose dynamic characteristics are reasonably well understood. Hydrogels undergo phase transitions (volume changes) in response to changing environmental conditions such as temperature,^{5,6} pH,⁷ solvent composition,⁸ and electrical stimuli.⁹ Conducting polymers also undergo chemical and physical changes in response to electrical stimuli. Ion exchange capacity,¹⁰ conductivity,¹¹ optical proper-

ties,^{12–15} and another interesting applications^{16–20} all change in response to the imposition of appropriate electrical potentials.

Recently, many researchers have focused on the superabsorbent polymer for developing new applications, such as, conducting materials, sensors, release materials, biomaterials, and wave-absorbing materials.^{21–25} Conducting composites or hydrogel with good conductivity can be formed by carbon,^{26–28} conducting organic monomer,^{29–31} and incorporating metal micropowder with superabsorbent polymer. The synthesis of hydrogel composites containing metal nanoparticles has gained considerable attention, owing to their interesting optical, electrical, and catalytic properties.³² However, the research on conducting composite by adding metal powder is fewer to be seen. Recently, a hydrogel conducting composite consisting of polyacrylamide and metal micropowder was also reported by Jihuai Wu.³³ Acrylate-based hydrogel often was prepared by free radical polymerization of monomers. The most commonly used type of polymerization procedure in preparation of acrylamide hydrogels is addition polymerization (free radical polymerization) initiated by free radical initiators such as azobisisobutyronitrile (AIBN) or potassium persulfate.³⁴ In this study, we synthesize a novel superabsorbent conducting composite consisting of polyacrylamide and Zn micropowder. The influence of preparation condition such as amount of crosslinker and initiator on electrical conductivity of hydrogel and thermal properties was discussed.

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EXPERIMENTAL

Materials

Acrylamide (AA), *N,N'*-(dimethylene)acrylamide, potassium persulfate, Zn-micropowder were purchased from Merck.

Instrumental measurements

Preparation of polyacrylamide/Zn composite

Optimization of preparation conditions of crosslinker. Polyacrylamide/Zn composite synthesized through methods with similar route reported in literatures.³³ Briefly, 0.2 g of Zn powder was dispersed in 15 mL of the monomer solution (containing 2 g acrylamide dissolved in 10 mL water), and then different amounts of crosslinker (0.02, 0.04, 0.06, 0.08, 0.1, and 0.12 g) were dissolved in the monomer/Zn mixture separately. The mixed solution was then degassed under vacuum for about 30 min. Totally, 50 mg of radical initiator potassium persulfate dissolved in 10 mL water then it was added to the solution consisting of monomer, Zn, and crosslinker. Under ambient atmosphere, the reaction mixture was stirred and heated to 80°C for 30 min after completion of the polymerization reaction; the mixture was filtered then immersed in excess distilled water to remove any impurities. The product was filtrated, dried under vacuum at 80°C for 5 h, finally a powdered polyacrylate/Zn composite was obtained.

Optimization of preparation conditions of initiator. For the optimization of initiator conditions, 0.2 g of Zn powder was dispersed in 15 mL of the monomer solution (containing 2 g acrylamide dissolved in 10 mL water), and 0.08 g of crosslinker (optimum condition obtained from section Optimization of preparation conditions of initiator) dissolved in 10 mL water then it was added to the solution consisting of monomer and Zn. Solutions of different amounts of initiator (0.003, 0.006, 0.015, 0.035, 0.05, and 0.06 g) in 10 mL water was added to above solution, separately. The mixed solution was then degassed under vacuum for about 30 min. Under ambient atmosphere, the reaction mixture was stirred and heated to 80°C for 30 min after completion of the polymerization reaction; the mixture was filtered then immersed in excess distilled water to remove any impurities. The product was filtrated, dried under vacuum at 80°C for 5 h, finally a powdered polyacrylate/Zn composite was obtained.

Optimization of preparation conditions of metal content. After the optimum condition of crosslinker and initiator were obtained from sections Optimization of preparation conditions of crosslinker and Optimization of Preparation Conditions of Initiator experiments, for the optimization of metal content,

different amounts of Zn (2.5, 5, 10, 12.5, 15, and 17.5 wt %) were prepared according above conditions.

Preparation of hydrogel

Zn-composite hydrogel was prepared through methods with similar route reported in literatures.³⁵ Briefly, the powdered composite of 4 g was immersed in distilled water of 300 mL at room temperature for at least 4 h to reach swelling equilibrium; the unabsorbed water was removed by filtrating with a 40 mesh stainless steel screen and hanging up for 25 min.

Electrical studies

For the measurement of electrical conductivity, the powdered conducting composite of 3 g was immersed in distilled water of 500 mL at room temperature for at least 5 h to reach swelling equilibrium. Then the unabsorbed water was removed by filtrating over a 40-mesh stainless steel screen and hanging up for 25 min. The electrical conductivity of hydrogel was measured by inserting a Pocket Conductivity Meter (HANNA 8733) in a cylinder containing a swollen sample about 20 g.

FTIR spectra analysis

FTIR spectra of hydrogels were measured on a Shimadzu model FTIR-8101M spectrometer by pelleting the finely grounded compound with KBr.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) was performed using STA-1500, Rheometric Scientific, UK. The scan rate of TGA was 10°C/min in air atmosphere.

Morphological studies

Morphology of the hydrogels was studied using a LED 14SSVP scanning electron microanalyzer. The air dried samples were gold sputtered prior to SEM analysis, in order to enhance contrast.

RESULTS AND DISCUSSION

Structural characterization

Infrared spectrography is a useful technique in characterizing structures of materials. The FTIR spectra are used to detect the characteristic bonds of the hydrogel structures. Figure 1 shows the FTIR spectra of polyacrylamide/Zn composites. The absorption peak at 3450 cm^{-1} and 2935 attributed to N—H and —CH₂— stretching, respectively. The absorption

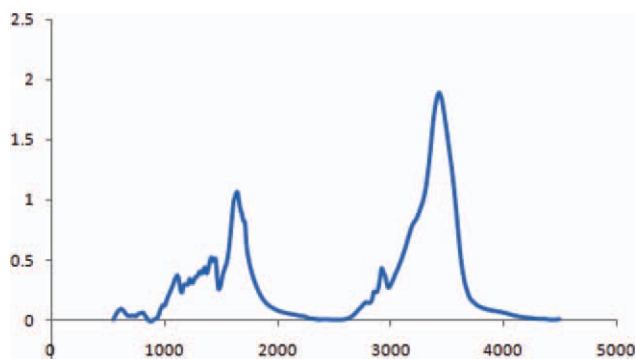


Figure 1 FTIR spectra of superabsorbent composite was obtained from optimum condition (15 wt % Zn, 0.08 g crosslinker, 0.035 g initiator). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

peak at 1658 cm^{-1} attributed to a C=O bending and 1303 cm^{-1} belonged to a C-H bending of polyacrylate, respectively. The C=C double bond stretching vibration for acrylamide monomer at 1613 cm^{-1} disappeared. The results indicated the formation of polyacrylamide in superabsorbent composite.

Influence of preparation conditions on conductivity of hydrogel

The conductivity of conducting hydrogel depends on a suitable mass ratio of crosslinker, initiator, monomer concentration, metal content. The preparation condition and structure of composite play an important role in the electrical conductivity of hydrogel. A suitable mass ratio of crosslinker to AA is important for the conductivity of hydrogel.

From Figure 2 it can be seen that the conductivity of hydrogel increase with increasing the amount of the crosslinker from 0.02 wt % to 0.08 wt %. Beyond a crosslinker amount of 0.08 wt % the conductivity of the hydrogel decrease. The electrical conductivity of hydrogel depends on the size of polymeric space

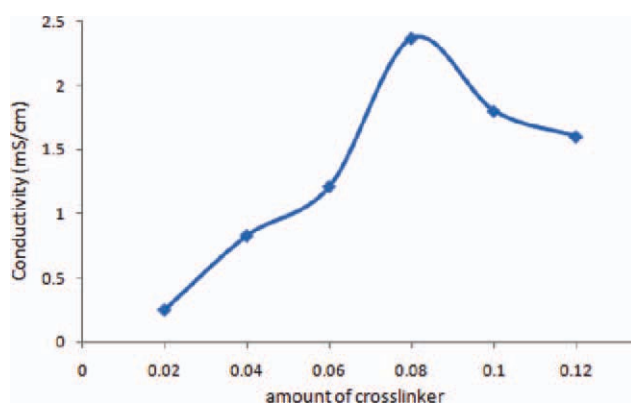


Figure 2 The conductivity of hydrogel versus the crosslinker amount in composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

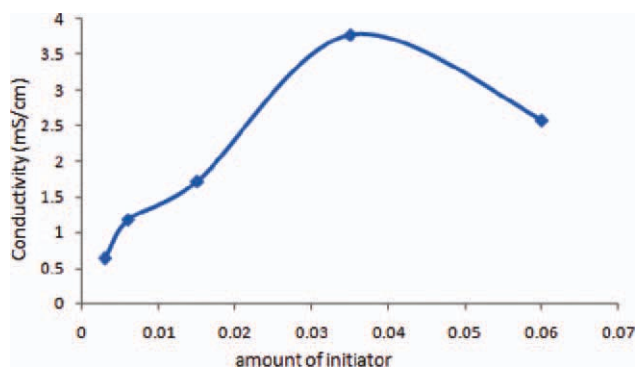


Figure 3 The conductivity of hydrogel versus the initiator amount in composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

network.³⁶ Clearly, a lower concentration of crosslinker does not produce enough crosslinker points to construct a polymeric three dimensional network to absorb Zn particles. Especially, when the crosslinker concentration is lower than 0.02 wt % the polymeric network does not form effectively. As a consequence the Zn micropowder are disposed in solution and washed out in the preparation process of superabsorbent composite. On the other hand, higher crosslinker concentrations result in the generation of more crosslink points and the smaller network space of the polymer,³⁷ which is not enough space to hold Zn particles.

The dependence of initiator on the electrical conductivity of hydrogel is similar to the crosslinker and the conductivity was more influenced by initiator concentration compared with crosslinker concentration. As shown in Figure 3, the electrical conductivity of the hydrogel increases with the increase of the amount of initiator. The optimum amount of initiator was 0.035 wt %. When the initiator concentration is low, the polymerization reaction takes place slowly. Polymeric network resulted larger space volume and in higher initiator concentration produces

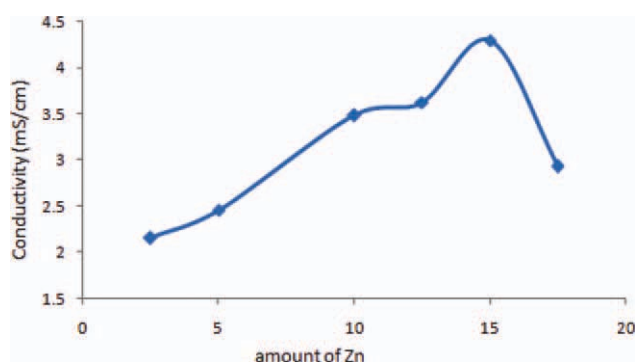


Figure 4 The conductivity of hydrogel versus the Zn amount in composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

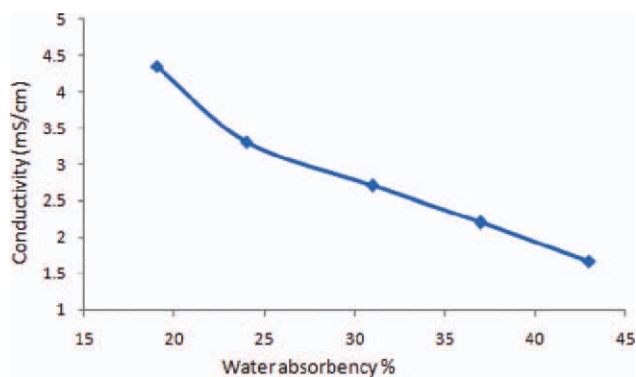


Figure 5 The conductivity of hydrogel versus the water absorbency in composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer network with smaller space size. Therefore, in the above two cases hydrogel cannot contain enough Zn particles to form conducting channels.

The influence of the Zn content on the conductivity of hydrogel is another factor affecting the conductivity of hydrogel. Figure 4 shows that the conductivity of hydrogel increases with the increase of Zn content. When Zn content is 15 wt % the conductivity of hydrogel reaches 4.35 ms cm^{-1} . Clearly when Zn content is lower, the connections between Zn particles are fewer, the electron transmission channels cannot run through effectively and conductivity is lower. On the other hand, when the Zn amount exceeds 15 wt %, the Zn particles aggregate gradually, or partly disperse in solution instead of absorbing on network of polymer, which results in a decline of electrical conductivity. The amount of Zn in hydrogels was determined by ICP. Sample containing 15 wt %, of Zn was evaluated with ICP method and the results showed that sample contains 13.5 wt % Zn which is rather low from theories value (15 wt %).

The influence of water absorbency of composite on the conductivity of hydrogel is shown in Figure 5. As shown in Figure 5, the conductivities of hydrogel decrease with the increase of the water absorbency of superabsorbent composite. The better conductivity achieve when the Q_{H_2O} (Swelling degree) is larger than 20 times. The conductivity of the hydrogel is based on the connections between Zn particles—when the water absorbency increases, the connections between Zn particles are diluted. Figure 6(a,b) shows the SEM micrographs of the PAA and Zn/PAA composites, respectively. Figure 6(b) exhibited a homogeneous surface morphology. It can be seen that the Zn particles disperse homogeneous in the hydrogel.

Influence of preparation conditions on thermal property of composite

Thermal stability of conducting hydrogel depends on a suitable mass ratio of crosslinker, initiator, monomer concentration, metal content. The preparation condition of composite plays an important role in the thermal stability of conducting hydrogel.

Figure 7(a–c) shows the thermogravimetric analysis curves of preparation condition effects on thermal stability of composite. According to the results, the degradation temperature of composite has been shifted to higher temperatures with the increasing of crosslinker amount. The end degradation temperature of composite with 0.04 wt % and 0.08 wt % from crosslinker were 600 and 614°C, respectively, but that of the composite with 0.1 wt % was 626°C. From Table I, it can be seen that the thermal stability of the conducting hydrogel increases with increasing the amount of the crosslinker.

The TGA data obtain for the initiator effect and metal content are summarized in Tables II and III.

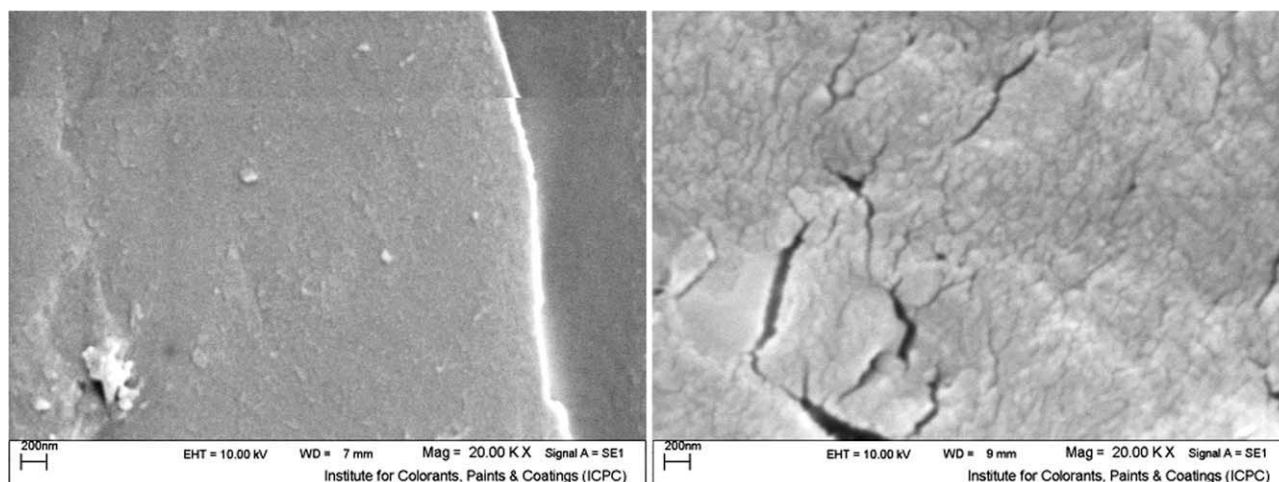


Figure 6 SEM image of (right) PAA (left) Zn/PAA composite.

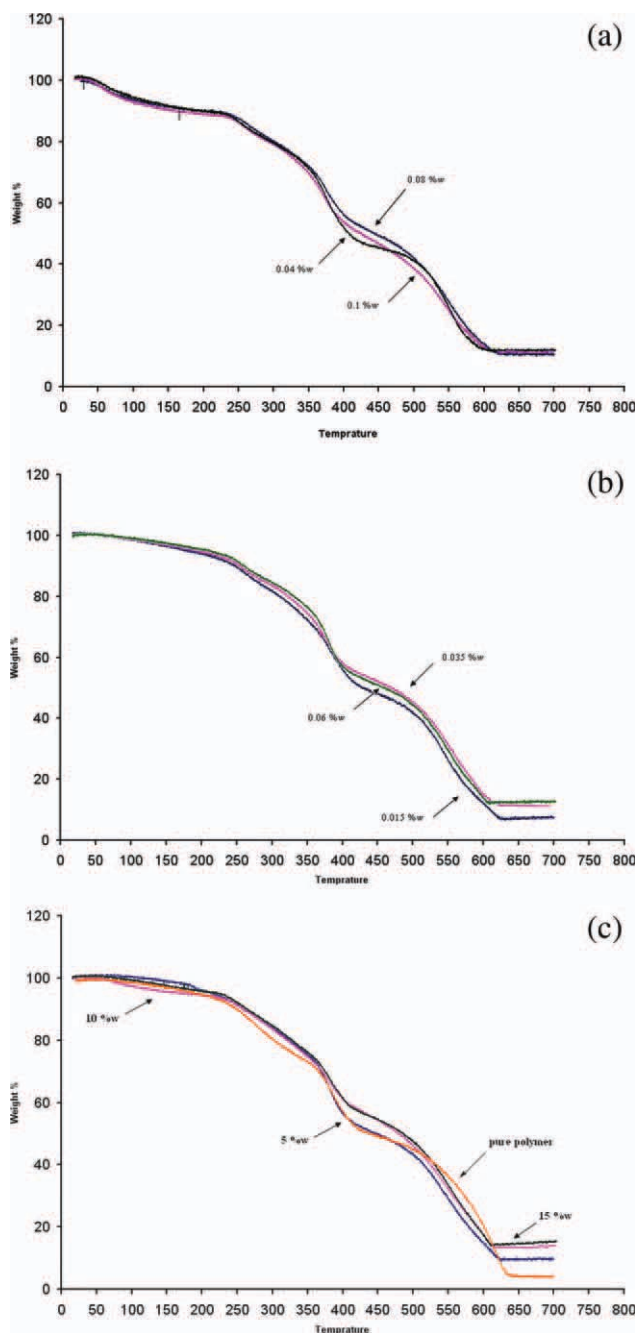


Figure 7 TGA diagrams of the effect of the (a) cross-linker amount, (b) initiator amount, (c) Zn amount. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The thermal stability of conducting hydrogel is not affected by the amount of the initiator. The end degradation temperature of composite with different amount of initiator is almost identical.

From Table III, it can be seen that the thermal stability of conducting hydrogels were influenced by metal content compared with pure polymer and increase with increasing the amount of metal content.

TABLE I
Percentage Weight of Thermal Degradation Data for Various Mass Ratio of Crosslinker in Composites (Containing 10 wt % Zn Were Prepared According to Section Optimization of Preparation Conditions of Crosslinker) Based on the TGA Results

%w crosslinker	$T_{0.15}^a$ (°C)	$T_{0.5}^b$ (°C)	End degradation temperature (°C)
(0.04 %w)	254	404	600
(0.08 %w)	257	423	614
(0.1 %w)	267	443.5	626

^a 15% degradation temperature ($T_{0.15}$).

^b 50% degradation temperature ($T_{0.5}$).

TABLE II
Percentage Weight of Thermal Degradation Data for Various Mass Ratio of Initiator in Composites (Containing 10 wt % Zn Were Prepared According to Section Optimization of Preparation Conditions of Initiator) Based on the TGA Results

%w initiator	$T_{0.15}^a$ (°C)	$T_{0.5}^b$ (°C)	End degradation temperature (°C)
(0.06 %w)	297	458	625
(0.035 %w)	288	468	615
(0.015 %w)	276	429	606

^a 15% degradation temperature ($T_{0.15}$).

^b 50% degradation temperature ($T_{0.5}$).

CONCLUSION

A conductive hydrogel composite-based polyacrylamide/Zn was prepared in aqueous solution by free radical polymerization. The preparation conditions were optimized. The effect of preparation condition on electrical and thermal properties was investigated. The highest conductivity of hydrogel was up to 4.30 mS cm^{-1} when the superabsorbent composite absorbed distilled water about 20 times.

TABLE III
Percentage Weight of Thermal Degradation Data for Various Mass Ratio of Zn in Composites (Were Prepared According to Section Optimization of Preparation Conditions of Metal Content) Based on the TGA Results

%w Zn	$T_{0.15}^a$ (°C)	$T_{0.5}^b$ (°C)	End degradation temperature (°C)
(5 %w)	292	446	609
(10 %w)	294	477	613
(15 %w)	298	483	625

^a 15% degradation temperature ($T_{0.15}$).

^b 50% degradation temperature ($T_{0.5}$).

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