Synthesis and Swelling Properties of Corn Stalk-Composite Superabsorbent

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ABSTRACT: A corn stalk-composite superabsorbent with water absorbency of 660 g/g within 30 min, was prepared by graft copolymerization with acrylic acid (AA), acrylamide (AM), sodium 4-styrenesulfonate (SSS), and corn stalk in aqueous solution after the pretreatment of corn stalks (CS), using N,N-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) and sodium bisulfite (SBS) as redox initiators. Factors influencing water absorbency and gel strength of the superabsorbent composite, such as the amount of corn stalk, the mass ratio of acrylic acid to acrylamide, the degree of neutralization for AA and the amount of crosslinker, were investigated. Morphologies and structure of the corn stalk-composite superabsorbents were characterized by FTIR, SEM and optical microscope. FTIR spectra indicate the structure of corn stalk graft-copolymer. SEM data show that the discontinuous sheet structures of corn stalks disappear and gel aggregates with many large microporous holes and small capillary pores are formed after corn stalk graft modification. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 698–703, 2013

INTRODUCTION

Superabsorbent polymers (SAPs) are lightly crosslinked networks of flexible polymer chains and can absorb a large amount of water compared with general water-absorbing materials in which the absorbed water is hardly removable even under some pressure. Because of their excellent characteristics, SAPs have been applied in many fields such as hygienic products,[1] agriculture,[2–4] waste water treatment,[5,6] and drug-delivery systems.[7,8] However, most of superabsorbents are based on fully petroleum-based polymers with high production cost and serious environment impact.[9]

Superabsorbents prepared with natural materials, such as cellulose,[10,11] starch,[9,12] chitosan,[13,14] guar gum,[15] and gelatin,[16] have attracted extensive attention due to their abundant resources, low production cost, and biodegradability. They are compatible to the natural environment and can be decomposed and used by microbiology and plants.

As by-product of corn crops, corn stalk is abundant biodegradable resource, and its main components are cellulose, hemicellulose and lignin. Up to now, most of the crops residues have been focused on burying them back to improve the fertility of the soil,

using them as the materials for paper industry and producing protein feed, alcohol and methane by microbial fermentation.[17] Wan[18] investigated effects of corn stalk amount on water absorbency and water retention properties of corn stalk-composite superabsorbent and found both water absorbency and water retention increased with corn stalk amount increasing to 10 wt %.

On the basis of our previous research on superabsorbent[19,20] and superabsorbent composite,[18,21,22] a corn stalk-composite superabsorbent was synthesized by aqueous solution copolymerization in this article. The objectives of the research are to investigate effects of corn stalk amount, crosslinker amount, neutralization degree of AA, and AA/AM mass ratio on water absorbency and gel strength, and characterize morphologies and structure of the corn stalk-composite superabsorbent by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and optical microscope.

EXPERIMENTAL

Materials

Acrylic acid (AA), analytical grade, was purified by distillation under vacuum. Acrylamide (AM), chemical grade, was purified by recrystallization. N-methylene-bis-acrylamide (MBA), analytical
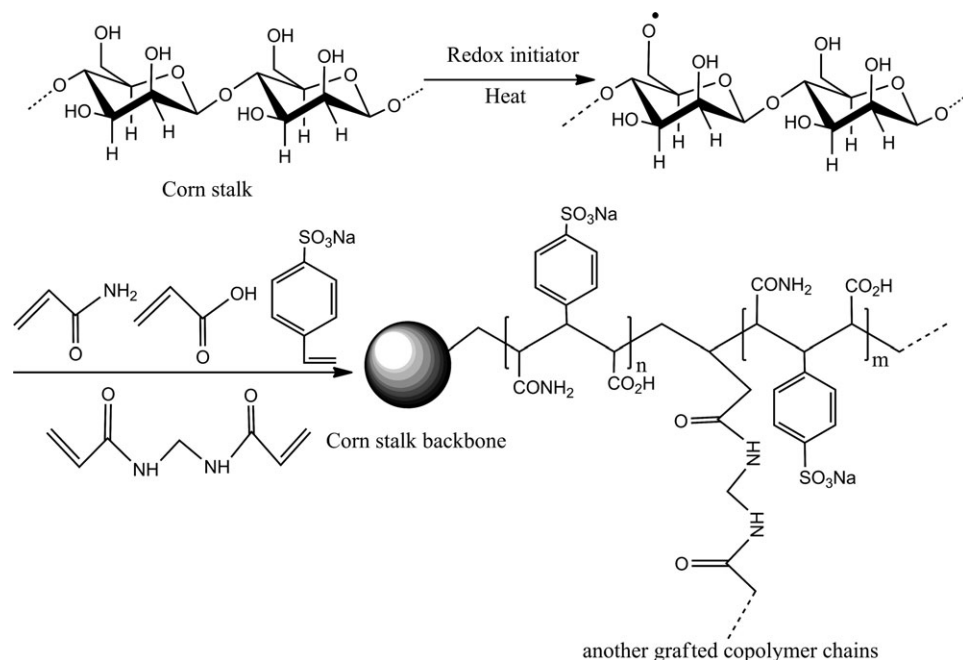
Scheme 1. Proposed mechanism for the formation of corn stalk-composite superabsorbent.

grade, was purified by recrystallization. Sodium 4-styrenesulfonate (SSS), chemical grade, was purified by recrystallization from 9:1 (v/v) mixture of methanol and water at 60°C and dried under vacuum. Ammonium persulfate (APS) and sodium bisulfite (SBS), analytical grade, were used without further purification. Corn stalk (CS) used in this study was agricultural residue of Chengdu, China. The stalks were crushed by disintegrator first and then ground to a 100 mesh particle size prior to use. All solutions were prepared with distilled water.

Preparation of Corn Stalk-Composite Superabsorbent

A series of corn stalk-composite superabsorbents with different amounts of corn stalk powder, crosslinker, and different AA/AM mass ratio were prepared by the following procedure: Typically, a weight quantity of corn stalk powder and distilled water were put in a 250-mL three-necked flask equipped with a stirrer, a condenser and a thermometer. The slurry was heated to 80–90°C for 30 min under nitrogen atmosphere. Redox initiator APS (88 mg) and SBS (28 mg) were then added when the temperature reached 55–65°C. After 30 min, 8 g of AA with 55–75% neutralization degree (neutralized with 20% sodium hydroxide solution in an ice bath), 6 g of AM, 2 g of SSS, and 48 mg of MBA were added into the flask. After reaction for 3 h at 55–65°C, the resulting product was washed several times with distilled water and ethanol and then dried at 70°C to a constant weight. The dried product was milled and screened, with a particle size of 100 mesh.

Water Absorbency Using Filtration Method

Approximately 50 mg of dried superabsorbents with a particle size of 100 mesh, were dispersed in 100 mL of deionized water for 30–60 min. Then, excess water was allowed to drain through a 300 mesh wire gauze. The weight of the superabsorbent containing absorbed water was measured after draining for 1 h,

water absorbency were calculated according to the following equation:

$$\text{Absorbency (g/g)} = (W_2 - W_1)/W_1 \tag{1}$$

where W_1 and W_2 are the weight of the dry and swollen superabsorbent, respectively.

Gel Strength Evaluation of the Corn Stalk-Composite Superabsorbent

The apparent viscosity is a relative measure of gel strength of swollen composite superabsorbent and is determined on a NXS-11B type rotation viscometer (Chengdu, China).

Characterization of the Water Superabsorbent

The micrographs of superabsorbents were taken using SEM (JSM-5600LV, JEOL). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. FTIR spectroscopy was carried out on a Perkin–Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station. The samples were prepared as KBr pellets or as liquid films interposed between KBr discs.

RESULTS AND DISCUSSION

Synthesis and FTIR Analysis of the Corn Stalk-Composite Superabsorbent

The corn stalk-composite superabsorbent was synthesized by simultaneous graft copolymerization of AA and AM onto corn stalk by using of APS and SBS as redox initiators and MBA as a crosslinker. The mechanism for crosslinking graft copolymerization is shown in Scheme 1. Redox initiators are decomposed under heating to generate sulfate anion radicals and sulfite radicals. These radicals abstract hydrogen from the hydroxyl group of the polysaccharide substrate to form alkoxy radicals on the substrate. These macroradicals initiate AA/AM grafting onto
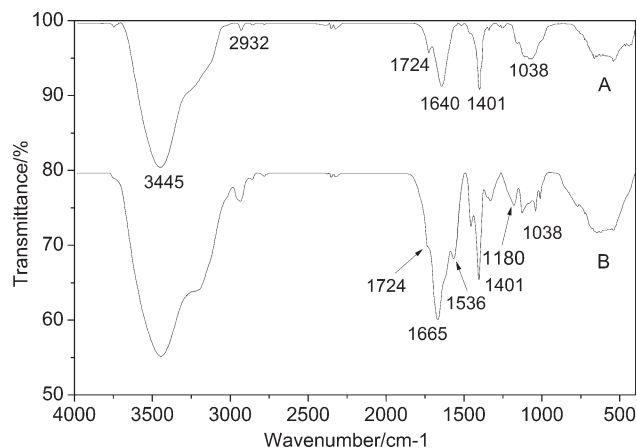
Figure 1. FTIR spectra of corn stalk (A) and corn stalk-composite superabsorbent (B) containing 10 wt % corn stalk.

corn stalk backbone and form a graft copolymer. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a crosslinked structure. FTIR spectroscopy was used to confirm the chemical structure of composite superabsorbent.

Infrared spectra of corn stalk and corn stalk-composite superabsorbent containing 10 wt % corn stalk are shown in Figure 1. The main components of corn stalk are cellulose, hemicellulose, and lignin. The raw corn stalk displays the following bands: the band at 3445 cm^{-1} is attributed to OH stretching in hydroxyl functional groups. The band at 2932 cm^{-1} is ascribed to C—H stretching absorption bands that might be present in methylene groups in cellulose. The band at 1724 cm^{-1} indicates C=O stretching from ketones and aldehydes. The bands at 1640 cm^{-1} and 1401 cm^{-1} are ascribed to the skeletal C=C stretching vibrations in the aromatic rings bands. The band at 1038 cm^{-1} is attributed to C—O stretching vibrations. In the infrared spectrum of corn stalk-composite superabsorbent, the absorption bands at 1665 cm^{-1} represents amide group stretching, and 1563 cm^{-1} is ascribed to asymmetric –COO- stretching; the band at 1180 cm^{-1} is attributed to the S=O stretching; the band at 1038 cm^{-1} (C—O stretching vibrations) and the band at1401 cm^{-1} (the skeletal C=C stretching vibrations in the aromatic rings) indicate the existence of corn stalk in composite. Therefore, the resulting product is a composite based on poly (AA/AM/SSS) incorporating with corn stalk.

Effects of Corn Stalk Amount on the Water Absorbency and Gel Strength of the Composite Superabsorbent

Corn stalk (CS) amount has great influence on the water absorbency and gel strength of the composite superabsorbent.[18] As shown in Figure 2, the water absorbency and gel strength of the composite superabsorbent increase with increasing corn stalk amount from 6 to 10 wt %, and then decrease with further increase in corn stalk amount. The incorporation of rigid CS chains into polymeric network can prevent intertwist of graft polymeric chains and improve polymeric network. Thus, the water absorbency and gel strength can be enhanced by the introduction of moderate amounts of CS. However, when the amount of CS exceed 10 wt %, more CS powders are physically filled in the network, which decrease the ratio of hydrophilic

groups in unit volume and lead to the decrease of hydrophilicity of composite superabsorbent. Consequently both water absorbency and gel strength of the composite superabsorbent decrease.

Effects of Crosslinker Amount on the Water Absorbency and Gel Strength of the Composite Superabsorbent

The relationship between the volume swelling ratio $Q^{5/3}$ and network structure parameters given by Flory-Rehner theory[23] is usually used as the following equation:

$$Q^{5/3} = \left[\left(\frac{i}{2V_u I^{1/2}} \right)^2 + \frac{1/2 - X_1}{V_1} \right] / v_e / V_0 \qquad (2)$$

Here, i/V_u is the concentration of the fixed charges referred to the unswollen polymer, and I is ionic strength in the external solution; the term $(1/2 - \chi_1)/V_1$ represents the interaction parameter, i.e., affinity of the gel to water and v_e/V_0 is the crosslink density of the gel.

According to eq. (2), the volume swelling ratio $Q^{5/3}$ should increase as the square of concentration of the fixed charge and as the reciprocal of I, and decrease as the crosslink density. Increase in crosslinker amount leads to high crosslink points and high crosslink density, which restrain the expansion of network and result in high gel strength and low swelling capacity, as indicated in Figure 3.

Effects of Neutralization Degree of AA on the Water Absorbency and Gel Strength of the Composite Superabsorbent

Figure 4 demonstrates the effects of neutralization degree of AA on the water absorbency and gel strength of corn stalk-composite superabsorbent. Water absorbency and gel strength of the composite superabsorbent increase as neutralization degree of AA increased from 55% to 65%, while decrease with further increase in the neutralization degree of AA, as shown in Figure 4.

According to eq. (2), the volume swelling ratio $Q^{5/3}$ should increase as the square of concentration of the fixed charge and as the reciprocal of I. With increase in neutralization degree of
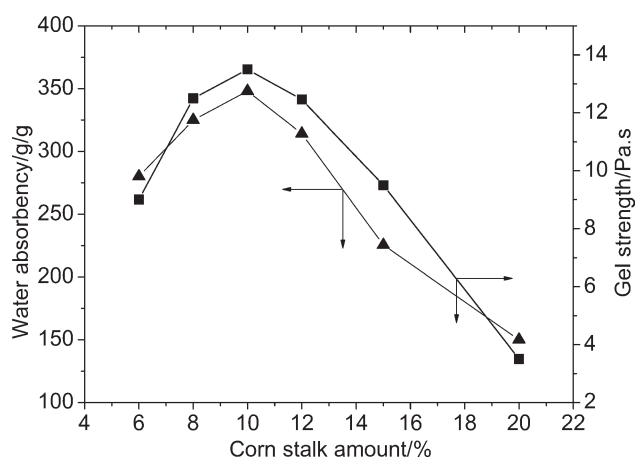

Figure 2. Effects of corn stalk amount (based on monomer weight) on the water absorbency and gel strength of corn stalk-composite superabsorbent.
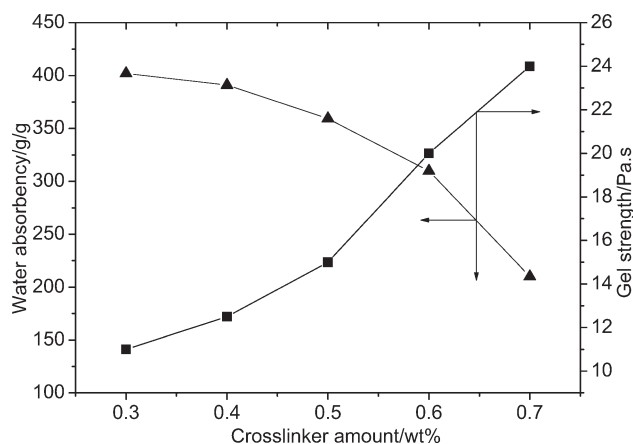
Figure 3. Effects of crosslinker amount on the water absorbency and gel strength of corn stalk-composite superabsorbent.

Figure 5. Effects of AA/AM mass ratio on the water absorbency and gel strength of the composite superabsorbent.

AA, more carboxylic groups are ionized, which results in an increasing electrostatic repulsion tending to expand the chain network. Consequently water absorbency and gel strength are enhanced. On the other hand, however, more and more carboxylic groups on the polymer network are ionized with the neutralization degree of AA beyond 65%, which results in higher counter ions concentration inside the network, weaker electrostatic repulsions,[24] and weaker hydrogen-bonding interactions among COOH and amide groups. Consequently both the water absorbency and gel strength of the composite superabsorbent decrease.

Effects of AA/AM Mass Ratio on the Water Absorbency and Gel Strength of the Composite Superabsorbent

Effects of AA/AM mass ratio on the water absorbency and gel strength of the composite superabsorbent are presented in Figure 5, from which it can be clearly observed that the water absorbency increases constantly with increasing AA/AM mass ratio in the feed mixture. However gel strength of the composite superabsorbent increases as AA/AM mass ratio rose from 30:70 to 60:40, and decreases with further increase in AA/AM mass ratio. The increase of AA/AM mass ratio can increase charges
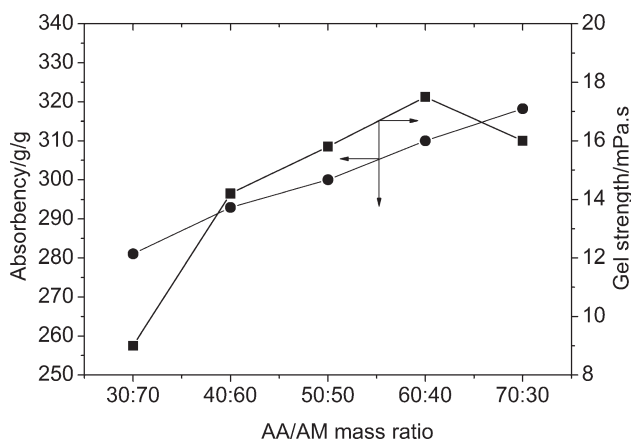
on the polymer chains which will set up an electrostatic repulsion tending to expand the chain network, increase chain stiffness and therefore cause an increase in both water absorbency and gel strength. On the other hand, the reduction in gel strength of the composite superabsorbent with AA/AM mass ratio beyond 60:40 might be ascribed to the weaker hydrogen-bonding interactions among COOH and amide groups.

Swelling Kinetics of the Composite Superabsorbent

The swelling capacity of the hydrogel was measured in distilled water at consecutive time intervals. Figure 6 represents the dynamic swelling behavior of the corn-stalk composite superabsorbent with the composition of 10 wt % corn stalk, 2 wt % initiator, 0.4 wt % crosslinker, 65% degree of neutralization, AA/AM mass ratio of 60: 40 and 15wt % SSS. Initially, the rate of water absorbency sharply increases and then begins to level off. The equilibrium swelling with water absorbency of 660 g/g is achieved after 30 min. A power law behavior is obvious from Figure 6. The swelling kinetics can be expressed by the Voigt-based viscoelastic model (eq. 3):[25,26]
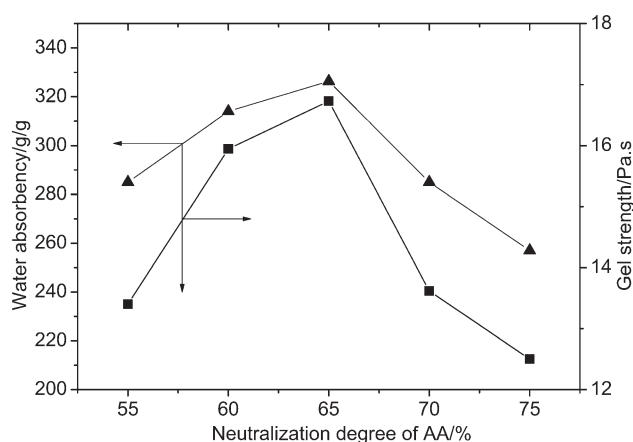
$$Q_t = Q_e(1 - e^{-t/r}) \qquad (3)$$

Figure 4. Effects of neutralization degree of AA on the water absorbency and gel strength of the composite superabsorbent.
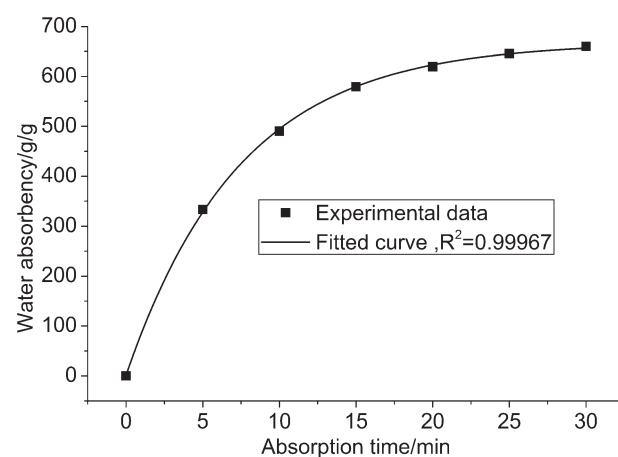

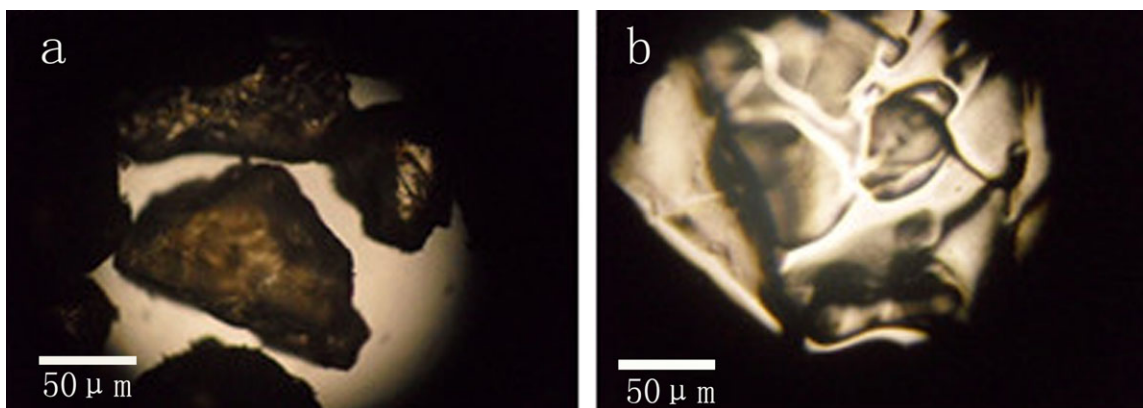**Figure 6.** Water absorbency rate of corn stalk-composite superabsorbent.

Figure 7. Morphologies of corn stalk-composite superabsorbent under optical microscope with 400 times magnification; a: dried composite superabsorbent; b: swollen composite.

where Q_t (g/g) is the degree of swelling at time t, Q_e is the equilibrium swelling (power parameter, g/g), t is time (min) for swelling Q_t, and r (min) stands for the " rate parameter," denoting the time required to reach 0.63 of equilibrium water absorbency.

The data obtained from the equilibrium water absorbency and the swelling rate are fitted into the eq. (3) to obtain the rate parameter r and power parameter Q_e. The rate parameter and power parameter for the composite superabsorbent are found to be 7.24 min and 671g/g, respectively. Because the rate parameter r is a measure of resistance to water permeation, a low calculated r value (7.24 min) reflects a high swelling rate of the composite superabsorbent.[27]

Morphologies of the Composite Superabsorbent
Figure 7 shows the morphologies of dried and swollen composite superabsorbent under optical microscope with 400 times magnification. As can be seen from Figure 7, dried composite superabsorbent has many gaps between the solid particles with irregular shapes. After absorbing water, the swollen composite superabsorbent forms a network-like structure filled with water. This indicates that corn stalk-composite superabsorbent has good water absorption.

The micrographs of dried corn stalk and dried corn stalk-composite superabsorbent are depicted in Figure 8, respectively. It can be observed that dried corn stalk displays a discontinuous sheet structures. However, composite superabsorbent presents an undulant and coarse surface with many large microporous holes and small capillary pores after corn stalk graft modification, which can facilitate the permeation of water into the polymeric network.[28]

CONCLUSIONS

Corn stalk-composite superabsorbent was prepared by graft copolymerization among corn stalks, acrylamide (AM), acrylic acid (AA), and sodium 4-styrenesulfonate (SSS) in aqueous solution. Influences of corn stalk amount, the mass ratio of acrylic acid to acrylamide, the degree of neutralization for AA and crosslinker amount, on water absorbency and gel strength of the superabsorbent composite, were investigated. The superabsorbent composite has water absorbency of 660 g/g within 30min with the composition of 10 wt % corn stalk, 2 wt % initiator, 0.4 wt % crosslinker, 65% degree of neutralization, AA/AM mass ratio of 60: 40, and 15 wt % SSS. FTIR spectra confirm the formation of corn stalk-composite superabsorbent by exhibiting all the characteristic bands of both corn stalk and monomer units. Composite superabsorbent has an undulant and coarse surface with many large microporous holes and small capillary pores.
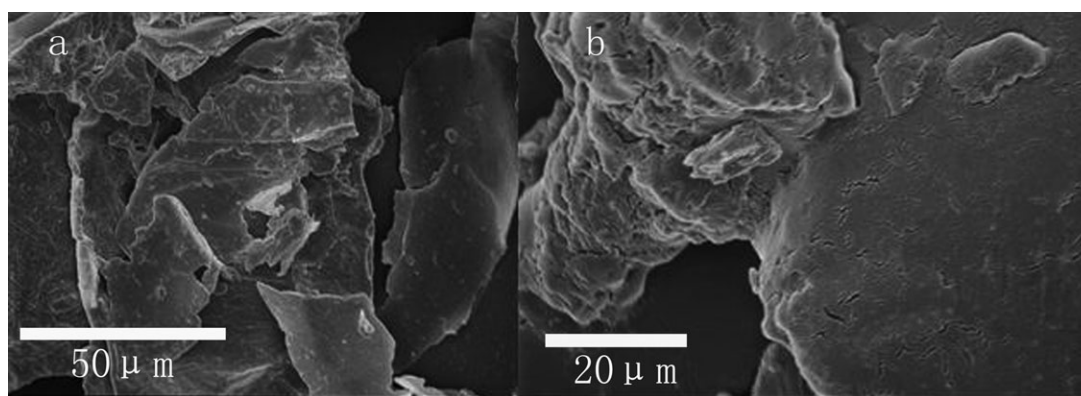

Figure 8. SEM morphologies of corn stalk-composite superabsorbent; a: dried corn stalk; b: dried corn stalk-composite composite superabsorbent.

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