



Synthesis and characterization of a novel super-absorbent based on chemically modified pulverized wheat straw and acrylic acid

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ABSTRACT

In order to develop an eco-friendly polymer, the material was prepared from pulverized wheat straw by chemical methods. And a super-absorbent hydrogel has been synthesized with chemically modified pulverized wheat straw (CMPWS) and acrylic acid (AA) in aqueous solution. Factors, such as weight ratio of AA to CMPWS, the amount of initiator and cross-linker, temperature and neutralization degree of AA that influence absorbencies of super-absorbent were investigated. Moreover, the super-absorbent had been proved with expectant polymerization structure and good thermo-stability via IR spectrum and TGA analysis. The morphological features were evidenced by SEM images. The excellent product was obtained with the absorbencies of 417 g/g in distilled water and 45 g/g in 0.9 wt% NaCl solution.

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1. Introduction

Super-absorbent hydrogels are known due to their loosely cross-linked network with excellent hydrophilic capacity (Aloulou, Boufi, & Labidi, 2006; Bajpai & Johnson, 2005). It can absorb water as much as more than thousand times of its original weight and the swelling equilibrium composite can retain liquid even under some pressure (Chen & Park, 2000). Because of their superior properties comparing with traditional water absorbing materials, the super-absorbent hydrogels have been widely used in hygiene, agriculture, horticulture, drug delivery and food storage (Chen, Liu, & Qi, 2007; Dadhaniya, Patel, & Patel, 2006). About 90% of super-absorbents are used in disposable articles (Blagodatskaya, Ermolaev, & Myakshina, 2004; Chen & Tan, 2006). Most of them are synthetic polymers, which are poor in degradability and remains environmental problems (Zhang, Li, & Wang, 2006; Zhang, Wang, & Wang, 2007). For these reasons, material's biodegradability has been widely focused because of the renewed attention to environmental protection issues. So traditional super-absorbents from synthetic polymers, such as poly (sodium acrylate) and polyacrylamide often have some limitations with poor biodegradability, and these flaws restrict its application (dos Santos et al., 2006; El-Sherbiny, Lins, Abdel-Bary, & Harding, 2005; Hwang & Damodaran, 1997). At present, various materials and

methods have been tried to improve absorbing properties and to avoid the environment problems.

The super-absorbent hydrogels with eco-friendly property and biodegradability are developed in the world. Particularly, the natural materials, such as starch, cellulose and chitosan have attracted great attention due to their abundant resources and degradability (Gao & Heimann, 1993; Gosavi, Deopurkar, & Ghole, 1999; Hosseinzadeh, Pourjavadi, Mahdavinia, & Zohuriaan-Mehr, 2005). The super-absorbent based on natural material could be decomposed and used by microbiology and plants, and it is compatible to the natural environment.

As by-product of grain crops, the wheat straws are abundant bio-resource, and it contains 40–60% natural cellulose and hemicellulose. However, most wheat straw is still burned and become wastes that contributes to pollution (Aloulou et al., 2006). In this work, the wheat straw was modified into the mixture of carboxymethyl cellulose and hemi-carboxymethyl cellulose through chemical method. The mixture can be used as skeletal material in copolymerization. And AA monomers can graft on these structural bodies to cross-link into super-absorbent composite (Chen & Tan, 2006; Davies, Novais, & Martins-Dias, 2004; Kim, Lee, & Yoon, 2002).

A simple and low cost super-absorbent based on AA and PCMWS with ammonium persulfate (APS) and *N,N'*-methylenebisacrylamide (MBA) as initiator and cross-linker was synthesized. The properties and synthesis conditions of the super-absorbent are also investigated to find the optimum synthesis conditions for an eco-friendly composite.

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2. Materials and methods

2.1. Materials

Acrylic acid (AA, chemically pure, distilled under reduced pressure before use), ammonium persulfate (APS, analytical grade, recrystallized from distilled water before use) and *N,N'*-methylenebisacrylamide (MBA, chemically pure, used as received) were supplied by Tianjin Reagent Corp (Tianjin, China). Other agents used were all of analytical grade and all solutions were prepared with distilled water. The wheat straw was acquired from Fumeng County, Liaoning Province.

2.2. Preparation of CMPWS

The wheat straws were chopped and dried in an 80 °C drying oven for 8 h. The dried wheat straws were then sieved with a 0.32 mm screen, and the fine wheat straw powder was weighed and dipped in a 2000 ml beaker with 20% sodium hydroxide solution. The aqueous suspension was heated and stirred at 80 °C for 4.5 h, and then the aqueous suspension filtered and washed with 95% ethanol solution. The filter residue was transferred into a beaker with 15% sodium hydroxide solution in water bath, and then interfused by chloroacetic acid, and being stirred and heated at 70 °C for 1 h. After that, the mixed solution was filtered with 75% ethanol solution, and the chemically modified pulverized wheat straw (CMPWS) was dried.

2.3. Preparation of the PAA-CMPWS super-absorbent composites

A series of samples with different amounts of chemically modified pulverized wheat straws (CMPWS), *N,N'*-methylenebisacrylamide (MBA), ammonium persulfate (APS) and acrylic acid (AA) with different degrees of neutralization were prepared by the following procedure. Appropriate amount of CMPWS was dissolved in 30 ml aqueous solution in a 500 ml four-neck flask, equipped with a mechanical stirrer, a reflux condenser, a funnel and a nitrogen line. After being purged with nitrogen for 30 min to remove the oxygen dissolved from the system, certain amount of APS was introduced in the mixture to initiate CMPWS to generate radicals, and a solution of 20.00 g AA after neutralization, certain amount of MBA and 10 ml de-ionized water was added. The water bath was kept at 70 °C for 1 h to complete polymerization. The resulting product was dried to a constant weight at 70 °C. In addition, the product was milled, and made into samples with a particle size in 0.42 mm.

2.4. Water absorbency measurement

A weighted quantity of the super-absorbent composite was immersed in distilled water and saline solution at the room temperature to swell equilibrium, respectively. Swollen samples were then separated from unabsorbed water by filtered over a 0.25 mm screen. The water absorbency (Q_{H_2O}) of super-absorbent composite was determined by weighing the swollen samples and calculated using the following equation:

$$Q_{H_2O} = \frac{m_2 - m_1}{m_1} \quad (1)$$

m_1 and m_2 were the weights of the dry sample and the water-swelling sample (g), respectively. Q_{H_2O} was expressed as grams of water per gram of sample (g/g).

2.5. Structural analysis

The FTIR spectra of samples were taken in KBr pellets using a TM FTIR spectrophotometer (Thermo Nicolet, NEXUS). The surface morphology of the gels were examined using scanning electron microscopy (SEM, JSM-5600LV, JEOL, Ltd.) on aluminum stubs and coated with a thin layer of palladium gold alloy. Thermal stability of the samples was studied on a TGA-7 thermo gravimetric analyzer (Perkin-Elmer Cetus Instruments, Norwalk, CT) with a temperature range of 25–800 °C at a heating rate of 10 °C/min using a dry nitrogen purge at a flow rate of 50 ml/min.

3. Results and discussion

3.1. Effect of ratio AA to CMPWS

The effect of weight ratio of PAA to CMPWS ranging from 1 to 15 on the absorbencies was investigated and showed in Fig. 1. It indicated that the hydrogel absorbencies increase continuously with the increase of weight ratio of PAA to CMPWS until the maximum absorbencies appeared at the ratio 10, which were 425 g/g in distilled water and 44 g/g in 0.9 wt% NaCl solution, respectively. Further increase of the weight ratio decreased absorbencies of the samples in both distilled water and saline solution. It can be explained as follows: as the weight ratio of PAA to CMPWS increases, the fraction of poly (AA) increases, which enhances hydrophilic groups, such as $-\text{COO}^-$ and $-\text{COOH}$ of the composite, and then the equilibrium water absorbencies were improved. In addition, more cations were generated in the polymeric network. Consequently, the osmotic pressure between the polymeric network and external solution increased. Moreover, both grafting and molecular weight of the poly acrylate chains increasing contributes to the improvement of the absorbencies. The decreasing of the absorbencies when the weight ratio exceeds 10 may be attributed to increasing dissoluble homo-polymer of poly acrylate at an invariable cross-linking density, which was not conducive to absorbencies.

3.2. Effect of initiator content

The effect of the initiator, ammonium persulphate (APS), on the water absorbencies of super-absorbent composite were also investigated and illustrated in Fig. 2. At 1.1 wt% of APS, the maximum absorbency (407 g/g in distilled water and 39 g/g in 0.9 wt% NaCl solution) were obtained, and the absorbencies increased with the increase of APS amount from 0.54 wt% to 1.1 wt%. When the amount of APS was higher than the optimum point (1.1 wt%), the swelling capacity of super-absorbent composite decreased with further increase of the amount of APS. It can be seen that the amount of initiator has great influence on the polymer absorbencies.

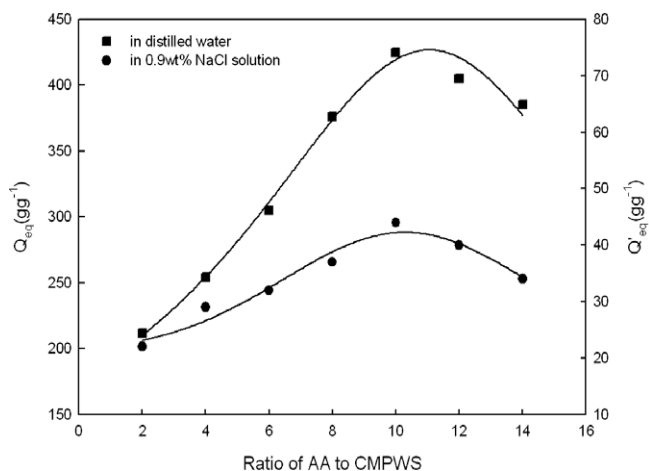


Fig. 1. Effect of AA to CMPWS ratio on absorbencies.

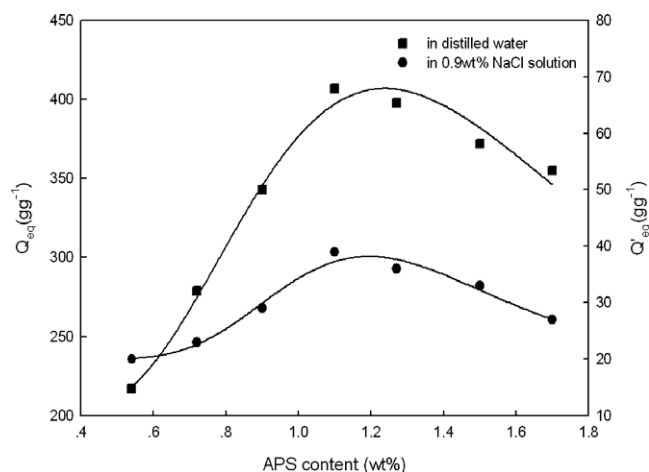


Fig. 2. Effect of APS content on the absorbencies.

This is accord with the relationship between average chain length and concentration of the initiator in the polymerization (Zhang et al., 2007). This can also be attributed to the fact that scarce radicals were generated less than due quantity. The molecular weight of the polymer backbone decreases with increasing the initiator concentration, and then more polymer chain ends are generated. Therefore, the water absorbency increases evidently with increasing the initiator content below the optimum value from 0.54 to 1.1 wt%. It has been reported that polymer chain ends do not contribute to water absorbency of super-absorbents. So further increasing the initiator concentration from 1.1 to 1.8 wt% is responsible for the decrease of water absorbency.

3.3. Effect of cross-linker content

In this study, the effect of cross-linker on absorbencies were investigated by changing the amount of *N,N'*-Methylenebisacrylamide (MBA) and shown in Fig. 3. The maximal absorbency was 413 g/g in distilled water and 42 g/g in 0.9 wt% NaCl solution at 0.15 wt% of the MBA content. Cross-linker amount, according to Flory's network theory, is also a crucial factor that influences the cross-linking density and fluid absorbency of the hydrogel.

It was evident that water absorbencies increase with tiny increasing of cross-linker content in the range of 0.02–0.15 wt%. According to Flory's theory, increasing cross-linker should increase

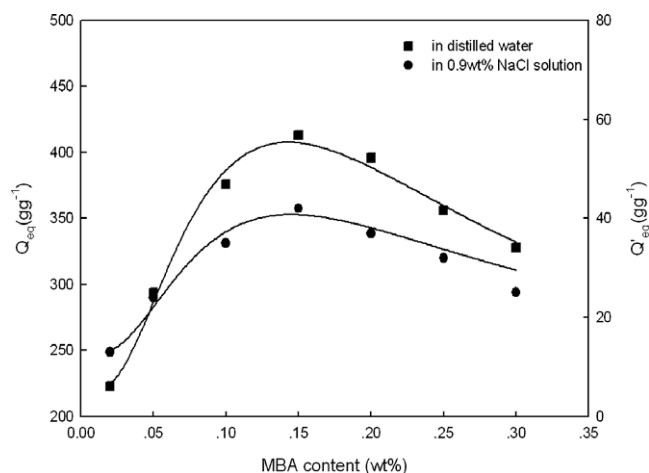


Fig. 3. Effect of amount MBA on the absorbencies.

the nodes of network and cross-linking density, which is favorable to the super-absorbent absorbing and retaining fluid (Pourjavadi, Barzegar, & Mahdavinia, 2006). It is attributed to the fact that the polymeric network of the composite cannot be formed perfectly and the composite exists as a water-soluble material. However, Fig. 3 showed that the water absorbencies decreased with further increase of cross-linker content from 0.15 to 0.27 wt%. This was because more cross-linker generates excessive nodes in the polymeric network, and results in a highly cross-linked, rigid structure that fail to expand to hold a large quantity of water.

3.4. Effect of temperature

Fig. 4 demonstrated the effect of the reaction temperature on swelling of PAA-g-CMPWS hydrogels. It shows that the absorbencies were also increased when the temperature was increased from 50 to 90 °C because of the improvement of polymerization rate, and the maximum absorbency was 417 and 45 g/g (the temperature was 75 °C) in distilled water and 0.9 wt% NaCl solution, respectively. When temperature further increased, the absorbencies decreased.

As it was a thermo-sensitive initiator, APS would release more radicals and result in more intense polymerization reaction with temperature increase. However, when the reaction system temperature passed over the optimum point (70 °C), an increase in the temperature favors the increasing of radical centers, causing high cross-linking points in the hydrogel. So, the swelling capacity of the hydrogel is decreased (Wu, Lin, Zhou, & Wei, 2000).

3.5. Effect of neutralization degree of AA

Hydrophilic groups, such as $-\text{COOH}$, $-\text{COONH}_2$ and $-\text{COO}^-$, gives an obviously influence on absorbencies in the PAA-g-CMPWS polymeric system, and the ratio of different hydrophilic groups can be changed by the neutralization degree of AA. The effects of neutralization degree of AA on water absorbency of the super-absorbent composite are illustrated in Fig. 5. It can be seen from Fig. 5 that water absorbencies of the composite increased with increasing neutralization degree of AA when the neutralization degree is less than 80%, and then decreases with further increasing the neutralization degree to 90%. The optimum absorbencies, 405 g/g in distilled water and 46 g/g in 0.9 wt% NaCl solution, appeared at 80% neutralization degree of AA.

According to previous works, the swelling ability and absorbencies were influenced by the rubbery elasticity, ionic osmotic, and

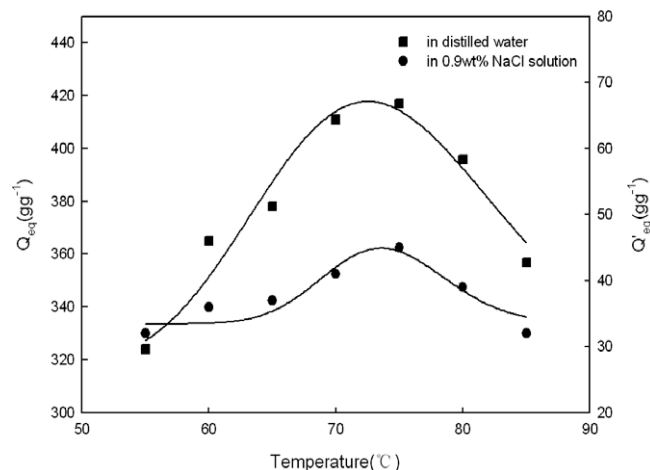


Fig. 4. Effect of temperature on the absorbencies.

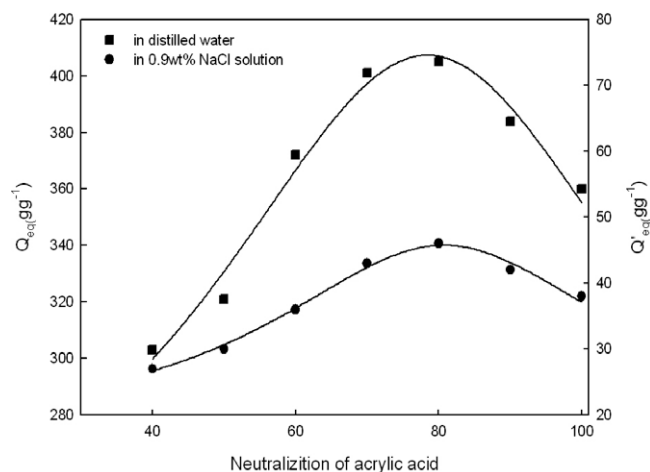


Fig. 5. Effect of AA neutralization on the absorbencies.

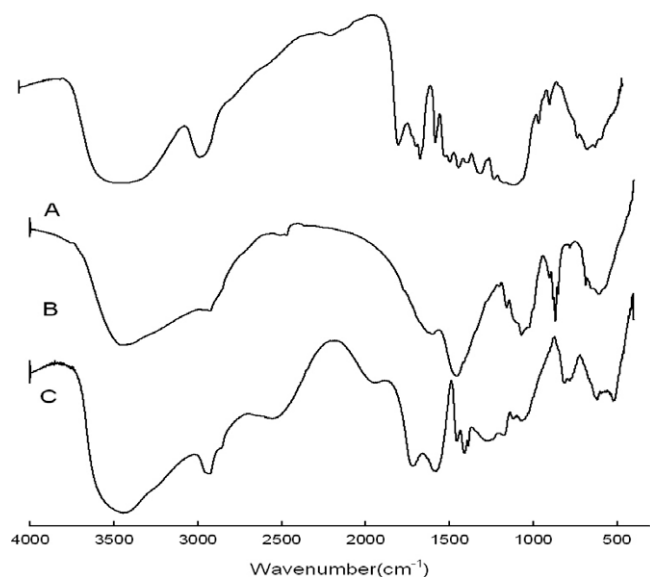


Fig. 6. FTIR spectra of PWS (A), CMPWS (B) and PAA-g-CMPWS (C) super-absorbent incorporated.

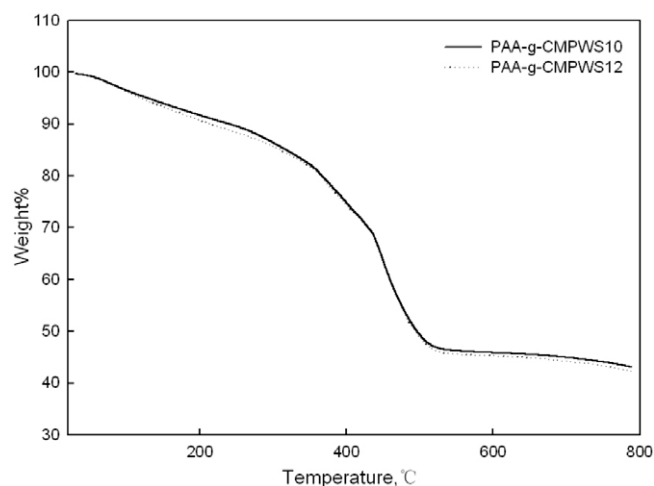


Fig. 7. TGA curves of PAA-g-CMPWS10 and PAA-g-CMPWS12 super-absorbent.

affinity of polymer toward water (Pourjavadi & Amini-Fazl, 2007). So AA is neutralized with sodium hydroxide, the hydrophilic groups of the composite and osmotic pressure increases, and it is conducive to expand the network. Moreover, neutralization degree increasing from 40% to 80% results in an increase of water absorbency for the composite. However, the neutralization degree over 80%, more Na^+ ions in the polymeric network reduces the repulsion by screening the negative charges of $-\text{COO}^-$ groups, thus resulting in the decrease of water absorbencies.

3.6. Infrared spectra

Fig. 6 shows the FTIR spectra of PWS (A), CMPWS (B) and CMPWS-g-PAA (C) super-absorbent copolymers. According to Fig. 6(A) and (B), the absorption was observed at 3400 cm^{-1} (hydroxyl stretch influenced by hydrogen bond), 1592 cm^{-1} and 1412 cm^{-1} (carbonyl stretch), 1068 cm^{-1} (β -1,4-glycosidic bond) and 2942 cm^{-1} and 2860 cm^{-1} (methylene), which were characteristic absorptions in cellulose and methylcellulose structures. In addition, as shown in Fig. 6(A) and (B), some absorption disappeared, which suggested that several compositions of pulverized wheat straw have been changed during the chemical modification. Compared with CMPWS IR spectra, CMPWS-g-AA super-absorbent copolymer had new absorption bands at 2540 cm^{-1} (amide group stretch), 1719 and 1575 cm^{-1} (amide group characteristic absorption), 1420 cm^{-1} (methylene shear vibration in carbonyl and methylene) and 1269 cm^{-1} (carboxyl in ethers), as shown in Fig. 6(C). This indicated that the acrylic acid have been grafted on the carboxyl methyl cellulose chain of the copolymer network. From the above FTIR information, it can be concluded that the grafting copolymerization between CMPWS and acrylic acid monomers has taken place during the reaction with ammonium persulfate as the initiator and *N,N'*-methylenebisacrylamide as the cross-linker.

3.7. Thermal stability

Thermo-gravimetric analysis (TGA) results of PAA-g-CMPWS super-absorbent composites are employed to characterize the thermal properties of the obtained graft copolymers and it shown in Fig. 7. The solid line and segment line described the ratio of PAA to CMPWS of 10 and that 12, respectively. The weight loss process exhibited three steps as the temperature increase from the room temperature to 437°C . Both PAA-g-CMPWS (10) and PAA-g-CMPWS (12) showed 4% weight loss below 102°C , suggesting the loss of absorbent and bound water in the hydrogels network. From approximately 102 to 343°C , both composites had significant weight losses similarly with 12.5% (343°C) and 12% (338°C), respectively, suggested complicated processes including the dehydration of carbohydrate chains and breaking of C–O–C glycosidic bond of the cellulose chain. Subsequent decomposition caused the two composites sharp weight loss—14.2% loss for PAA-g-CMPWS (10) and 14.4% loss for PAA-g-CMPWS (12)—with further temperature increase from 343 or 338 to 437°C . However, there was prominent difference between the two super-absorbents in higher temperature range. Thermal decomposition for PAA-g-CMPWS (10) occurred at next stages: first 18.8% weight loss corresponding to decomposition of the carboxyl group of PAA chain from 437 to 511°C and another 4% to the breakage of the chains of AA from 511 to 787°C . Similarly, PAA-g-CMPWS (12) first lose 19.2% weight from 437 to 511°C , and then lose 4.5.8% from 511 to 787°C . The result indicated that PAA-g-CMPWS (12) is more thermally stable for higher ratio of PAA-g-CMPWS in the network, perhaps due to the fact that the network can act as a heat barrier, and thus enhance the overall thermal stability of the composite.

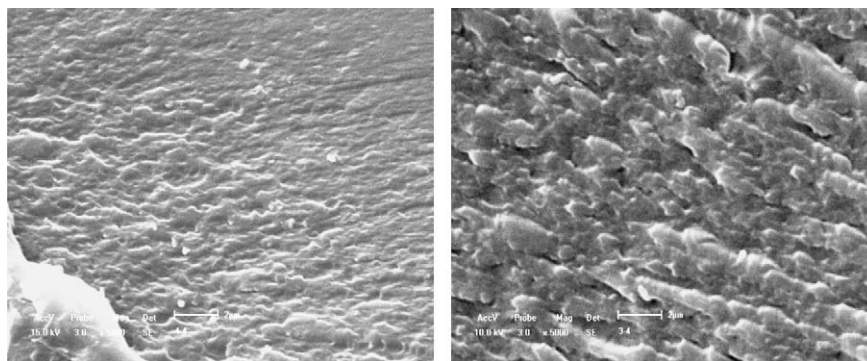


Fig. 8. Morphologies of SAP ratio of PAA-g-CMPWS 8 (left) and 10 (right).

3.8. SEM surface morphology

The SEM micrographs of the acrylic acid modified pulverized wheat straw samples are shown in Fig. 8. Tighter surface and less porous structure can be observed at the ratio of PAA to CMPWS 8 (left, Fig. 8), while broad network and more porous structure increase the surface area of the copolymer hydrogel at the ratio of 10 (right, Fig. 8). When the gel was dipped into an aqueous medium, the medium easily diffused into the gel mass through the micro porous gaps, leading to substantially increase of absorption rate. Therefore, the ratio of reactants had great influence on surface morphology of the super-absorbent. This observation was in good agreement with our water absorption results.

4. Conclusion

A novel PAA-g-CMPWS super-absorbent composite with eco-friendly property was prepared by grafted copolymerization through AA and MPCWS. Various factors have great influence on the absorbency and it demonstrated maximum absorbencies of 417 g/g in distilled water and 45 g/g in 0.9 wt% NaCl solution. The production cost was significant reduced than that of traditional cross-linked poly (acrylic-co-acrylamide) super-absorbent composite. But this water absorbencies and adsorptions under load should be proved in the future.

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