

Synthesis and Properties of Polyacrylamide/Hollow Coal Gangue Spheres Superabsorbent Composites

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ABSTRACT: Polyacrylamide/hollow coal gangue spheres (PAM/HCGS) superabsorbent composites were prepared by in situ aqueous solution polymerization using N,N'-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator. PAM/HCGS composites exhibit the good water and salt absorption with 5 wt % HCGS, 0.14 wt % crosslinker, and 0.56 wt % initiator. Water retention of PAM/HCGS (5 wt %) retains 43% at 60°C for 24 h, which is much better than that of pure polyacrylamide. It suggests that the addition of HCGS increase the strength of swollen gel. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2184–2187, 2013

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INTRODUCTION

Superabsorbent polymers (SAP) materials are capable of absorbing and retaining a large amount of water or aqueous solution, and the water absorbed is hardly removable even under pressure.^{1–3} The most important applications of superabsorbent materials are employed in hygienic uses,² and other important applications include the conservation of water in the agriculture and horticulture.⁴ For these applications, superabsorbent materials should possess not only high absorptive capacity, but also it should be rather strong in the swollen state in order to hold effectively the absorbed liquid.⁵ However, the strength of swollen polymer is very low, which impedes its wide applications.

Among SAP materials, polyacrylamide (PAM) has been widely studied and manufactured due to its high absorptive capacity. However, the strength of swollen PAM is very low and the absorptive capacity reduces significantly with repeated use. In order to solve this problem, PAM-based composites have been received intensive attention, such as PAM/attapulgit, ^{6–9} polyacrylamide/sodium alginate,^{10–13} PAM/poly(*N*-isopropylacrylamide) spheres,¹⁴ PAM/silica,¹⁵ etc.

The coal gangue is a kind of solid wastes generated in the processes of coal mining and washing. Scrap coal gangue occupies large farmland and deteriorates the environment as a hazardous byproduct without proper treatment. However, coal gangue has

the potential to be used as polymer filler. It is a mixture of inorganic and organic components with some unsaturated points and polar functional groups, such as hydroxyl, carboxyl, etc.¹⁶ Some coal gangue powder and its product through calcination or with surface treatment have been successfully used as rubber filler, even partially replaced the traditional rubber reinforcement, such as carbon black.¹⁷

In this article, hollow coal gangue spheres (HCGS) with open pores were prepared by spray granulation, and then sintered at 900°C. HCGS were embedded into the matrix of PAM by aqueous solution polymerization to improve its strength and reduce its cost. The effects of coal gangues, crosslinker, and initiator content on the absorption rate and retention of water of PAM/HCGS have been investigated.

EXPERIMENTAL

Preparation of the PAM/HCGS Superabsorbent Composites

A series of PAM/HCGS superabsorbent composites were synthesized according to Ref. 6. Typically, acrylamide monomer was dissolved in distilled water in a four-neck flask, equipped with a reflux condenser, a thermometer, and a nitrogen line. Cross linker N,N'-methylenebisacrylamide (MBA) was added into the monomer solution, and then an appropriate amount of HCGS was dispersed in the mixed solution. The mixed solution was heated to 40–60°C gradually under nitrogen atmosphere, and

then ammonium persulfate (APS) as an initiator was introduced into the mixed solution. The gel is immediately formed, and the product was saponified by sodium hydroxide, and stirred vigorously under nitrogen atmosphere for 3 h at 90°C. After saponification, the product was washed several times with water and methanol (1 : 9 in volume), and dried in an oven at 70°C.

Characterization of PAM/HCGS Composites

Microstructure of PAM/ HCGS. The fracture surface of PAM/HCGS composites was deposited a fine layer of gold metal by the radio frequency sputtering, and the microstructure was observed by scanning electron microscopy (Hitachi S-4700 SEM).

Measurement of Water Absorption. A weighted quantity of the PAM/HCGS (0.05 g) powders was immersed in excess distilled water (500 mL) at ambient temperature. After the swelling equilibrium is reached, the swollen samples were separated from unabsorbed water by filtering through a 100-mesh screen. The saturated absorption of superabsorbent composite, Q_{H_2O} , was calculated using the following equation:

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

where m_1 and m_2 were the weight of dry sample and swollen sample, respectively.

For the measurement of salt water absorption, the concentration of NaCl is 0.9 wt %.

Water Retention Capacity. Typically, the saturated swollen gel of PAM and PAM/HCGS composites was spread on the glass and placed in an oven at 60°C. The gel was weighed at each time interval and the loss of water was obtained to evaluate water retention capacity of the PAM and PAM/HCGS composites.

RESULTS AND DISCUSSION

The Microstructure of PAM/HCGS Composites

The microstructure and particle size distribution of hollow coal gangues spheres are shown in Figure 1(a). It shows that coal gangues spheres are hollow, and open pores are observed in the surface of hollow spheres. The grain size of spheres is 50–150 μm . The main composition of hollow coal gangue spheres is silicon and aluminum oxide that is hydrophilic compounds, and the spheres are hollow and porous, which is favorable to the absorption and retention of water. Figure 1(b) shows the morphology of PAM/coal gangues composites. The coal gangues were embedded in the polymer, and some coal gangues are broken due to the stirring during the preparation process.

Effect of HCGS Content on the Absorptive Capacity

Water absorption of PAM/HCGS composites embedded with different HCGS content in distilled water and 0.9 wt % NaCl

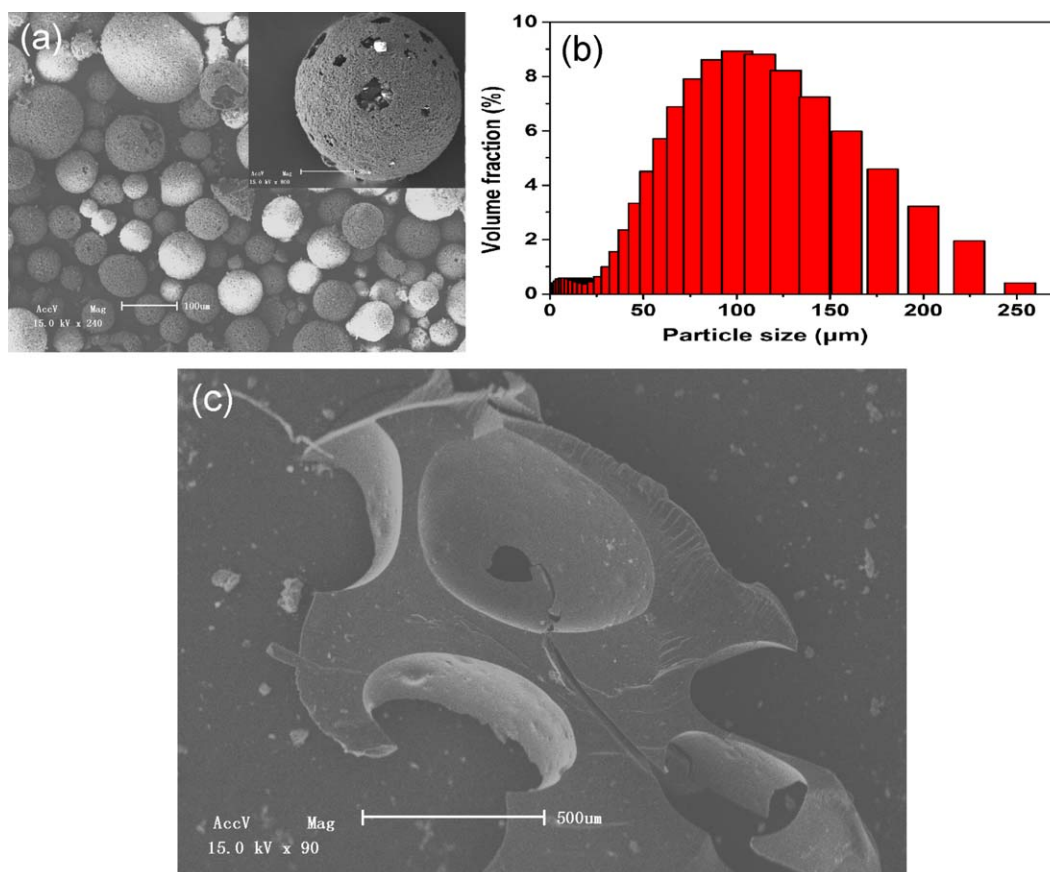


Figure 1. SEM pictures of (a) HCGS, (b) particle size, and (c) PAM/HCGS composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

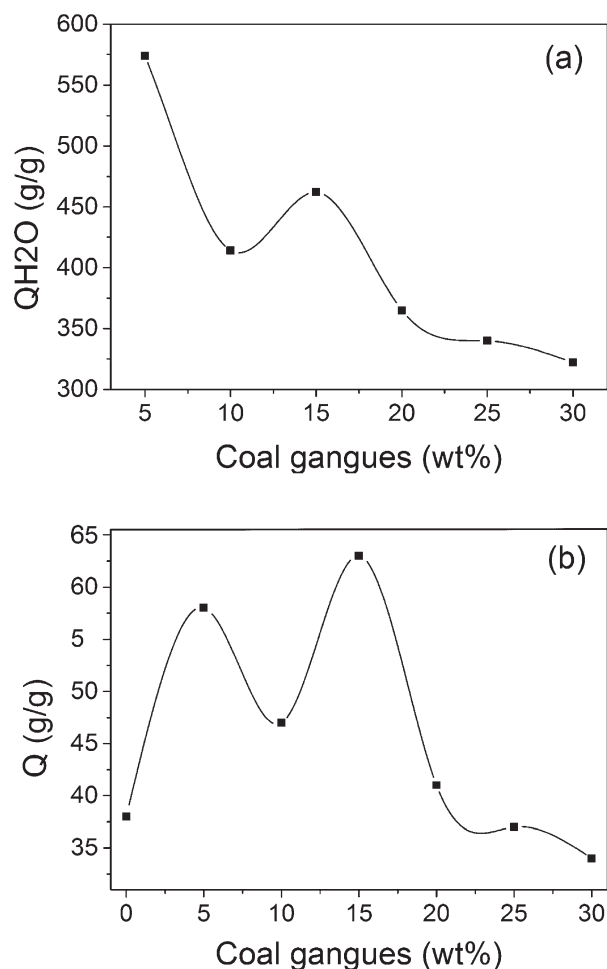


Figure 2. Water absorbency of PAM/HCGS composites with different coal gangues spheres content in (a) distilled water and (b) 0.9 wt % NaCl solution.

solution is shown in Figure 2. The HCGS content affects significantly the absorptive capacity of PAM/HCGS composites. As the amount of HCGS increases from 0 to 10 wt %, the water absorption decreases from 1474 to 432 g/g, and then increases to 475 g/g when the amount of HCGS increases to 15 wt %. The significant degradation of water absorption of PAM/HCGS composites with increasing HCGS content may be attributed to the fact that the additional HCGS results in the generation of more crosslink points in the polymeric network, which increases the crosslink density of composites, and then the elasticity of the polymer chains decreases.⁹ Additionally, the content of hydrophilic groups is lower at a higher HCGS content, and then the osmotic pressure difference decreases, which also results in the shrinkage of the composite. The density of HCGS (stacking density is 0.8 g/cm³) is much higher than that of dry PAM gel (stacking density is 0.4 g/cm³), but water absorption of HCGS (2 g/g) is much lower than that of PAM, which leads to the low water absorption for the same mass of PAM/HCGS composites with increasing HCGS content. In this study, the water absorption of PAM/HCGS composites is higher than the values of polyacrylate/glass spheres composites, and its maximum water absorption is 80 g/g¹⁸. It needs to note that the

grain size of glass spheres is 10 μm , and its density is only 0.125 g/cm³.

The salt water absorption of PAM/HCGS composites with different amounts of HCGS is shown in Figure 2(b). The variation trend of salt solution absorption is different with water absorption of PAM/HCGS. As the HCGS increases from 0 to 15 wt %, the salt water absorption increases to 63 g/g. The huge difference in absorption capability of composites between pure water and salt water is attributed to the decrease of osmotic pressure difference between the polymeric network and the external salt solution. In addition, the penetration of counterions (Na) into the network makes the screening effect of them on the anionic group ($-\text{COO}$) more evident, which will also decrease water absorbency of the PAM composite.¹⁹

Effect of Crosslinker and Initiator Contents on Water Absorption

Crosslink density is an important factor of water absorption, and water absorption of superabsorbent can be influenced greatly by the amount of crosslinker.¹² The effect of crosslinker content on water absorption of PAM/HCGS composites is shown in Figure 3. It can be seen that the water absorption decreases with increasing crosslinker from 0.14 wt % to 0.23 wt %. This is attributed to the fact that the crosslink density increases with increasing crosslinker content, and then the space in the polymeric network to hold water is reduced. According to Flory network theory,²⁰ water absorption of superabsorbent is in inverse proportion to crosslink density. Therefore, the increase of crosslinker content results in the decrease of water absorption of PAM/HCGS superabsorbent composites. As the crosslinker content decreases from 0.14 wt % to 0.056 wt %, polymer cannot form a good network, and the gel of swollen polymer composites is very weak, which leads to low water absorption.

The effect of initiator content on water absorption of PAM/HCGS composites is shown in Figure 4. The variation trend is similar to that of crosslinker content. According to Allcock et al.,²¹ the average kinetic chain length is in inverse proportion to the square root of the initiator concentration in free-radical polymerization. Therefore, the molecular weight of the polymer

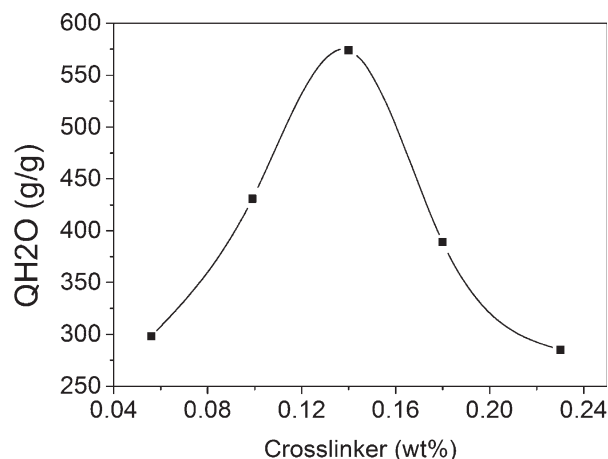


Figure 3. Effect of crosslinker content on water absorbency of PAM/HCGS composites (5 wt % HCGS).

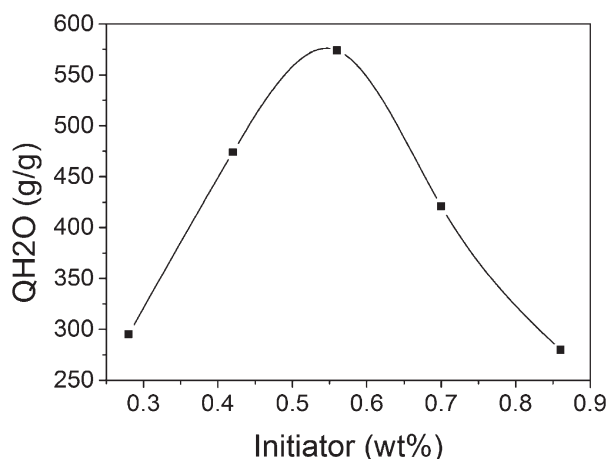


Figure 4. Effect of initiator content on water absorbency of PAM/HCGS composites (5 wt % HCGS).

backbone decreases with increasing the initiator concentration, and then more polymer chain ends are generated. It has been reported that the polymer chain ends do not contribute to water absorption of superabsorbent.²² Thus, the further increase of the initiator concentration from 0.56 wt % to 0.86 wt % is responsible for the decrease of water absorption. However, the water absorption decreases evidently with decreasing the initiator content below the optimum value from 0.56 wt % to 0.28 wt%. This can also be attributed to the formation of more water-soluble polymers owing to the fact that deficient radicals were generated as less initiator was charged.

Water Retention of PAM/HCGS Composites

The water retention of PAM and PAM/HCGS composites with time at 60°C is shown in Figure 5. It can be seen that the water retention of PAM/HCGS composites is much better than that of PAM. The water of swollen PAM has lost completely at 60°C for 7 h. However, the water of swollen PAM/HCGS decreases at 60°C from 0 to 10 h, and then retains about 45% for 24 h. It suggests that the addition of HCGS is favorable to increase the strength of PAM and lead to high water retention.

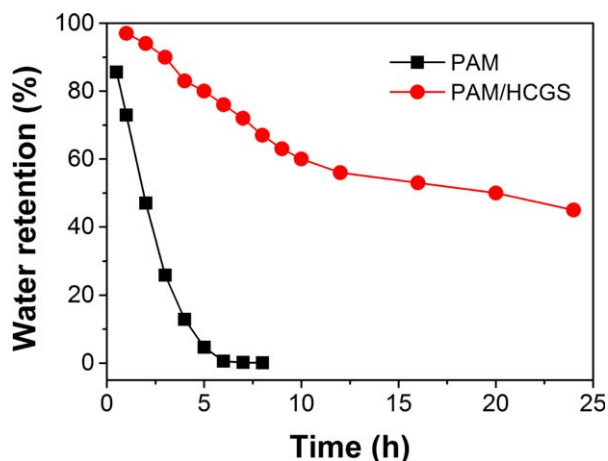


Figure 5. The evolution of water retention of PAM and PAM/HCGS composites (5 wt % HCGS) with the prolongation of time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSION

PAM/HCGS superabsorbent composites are prepared by aqueous solution polymerization, N,N'-methylenebisacrylamide (MBA) as crosslinker, and ammonium persulfate (APS) as an initiator. PAM/HCGS composites exhibit the good water absorption and water retention with 5–15 wt % HCGS, 0.14 wt % crosslinker, and 0.56 wt % initiator. Although the water absorption of PAM/HCGS decreases comparing to PAM, the addition of HCGS not only reduces the cost, but also increases the strength and salt water absorption.

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