

# Synthesis and Swelling Behaviors of Poly(sodium acrylate)/Hydroxyapatite Superabsorbent Nanocomposites

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**Abstract.** Superabsorbent nanocomposites based on partially neutralized acrylic acid (AA) and hydroxyapatite (HP) were prepared by free radical solution polymerization using *N, N'*-methylenebisacrylamide (MBA) as the crosslinker and ammonium persulfate (APS) as the initiator. The developed nanocomposites were characterized by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The effects of HP content on water absorbency of the nanocomposites were investigated, and the swelling behaviors of the nanocomposites in various pH solutions and their reswelling capability in distilled water were also systematically evaluated. FTIR spectra revealed that the P–OH groups of HP participated in graft polymerization reaction with AA. TEM analysis showed the needle-like crystals of HP present in the PAA/HP nanocomposite with a diameter of about 40 nm and a length of about 270 nm. The swelling rate and reswelling capability of the superabsorbents were improved due to the introduction of HP into PAA polymeric network, and this result implied that the nanocomposites acted as a recyclable water-saving material.

## 1 Introduction

Superabsorbents are slightly crosslinked hydrophilic polymers that can absorb and retain aqueous solutions up to hundreds of times their own weight even under some pressure. Superabsorbents have been widely applied in various fields, such as hygienic products, agriculture, horticulture, cosmetics and drug-delivery systems <sup>[1]</sup>, etc. Since the first superabsorbent was developed by US Department of Agriculture in the early 1970s <sup>[2]</sup>, considerable efforts have been made to improve the absorbing properties and expand the application fields of superabsorbents <sup>[3]</sup>. Recently, the preparation of organic–inorganic superabsorbent composites has attracted great attention. Inorganic fillers, including montmorillonite <sup>[4]</sup>, attapulgite <sup>[5]</sup>, kaolin <sup>[6]</sup>, mica <sup>[7]</sup>, diatomite <sup>[8]</sup> and rectorite <sup>[9]</sup>, etc. have already been used for the preparation of superabsorbent composites, and the resultant materials exhibited improved swelling capability, thermal stabilities and low production cost. However, the reswelling capabilities of organic–inorganic superabsorbent composites are expected to be further improved.

Hydroxyapatite (HP) is a naturally occurring form of calcium apatite with the formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , which is available in nature, abundant and economically utilizable. HP can easily be modified by grafting polymerization of vinyl phosphonic acid because it's abundant P–OH functional groups. Therefore, HP is a reactive inorganic component, and it is expected that HP can act as an assistant crosslinker during the polymerization reaction to form the desired superabsorbents. For these reasons, a series of poly(sodium acrylate)/hydroxyapatite (PAA/HP) superabsorbent nanocomposite with various HP contents were synthesized and characterized. The effects of HP on water absorbency and swelling rate of the nanocomposites were investigated. The

swelling behaviors in various pH solutions and the reswelling capabilities of the superabsorbent nanocomposites were also studied systematically.

## 2 Experimental

**Materials.** Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China), *N,N'*-methylenebisacrylamide (MBA, chemically pure, Shanghai Chemical Reagent Corp., Shanghai, China) and Hydroxyapatite (HP, 40 nm, 97%, Nanjing Emperor Nano Material Co., Ltd., Jiangsu, China) and were used as received. Other reagents used were of analytical grade and all solutions were prepared with distilled water.

**Preparation of PAA/HP Superabsorbent Nanocomposites.** Typically, 7.2 g AA was dissolved in 14 mL distilled water and neutralized with 15 mL of NaOH solution (4 mol/L) in a four-neck flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line, and then 8.0 mg of MBA and an appropriate amount of HP nano-powder were introduced. After being purged with N<sub>2</sub> for 30 min to remove oxygen in the solution, the mixed solution was heated to 40 °C and then 24.0 mg of APS was introduced. Finally, the temperature was slowly risen to 70 °C with vigorous stirring and kept for 3 h to complete reaction. The gels obtained were dried to constant weight at 70 °C. Dried product was milled and screened to keep a particle size of 40–80 mesh. PAA was prepared according to a similar procedure except without HP.

**Measurement of Water Absorbency.** Superabsorbent sample (0.05 g) was immersed in excess distilled water or various pH solutions (adjusted using 0.1 mol/L HCl or 0.1 mol/L NaOH solutions) at room temperature for 4 h to reach the swelling equilibrium. Swollen samples were separated from unabsorbed water by filtering with 100-mesh stainless screen and then drained on the screen for 10 min. The equilibrium water absorbency of superabsorbent nanocomposite,  $Q_{eq}$  (g/g), was derived from the mass change before and after swelling. All samples were carried out three times repeatedly and the averages are reported.

**Measurement of Swelling Rate.** The swelling rate of the samples was measured according to the following process. Sample (0.05 g) was immersed in certain amount of distilled water in several 500 ml beakers. At certain time intervals, the water absorbency ( $Q_t$ ) of the sample was measured. The measurement condition is the same as that for equilibrium water absorbency.

**Measurement of Reswelling Capacity.** The specimen (0.05 g) was immersed into slightly excess distilled water to achieve the swelling equilibrium. The swollen gel was placed in an oven at 105 °C until the gel was thoroughly dried. Then an equal amount of distilled water was added to the dried gel and placed in the oven again. A similar procedure was repeated, and then the equilibrium water absorbency of the sample after reswelling for several times was obtained.

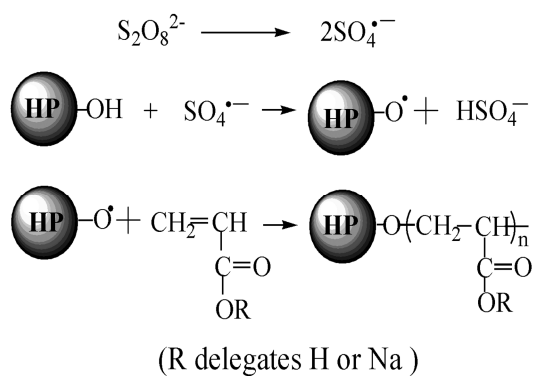
**Characterizations.** FTIR spectra of the superabsorbent nanocomposites were recorded on a FTIR (Thermo Nicolet, NEXUS, TM) spectrophotometer in the range of 4000–400 cm<sup>-1</sup>, using KBr pellets. SEM studies were carried out in a JSM-5600LV SEM instrument (JEOL, Ltd.) after coating the sample with gold film using an acceleration voltage of 20 kV. TEM was performed on an instrument of JEM1200EX (Japan). The powdered specimen was placed on the copper grids after sonicating its suspension in absolute ethanol for 300 s.

## 3 Results and Discussion

### FTIR Analysis

The FTIR spectra of HP, PAA and PAA/HP are shown in Fig. 1. The absorption bands of HP at 1033 and 961 cm<sup>-1</sup> and at 602 and 562 cm<sup>-1</sup> are ascribed to the stretching vibrations and deformation vibrations of phosphate groups, respectively. The band at 3570 cm<sup>-1</sup> is attributed to free hydroxyl ions in crystal lattice sites. The broad band at 3000–3700 cm<sup>-1</sup> and the small band at 1635 cm<sup>-1</sup> are assigned to the stretching vibration and the bending vibration of bonding H<sub>2</sub>O molecule, respectively [10]. Compared with the FTIR spectrum of HP, a series of new absorption bands at 2924 cm<sup>-1</sup> (C–H stretching), 1712 cm<sup>-1</sup> (C=O stretching of –COOH group), and 1456 cm<sup>-1</sup>

(symmetric stretching  $-\text{COO}^-$  groups) appears in the spectra of PAA/HP (Fig. 1c and Fig. 1d), indicating the existence of PAA chains. The absorption bands of HP at  $3570\text{ cm}^{-1}$  and  $961\text{ cm}^{-1}$  were absent and the absorption band at  $1033\text{ cm}^{-1}$  was obviously weakened in the spectra of PAA/HP, suggesting that HP participated in the polymerization reaction through its active functional P-OH group (Scheme 1).



Scheme 1. Schematic reaction of HP and AA

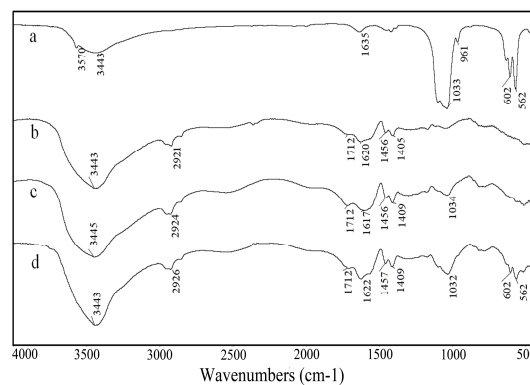


Fig. 1. FTIR spectra of (a) HP, (b) PAA, (c) PAA/HP (10 wt%), and (d) PAA/HP (30 wt%)

### Morphology Analysis

The SEM micrographs of PAA and PAA/HP (10 wt%) nanocomposites are shown in Fig. 2. It can be observed that the surface morphologies of superabsorbents changed greatly after the incorporation of HP. PAA displays a dense, tight and smooth surface (Fig. 2a); while the nanocomposite PAA/HP (10 wt%) present an undulant and coarse surface (Fig. 2b). The improved surface roughness may facilitate the permeation of water into the polymeric network and improve the swelling ability of the superabsorbents. Furthermore, SEM micrographs revealed that HP power were almost embedded within the polymeric networks and more finely dispersed in the polymer matrix, which can be further evidenced by TEM analysis (Fig. 3). It can be clearly observed that HP existed in the composite in the form of needle-like crystals having a diameter of 42 nm and a length of 270 nm, indicated the nanoscale dispersion of HP in the nanocomposite.

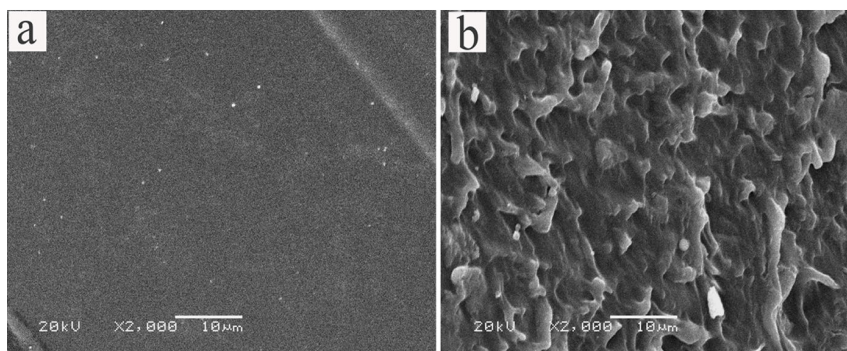


Fig. 2 SEM micrographs of (a) PAA and (b) PAA/HP (10 wt%)

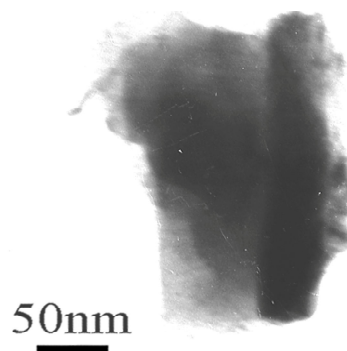


Fig. 3 TEM micrographs for the PAA/HP (10 wt%)

### Effect of HP Content on Water Absorbency

The influence of HP content on the water absorbency is shown in Fig. 4. It is clear that HP content plays an important role to the equilibrium water absorbency of the nanocomposites. The equilibrium water absorbency of the nanocomposite slightly decreased when the content of HP is less than 10 wt% and then decreases rapidly with the further increase of HP content. This may be attributed to

the fact that HP could react with AA and result in the generation of more crosslink points in the polymeric network, which decreased the elasticity of the polymer chains. Additionally, excess HP was physically filled in the polymeric network and the amount of hydrophilic groups on the polymeric backbone decreases with the increase of HP content. As a result, the osmotic pressure difference between the polymeric network and external solution was decreased, causing a decrease of water absorbency.

### Swelling Kinetics

The swelling kinetics of PAA and PAA/HP are shown in Fig. 5. It can be seen that the swelling rate of the superabsorbent nanocomposite underwent a great change in the first 30 min, and then the curves of the swelling rate became flatter. In this section, the swelling kinetics was studied by means of a Voigt-based viscoelastic model,  $Q_t = p(1 - e^{-t/r})$  (Eq. 2) [11].  $Q_t$  is the swelling capability at time  $t$  (g/g);  $p$  is the power parameter (g/g), denoting the theoretical equilibrium water absorbency;  $r$  is the rate parameter, denoting the time required to reach 0.63 of equilibrium water absorbency.  $r$  and  $p$  values can be obtained by fitting experimental data using Eq. 2.

The rate parameter  $r$  is a measure of the swelling rate, and a lower  $r$ -value can mirror a higher swelling rate. Thus, according to the calculated  $r$  value (4.03 min, 3.21 min, 3.71 min and 3.74 min for PAA for PAA/HP (10, 20 and 30 wt%), respectively), it can be concluded that the swelling rate for each sample decreased in the order: PAA/HP (10 wt%) > PAA/HP (20 wt%) > PAA/HP (30 wt%) > PAA. As discussed above, the incorporation of HP can improve the surface structure of the resulting superabsorbent nanocomposites (Fig.2b), and therefore facilitate the permeation of water into the polymeric network, resulting in a higher swelling rate. However, the swelling rate is decreased when the content of HP exceeds 10 wt%. This is due to that excess HP is physically filled in the polymeric network which can hinder the diffusion of water molecules, and thus decreased the swelling rate. From this discussion, it was concluded that the moderate incorporation of HP into PAA network can improve the swelling rate of superabsorbent.

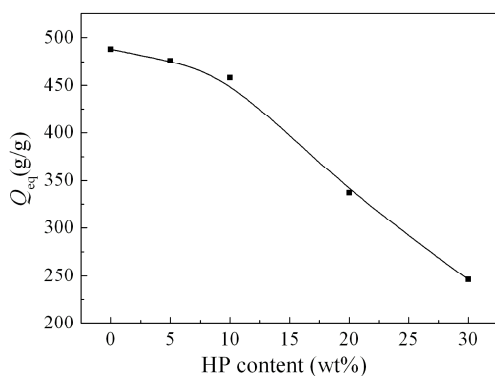


Fig. 4 Effect of HP content on water absorbency

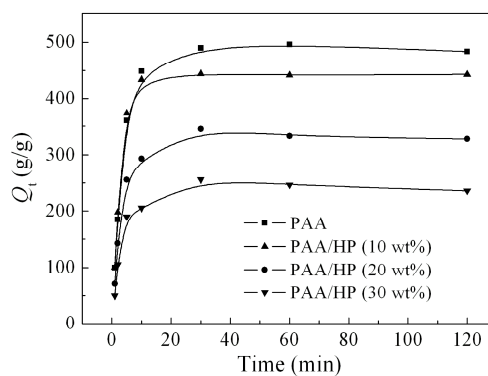


Fig. 5 Swelling kinetics of PAA and PAA/HP superabsorbent nanocomposites

### Effect of External pH on Water Absorbency

The effect of pH values on water absorbency is shown in Fig. 6. The equilibrium water absorbencies for both PAA and PAA/HP nanocomposites keep roughly constant in the pH range from 4 to 11. This behavior was interpreted as a buffer action of  $-\text{COOH}$  and  $-\text{COO}^-$  groups [12, 13]. However, at lower pH values ( $\text{pH} < 4$ ), the  $-\text{COO}^-$  groups are protonated to  $-\text{COOH}$  groups, and the hydrogen bonds between  $-\text{COOH}$  groups are formed, which result in a decrease in swelling ratio. Moreover, at higher pH values ( $\text{pH} > 11$ ), most of  $-\text{COOH}$  changes into  $-\text{COO}^-$ , and thus the screening effect of the counter ions, i.e.,  $\text{Na}^+$ , may shield the charge of the  $-\text{COO}^-$  anions and decrease the repulsion of polymeric chains. So, a remarkable decrease in equilibrium swelling was also observed. The incorporation of HP into PAA polymeric network would not influence the water absorbency of superabsorbent nanocomposites in different pH values, which will be in favor of its practical application in many fields.

### Effect of HP on Reswelling Capability

The reswelling capabilities of PAA hydrogel and PAA/HP nanocomposites with various amounts of HP were evaluated and shown in Fig. 7. The equilibrium water absorbency of PAA decreases gradually with increasing reswelling times. This may be attributed to the breakage of crosslinking points of the crosslinked network in the repeating process of swelling-deswelling. Thus, the polymeric network for holding water diminished and the equilibrium water absorbency decreased. However, the equilibrium water absorbency of PAA/HP nanocomposites slightly increased, and then decreased with further increasing reswelling times. The reasons may be as follows: the crosslinking density of PAA/HP is relatively higher than PAA because HP can act as crosslinking points in polymeric network. As increasing reswelling times, some crosslinking points were broken and the resulting superabsorbents had a proper crosslinking density to hold a relatively more water. However, the crosslinking density decreases sequentially with further increasing reswelling times and ultimately results in the decrease of water absorbency. The equilibrium water absorbency of PAA decreases from 491 to 382 g/g after reswelling for five times, and only 77.8% of its initial saturated water absorbency is retained; whereas the nanocomposite doped with 10 wt% HP retained 87.6% of its initial equilibrium water absorbency after reswelling for five times. The above result allowed the suggestion that HP can act as an assistant crosslinker in the polymeric network. This characteristic makes the resulting nanocomposite show an excellent reswelling ability and thus is proved to be a useful recyclable superabsorbent material.

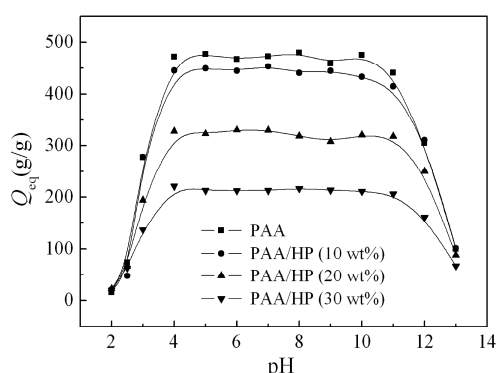


Fig. 6. Water absorbency of the superabsorbents as a function of pH values

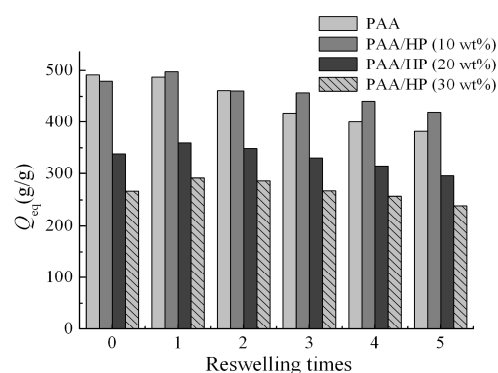


Fig. 7. Water absorbency of the superabsorbents as a function of reswelling times

## 4 Summary

A series of new superabsorbent nanocomposites were prepared by solution polymerization of partially neutralized acrylic acid (AA) and hydroxyapatite (HP). FTIR spectra reveal that HP participated in graft copolymerization reaction through its reactive P-OH groups. TEM analysis confirms the nanoscale dispersion of HP in the nanocomposite. All testing samples keep constant water absorbency in a wide range of pH from 4 to 11, which is beneficial to their application in agriculture for various soils. HP had greatly influenced the equilibrium water absorbency, swelling rate, and reswelling capability of the superabsorbent nanocomposites. In spite of the equilibrium water absorbency decreases with increasing HP content, the introduction of HP nanopowder into PAA polymeric network could not only enhance the swelling rate, but also improve the reswelling capability of the nanocomposites. The nanocomposite doped with 10 wt% HP could retain 87.6% of its initial equilibrium water absorbency after reswelling for five times. These results indicate that HP not only acts as a substrate, but also serves as an assistant crosslinker in the polymeric network.

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