

Novel Degradable Superabsorbent Materials of Silicate/Acrylic-Based Polymer Hybrids

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ABSTRACT: Novel superabsorbent materials, inorganic-organic hybrids, were synthesized by polymerizing acrylic acid or acrylamide with sodium silicate without any other crosslinking agent. The crosslinking bonds of Si—O—C form through the reaction of carboxyl groups with silanol groups (Si—OH) existing in reaction system. Results of FTIR, swelling, and degrading experiments show that the crosslinking degree increased as the mol ratio of silicate increased in a certain range. The hybrids possess the properties of high absorbency and high absorption rate in both distilled water and normal saline solution. Because of the

hydrolysis of Si—O—C bonds in aqueous solution, the hybrid hydrogels can degrade in days, and maybe beneficial to environment protection. This property is quite different from those superabsorbent polymer crosslinked with organic crosslinking agent. By monitoring the temperature of the reaction system, sodium silicate was also found to facilitate the Trommsdorff effect in polymerization process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 936–940, 2004

Key words: water-soluble polymers; inorganic materials; crosslinking; composites; swelling

INTRODUCTION

The earliest superabsorbent polymers appeared in the 1960s. Because of their exceptional absorbent capability and potentials in biomedical applications, synthetic superabsorbent polymers have attracted significant attention, especially in the last 30 years.¹ Superabsorbents can be prepared from most of the water-soluble monomers by covalent crosslinkage. The most common route to covalent crosslinking is to copolymerize primary monomer with a multifunctional comonomer such as *N,N'*-methylenebisacrylamide.² In this work, novel degradable superabsorbent composites were synthesized based on inorganic silicate/acrylic polymer hybrids, in which inorganic silanols in the reaction solution played the role of crosslinking agent.

Sodium silicate is very cheap and easily obtained. It can be used to prepare silica-containing organic derivatives directly.^{3–5} Dissociated silanols are formed in the aqueous solution of sodium silicate by adjusting the pH value, and they have better activity compared with methanol, whose structure is similar to silanol.³ Silanols tend to form a Si—O—Si network via condensation catalyzed by acid. If the acid condition is offered by an organic acid with a COOH groups, silanols can react with COOH groups and result in the formation of Si—O—C links.^{6,7} Therefore, sodium silicate is

proposed to be able to crosslink acrylic-based polymers during the polymerization process. In case acrylic acid is partly neutralized, sodium silicate will hydrolyze and condense to form lots of small aggregates of inorganic Si—O—Si networks. On the other hand, the partly uncondensed Si—OH groups on the surface of the aggregates can react with the COOH groups on polymer chains resulting in the crosslinking networks of poly(acrylic acid). The hybrid superabsorbent material with intercrossing inorganic Si—O—Si networks and polymer network structure could be obtained.

For the reason that poly(acrylic acid-*co*-acrylamide) superabsorbents has good absorbent capability in saline solution compared with poly(acrylic acid), the hybrids of silicate/poly(acrylic acid-*co*-acrylamide) were also synthesized and studied. In the present work, FTIR spectra, swelling, and degrading behaviors and heat effects of the hybrids were investigated.

EXPERIMENT

Materials

Acrylic acid (AA) (Tianjin Chem. Co., China) was purified by distillation under the reduced pressure. Acrylamide (AM), potassium persulphate (KPS), sodium hydroxide (NaOH) (Guangzhou Chem. Co., China, analytical grade), and sodium silicate (SS) (Shantou Guanghua Chem. Co., China, analytical grade) were used as received.

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Preparation of superabsorbent hybrids

Two systems of silicate/poly(acrylic acid) hybrids and silicate/poly(acrylic acid-co-acrylamide) hybrids were prepared. The total monomer concentrations were the same in all samples as 40% (w/w). Acrylic acid was neutralized to the degree of 80%. The mol ratios of SS/AA were 0, 0.025, 0.038, 0.051, and 0.058, respectively, and the weight ratios of SiO₂/Na₂O in the initial sodium silicate alkaline solutions were 0, 0.06, 0.08, 0.11, and 0.12, respectively. Potassium persulphate aqueous solution was prepared (0.003–0.155 g/mL).

In a typical synthesis process, the stirring acrylic acid (AA) aqueous solutions (10 g acrylic acid in 5 g distilled water) cooled in an ice bath were neutralized with sodium hydroxide and sodium silicate (SS) solution. After neutralization, the pH values of the mixtures were about 6.3–6.7. In the system of an acrylic acid-acrylamide copolymer, acrylamide (AM) with the mol ratio of AA/AM equaled to 2.3, was dissolved in the solution after neutralization. The pH values of the mixtures were about 6.4–6.8. Then the initiator was added into the solutions. After mixing, the solutions were moved into test tubes and then sealed. The mixtures were kept under 75°C for 1.5 h. The resulted products (transparent gel) were cut into small pieces, washed with ethanol, and dried at 80°C to constant weight. The dried products were powdered with a minigrinder and screened with sieves.

Swelling measurement

An accurately weighed 0.5 g dry sample (150–250 μm) was dispersed in 1 L of distilled water. The swollen gel was taken out at different times and filtered through a 100-mesh nylon gauze. The swollen gel was weighted. The water absorbency at time *t* (*Q_t*) was calculated using the following equation:

$$Q_t = (W_t - W_0) / W_0 \text{ (g/g)} \quad (1)$$

where *W_t* is the weight of the swollen gel at a certain time, and *W₀* is the weight of the dry sample. The equilibrium swelling absorbency for the normal saline solution was determined by the following method; the accurately weighed 0.5-g dry sample was dispersed in 150 mL 0.9% sodium chloride aqueous solution. Swelling capacity was measured after absorbing for 5 h.

Infrared measurement

The Fourier transform infrared (FTIR) analyses were performed on a Bruker Optik Vector 33-MIR spectrometer. Synthesized superabsorbents powder (5.0 wt %) were mixed with KBr and pressed into discs for

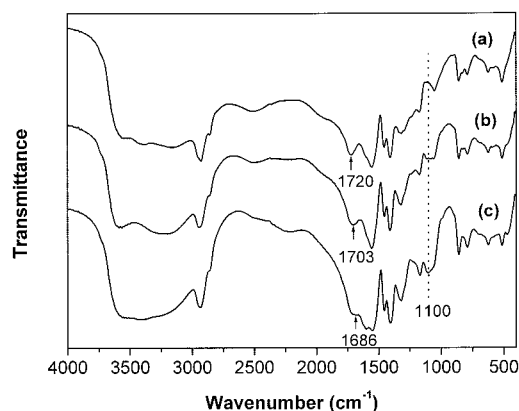


Figure 1 FTIR spectra of SS/PAA hybrids. The mol ratios of SS/AA are (a) 0, (b) 0.025, and (c) 0.051, respectively.

inspection. Transmittances were recorded between the wave numbers of 4000 and 450 cm⁻¹.

RESULTS AND DISCUSSION

FTIR analysis

FTIR spectra of SS/PAA hybrids samples with increasing proportion of sodium silicate are shown in Figure 1. The mol ratios of SS/AA are (a) 0, (b) 0.025, and (c) 0.051, respectively. The absorption regions of PAA and silicon can be observed from these spectra: for PAA partially neutralized, the stretching vibration absorption bands of C=O belonging to COOH (1720 cm⁻¹) and COONa (1556 cm⁻¹ for the symmetrical stretching vibration, 1410 cm⁻¹ for the asymmetrical stretching vibration) are observed in spectra.^{8,9} The absorption at 1170 cm⁻¹ is assigned to the stretching vibration of C—O bonds of COOH.^{8,9} For the samples with inorganic silicate (b and c), a new absorption is observed at 1100 cm⁻¹ (marked with a dot line), and the relative absorption of this band increase with the amount of inorganic silicate proportion. As is known, the bands between 1100–1000 cm⁻¹ can be assigned to Si—O—C bonds.^{8,10} Moreover, the stretching mode absorption of Si—O—Si also locates within the same region.^{5,8,11} Here, the adsorption in this band could be the superposition of Si—O—C and Si—O—Si bonds absorptions. Considering this, the absorption at 1100 cm⁻¹ is not an enough proof for the existence of Si—O—C bonds. Theoretically, the polycondensation reaction of COOH with Si—OH will result in the formation of COOSi bonds, during which the chemical environment of the bridging oxygen atoms in carboxyls will change from OC—O—H to OC—O—Si. As a consequence, the chemical environment of carbonyl groups in carboxyls will also change, resulting in the widening and partially shift of C—O bonds absorption in the spectra of FTIR.¹² This conclusion is well supported by the results of my experiments. With the

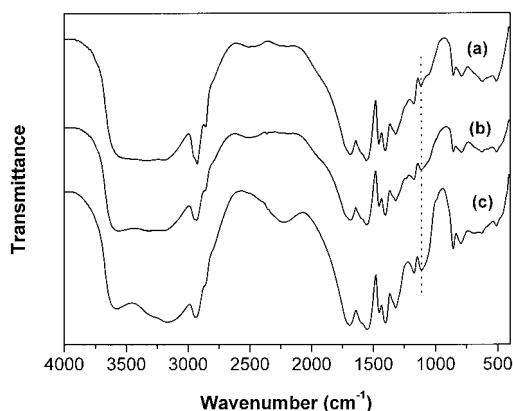


Figure 2 FTIR spectra of SS/P(AA-co-AM) hybrids. The mol ratios of SS/AA are (a) 0, (b) 0.025, and (c) 0.051, respectively.

amount of inorganic silicate increasing, the absorptions of Si—O—Si and Si—O—C bonds in superposition area increase. Furthermore, widened and partially shifted absorption of C=O bonds from 1720 cm^{-1} (pure PAA) to 1703 and 1686 cm^{-1} were also observed in spectra b and c, respectively. This widening and shift can be attributed to the influence of the formation of Si—O—C bonds.

The case of the FTIR spectra of SS/P(AA-co-AM) hybrids showed in Figure 2 is similar to that of SS/PAA hybrids. The absorption at 1100 cm^{-1} is increased as the amount of silicate increasing. No obvious bands shift of C=O stretching vibration can be noticed in the spectra due to the superposition of amide groups absorption (1690 cm^{-1}) and C=O in COOH (1720 cm^{-1}).^{8,9}

More evidences for the existence of Si—O—C crosslinking structure were obtained from the results of swelling and degrading experiments.

Swelling and degrading behavior of hybrids

The results of swelling experiments support that silicate can crosslink PAA, and the crosslinking degree will increase when the amount of silicate in the systems increases in a certain range. Figure 3 shows the dynamic water swelling of SS/PAA hybrids within 50 min. The mol ratios of SS/AA are (a) 0, (b) 0.025, (c) 0.038, (d) 0.051, and (e) 0.058, respectively.

Sample (a), without silicate, has no chemically crosslink in the structure and can dissolve completely within 30 min after being immersed in water. With a mol ratio of 0.025 for SS/AA, sample (b) is partly crosslinked, and can dissolve completely within several hours. As the ratios are within 0.038–0.058, crosslinking degree increases to a certain degree resulting in the products of superabsorbent materials. The equilibrium swelling absorbencies of all these

three samples (c, d, e) are about 1600 g/g . All of the three samples can absorb water by about 1400 times more than its dry weight in 5 min. It seems that the crosslinking degree has no obvious change according to absorbency as the addition of SS increase from 0.038 to 0.058. The reason can be that the polycondensation between silanols is strongly favored when the mass ratio of SS/AA is beyond 0.038, and the majority of silanols in the system is involved in the formation of Si—O—Si networks, while the amount of Si—O—CO bonds is less improved. When the ratio of sodium silicate is beyond 0.058, the systems come into turbid and heterogeneous. This phenomenon can be explained as the macroscopic phase separation occurs in the systems.¹² The large domain size of the inorganic Si—O aggregates cause light scatter; as a result, the system will become turbid and semitransparent. The hybrids with small amount of silicate are transparent because the domain size of inorganic Si—O aggregates are small and the amount of Si—O—C covalent crosslinking bonds are enough to inhibit the macroscopic phase separation.

When the mol ratio of SS/AA is 0.051, the equilibrium absorbencies of superabsorbent hybrids in the 0.9% NaCl aqueous solution are 110 g/g for SS/PAA and 140 g/g for SS/P(AA-co-AM).

The hydrogels of the hybrids have distinct degradable property. The crosslinking structures of the hybrids resulted from Si—O—CO bonds between PAA chains and silicate. For Si—O—CO bonds hydrolyzed in aqueous solution, the hybrids tend to degrade in aqueous solution.¹³ Figure 4 shows the degrading behavior of saturated-swollen SS/PAA hybrids. The mol ratios of SS/AA are (c) 0.038, (d) 0.051, and (e) 0.058, respectively. After 24 h, these three samples lose weight of 45, 37, and 35%, respectively. Forty-eight hours later, the lost weight percentages are 95, 88, and 73%, respectively; and the weights left are 80, 185, and 420 times of its dry weight, respectively. Although the

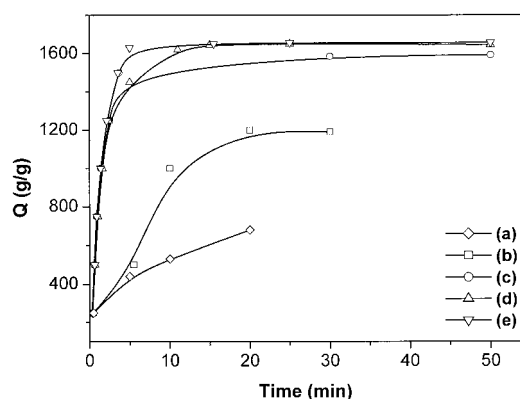


Figure 3 Evolution of water absorbency of SS/PAA hybrids within 50 min. The mol ratios of SS/AA are (a) 0, (b) 0.025, (c) 0.038, (d) 0.051, and (e) 0.058, respectively.

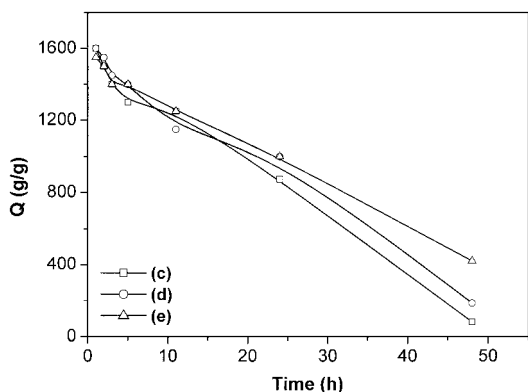


Figure 4 Degrading behavior of saturated-swollen SS/PAA hybrids. The mol ratios of SS/AA are (c) 0.038, (d) 0.051, and (e) 0.058, respectively.

equilibrium absorbencies of the three samples are close, the degrading rates slow down as the amount of silicate increases, which may result from the increase of the amount of Si—O—Si networks in the system.

Figure 5 shows the evolution of water absorbency of SS/P(AA-co-AM) hybrids. The mole ratio of SS/AA is 0.051. The maximal absorbency is about 1600 g/g. The reactions of side functional groups on the PAM can produce part crosslinking bond, so the hybrids of SS/P(AA-co-AM) have higher crosslinking degree.¹⁴ Its absorption rate is slower than that of SS/PAA as about 1400 g/g in 12 min. The degrading rate is also slower than that of SS/PAA. After 24 h, the lost weight is 11%, and left weight is about 1450 times of its dry weight. After 48 and 72 h, the left weight is 865 and 330 times, respectively.

The above-mentioned degradation experiments were all carried out under a saturated swelling state. If the hybrids absorb water less than the saturated amount, the degrading rate will decrease steadily. The hybrids particles with bigger size also have a lower degrading rate.

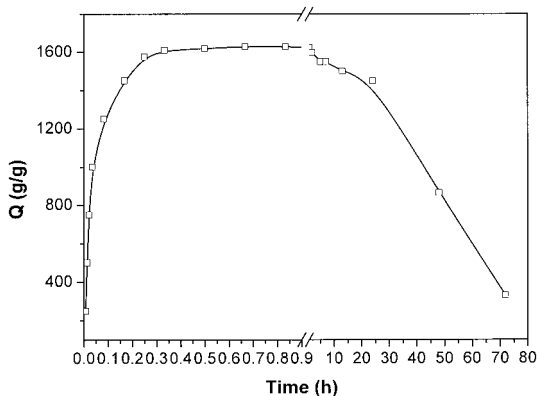


Figure 5 Evolution of waer absorbency of SS/P(AA-co-AM) hybrids vs time. The mol ratio of SS/AA is 0.051.

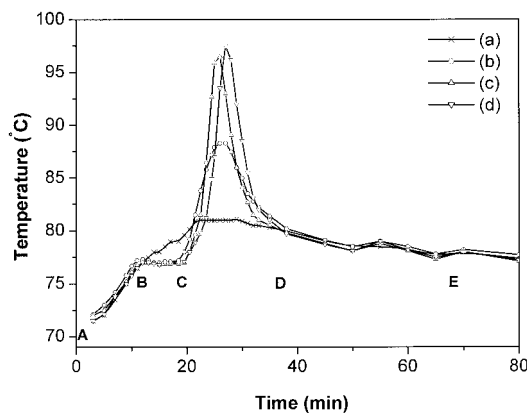


Figure 6 System temperature evolution of SS/PAA hybrids during polymerization. The mol ratios of SS/AA are (a) 0, (b) 0.038, (c) 0.051, and (d) 0.058, respectively.

The degradable property of the synthesized hybrid hydrogels is faster than those crosslinked by organic crosslinking agents, which cannot be totally decomposed even after several months. Consequently, these synthesized environment beneficial hybrids can be applied in those fields of one-off and of short time use with requests of high absorbency and high absorption rate, such as absorbent paper towel, sanitary napkin, or paper diaper.

Heat effect during reaction process

Reaction process of superabsorbent polymer can be traced by monitoring the heat effect with a calorimeter or thermometer.^{15,16} Figures 6 and 7 show the evolution of temperature vs reaction time for SS/PAA hybrids and SS/P(AA-co-AM) hybrids, respectively. In a general reaction of superabsorbent polymer, the heat effect curve can be divided into four parts. In the A → B region, the temperature of the reaction solutions rise

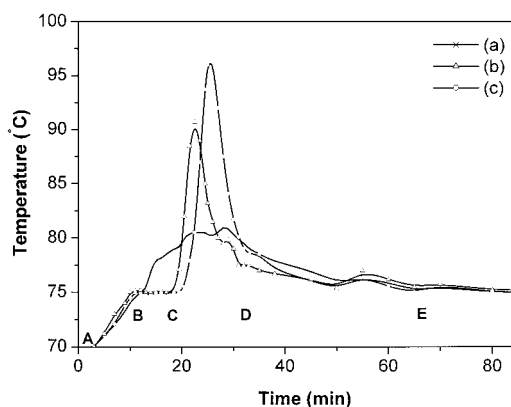


Figure 7 System temperature evolution of SS/P(AA-co-AM) hybrids during polymerization. The mol ratios of SS/AA are (a) 0, (b) 0.038, and (c) 0.051, respectively.

to the preestablished reaction temperature. The B \rightarrow C region is the inhibition period of the reaction. Due to the retardant effect of oxygen or other impurities, there are not enough radical initiators to start the polymerization. In the region of C \rightarrow D, polymerization starts accompanied with an exothermic effect when a sufficient amount of the initiator decomposes. As the viscosity of the reaction system rises, it is difficult for the radicals to diffuse. As a result, the constant of termination reaction becomes smaller, the rate of polymerization is accelerated, and the heat effect is intensified. There appears an obvious exothermic peak on the heat effect curve, and the highest point of the peak is assigned to the gelation point. This phenomenon is called the trommsdorff effect or auto-accelerating effect.¹⁷ The D \rightarrow E region is postgelation period.

Sodium silicate, to radical polymerization, is a kind of impurity. It can trap the initiator radicals temporarily at the beginning of polymerization, so the start of polymerization is retarded (B \rightarrow C region). Once polymerization begins, crosslinking structures formed, leading to higher viscosity of the system. The trommsdorff effect will be intensified, and the higher gelation temperature appears (C \rightarrow D region). By measuring the temperature of the reaction systems, the addition of sodium silicate is found to facilitate the trommsdorff effect in the polymerization process, and the greater amount of silicate, the greater intensity the exothermic reaction will be.

CONCLUSION

The superabsorbent materials of silicate/acrylic-based polymer hybrids were synthesized. These hybrids have the crosslinking structures achieved by the reaction between carboxyl groups and silanol groups existing in the mixtures. Results of FTIR, swelling, and degrading experiments show that the crosslinking degree increased as the mol ratio of silicate increasing in a certain range.

In both systems of acrylic acid and acrylic acid-acrylamide copolymer, the optimum hybrids have high absorption rate, high water absorbency, and high absorbency in the normal saline solution. The addition

of SS is found to intensify the trommsdorff effect during polymerization process.

The hybrid superabsorbents tend to degrade due to the hydrolysis nature of Si—O—C bonds. The degrading rate of the hybrid superabsorbents is easily controlled. These environmental beneficial superabsorbents show promising prospects in the fields of one-off and of short time use with requests of high absorbency and high absorption rate, such as absorbent paper towels, sanitary napkins, or paper diapers.

In future works, other measurement such as ²⁹Si-NMR should be taken to study the kinetics of the formation and decomposition of Si—O—C bonds in this system. By accurately adjusting the crosslinking structure, more efficient SS/PAA and SS/P(AA-AM) hybrid superabsorbents are anticipated to be prepared.

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