Preparation and Performance of a Superabsorbent with Core-shell Structure

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Abstract

Core-shell organic-inorganic composite nano-hydrogels based on sodium silicate (SS)/ polyacrylic acid (PAA)/chitosan(CS) of about 200 nm were prepared by sodium silicate(SS) sol-gel process and acrylic acid polymerization. The result showed a core-shell structure was formed with SiO2 inner core and CS-PAA/acrylic acid (AA) outer shell. That is, the processes of sol-gel, polymerization and self-assembly between the components were simultaneous. The structure and morphology of the obtained systems were investigated by Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM). Their strength have significant improvement compared to the conventional hydrogel, meanwhile, swelling capacity in salt solutions with different concentration was investigated. The hydrogels are pH-sensitive: their swelling capacity first increase and then decrease as pH value increases.

Keywords

Hydrogel; Sodium silicate; Mechanical property; Sol-gel; Core-shell structure.

1. Introduction

A wide range of industrial and biomedical applications has been proposed for hydorgels made from either natural or synthetic sources. However, most of them are confront with the problem of the lack in mechanical toughness. For a long time, many efforts have been focused on improving mechanical properties of hydrogels(Li et al., ; Luo et al., ; Tanaka et al., 2005; Xia et al., 2003). In recent years, four kinds of hydrogels have been developed with novel structure and high mechnical properities. Okumura et al. have report a new kind of topological gel that was synthesized from a polyrotaxane in which a PEG chain with large molecular weight is sparsely populated with a-cyclodextrins(Okumura and Ito, 2001). In this gel, the polymer chains with bulky end groups are neither covalently cross-linked like chemical gels nor do they interact attractively like physical gels, instead they are topologically interlocked by figure-of-eight cross-links. It is expected that these cross-links can pass along the polymer chains freely to equalize the ‘tension’ of the threaded polymer chains just like pulleys. Therefore, it can bear high stress. In 2002, Haraguchi reported the creation of a novel “nanocomposite hydrogel” with a unique organic–inorganic network structure by extending the concept of NC to the field of soft hydrogel materials(Haraguchi and Takehisa, 2002). They have synthesized organic/inorganic nanocomposites by introducing inorganic nano-particles(clay platelets) to act as multifunctional crosslinkers(Haraguchi et al., 2003; Haraguchi et al., 2002). Gong et al. reported that a novel method to construct a double network (DN) structure for various combinations of hydrophilic polymers(Gong et al., 2003). The DN gels are comprised of two independently cross-linked networks. The first network is highly cross-linked and the second network is slightly cross-linked; the hydrogels with high mechanical strength were obtained(Kaneko et al., 2005). A macromolecular microsphere composite (MMC) hydogel with a novel, well-defined network structure and high mechanical strength was reported by Wang et al. (Huang et al., 2007). The MMC hydrogels did not break, even at a stress of 10.2 MPa and a water content of 89%.

In our work, we synthesized a kind of core-shell organic-inorganic composite nano-hydrogels with high mechanical strength through sol-gel progress and acrylic acid polymerization. The sol-gel process has been widely used in the fields of mesoporous materials(Ha et al., 2008)，membrane materials(Kim et al., 2005) and intelligent hybrid hydrogels(Cupane et al., 2002), but it is seldom reported in synthesis of super absorbent hydrogels. In addition, most of the used silica precursors do not dissolve enough in water, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS)(Pereira et al., 2000; Sahiner, 2006), co-solvents and catalysts are often needed due to the low water solubility and reactivity of these compounds. Sodium silicate (SS) is chosen, in this work, as a water-soluble inorganic silica precursor due to the low cost and good degradability. Chitosan, a kind of nature polysaccharide, having structural characteristics similar to glycosaminoglycans, is non-toxic and biodegradable(Muzzarelli et al., 1988). All these important properties make chitosan a very interesting component of hydrogels in the medical and pharmaceutical fields. Nowadays, chitosan is widely used in synthesis of chitosan-poly(acrylic acide) nanoparticals(Chen et al., 2005; Ding et al., 2006; Hu et al., 2005; Hu et al., 2002), in our work, chitosan was introduced to form PAA-CS polyelectrolyte complex as one part of the shell for improving mechanical properties of hydrogels.

2. Experimental

2.1 Materials

Acrylic acid was purchased from Tianjin Guangfu chemistry reagent factory, sodium silicate was purchased from Shanghai shisihewei Chem. Co. N, Chitosan was purchased from Tianjin Geleiman chemical institute, the degree of deacetylation was about 90%. N'-methylene bisacrylamide (MBAM) and ammonium persulfate (APS) were purchased from Shanghai Chemical Co and Xi'an Chemical Co respectively. All reagents were of analytical grade and used directly without further purification.

2.2 Preparation of hybrid hydrogel

The chitosan was dissolved in 15 mL 1 wt% AA. Sodium silicate (SS) and sodium hydroxide solution were added to the chitosan solution. The stirring acrylic acid (AA) solutions cooled in an ice bath were neutralized by the above solution. The amount of AA was maintained constantly at 5 g in all experiments. The MBAM and APS were added and fully mixed. Then the mixture was stirred at room temperature for 24 h to get the homogeneous solution. The solutions were transferred into plastic tubes and sealed, and then standed at room temperature to react. Then the products were washed with deionized water to remove the soluble monomers and polymers. The resulting hydrogel was dehydrated with ethanol then dried at 80 ℃ to a constant weight. The dried product was milled to 20-40 mesh.

2.3 Swelling measurement

0.1 g sample was immersed in 250 mL deionized water or 100 mL sodium chloride solution for 12 h to reach swelling equilibrium. The swollen sample was filtered by 100 mesh nylon gauze. Swelling ratio (SR) of hydrogels was calculated as follows:

$$SR = \frac{m_1 - m_0}{m_0}$$

m_1 and m_0 are the weights of swollen gel and the dry sample respectively.

2.4 Mechanical strength measurement

Mechanical performance of hydrogel was evaluated through compression test using homemade equipment, which was made following the previous reference(Ramazani-Harandi et al., 2006). The swollen sample was cut into a disk with a thickness of 10 mm and a diameter of 30 mm.

2.5 Characterization

FTIR measurements were performed on a BRUKER EQINOX55 FTIR spectrometer. All spectra in the range 400-4000 cm^{-1} with 2 cm^{-1} spectral resolution were obtained from compressed KBr pellets in which the samples were evenly dispersed. TEM observation was conducted on a HITTACHI H-600 transmission election microscope at an acceleration voltage of 75 kV.

3. Results and discussion

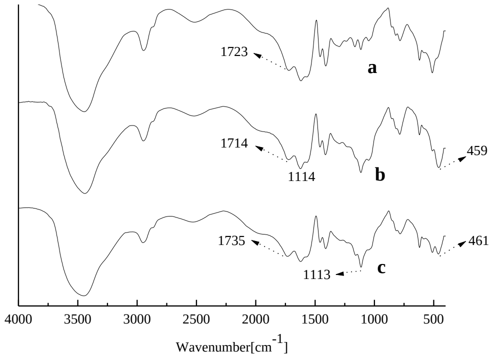


Fig. 1. FTIR spectra of hydrogel.(a)AA; (b)SS/AA; (c) SS/PAA/CS.

IR spetra of AA, SS/AA and SS/AA/CA were shown in Figure 1. In the spectra of AA, the absorption bands at 3444 and 1722 cm^{-1} are ascribed to hydroxyl groups and carbonyl groups of AA respectively. However, the absorption bands shift to 3440 and 1713 cm^{-1} after SS was introduced, which reveals that strong hydrogen-bonding interaction between carboxyl groups of AA and hydroxyl groups on the surface of silica cores. Meanwhile a strong peak at 1113 and a middle peak at 458 cm^{-1} corresponding to the symmetrical and bending stretching vibration of Si-O-Si. In the spectra of SS/AA/CS, we can see the significant shift from 3440 and 1713 cm^{-1} to 3448 and 1734 cm^{-1} respectively, which indicates that the existence of amino groups weakens hydrogen-bonding interaction between carboxyl groups and hydroxyl groups dramatically.

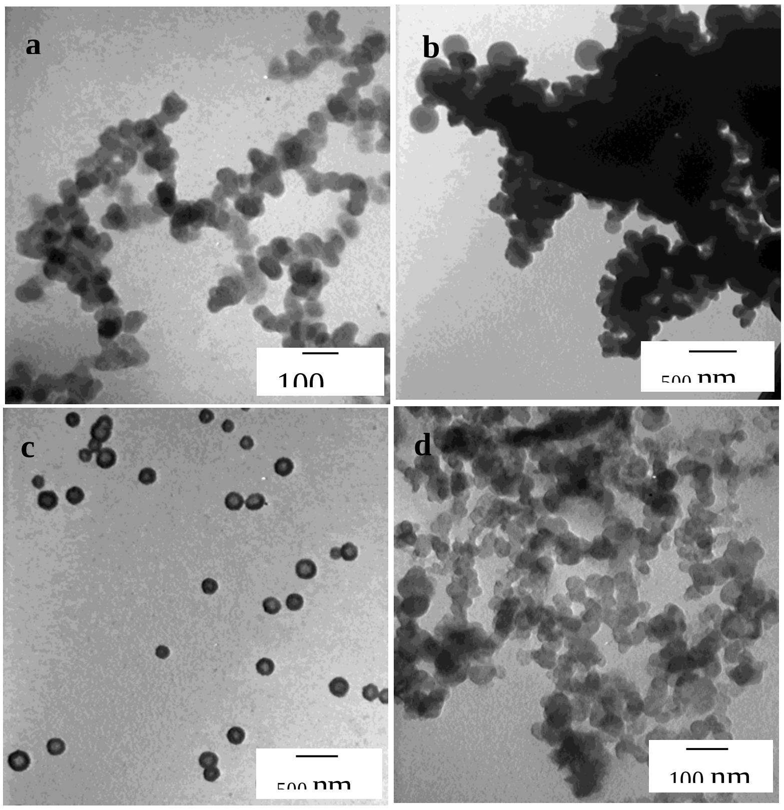
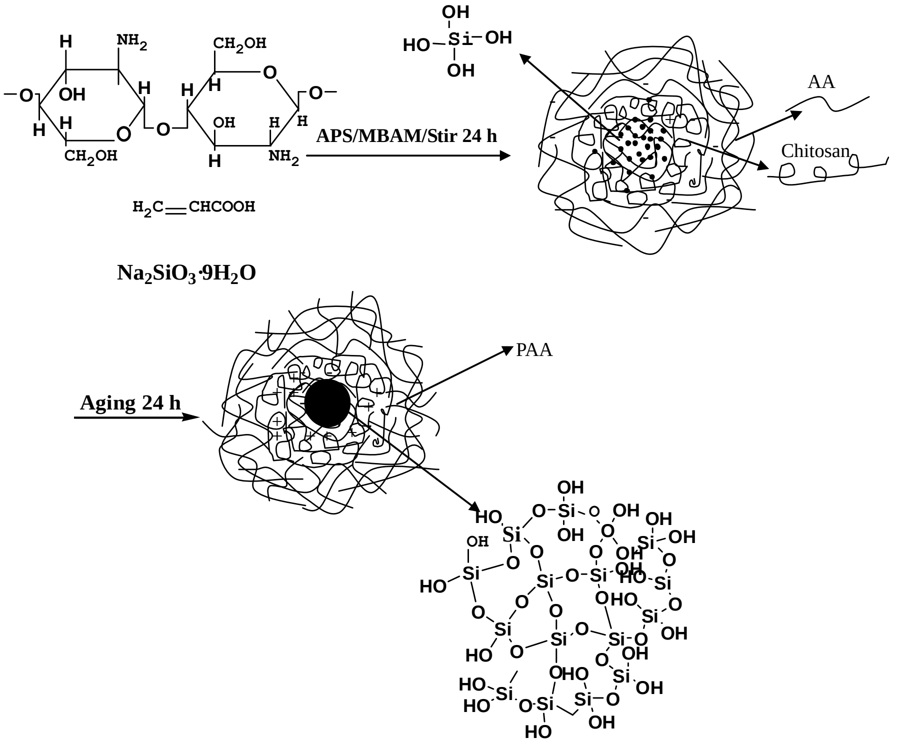


Fig. 2. Morphology of hydrogels(mass ratio of CS/AA was 0.09). a: AA/CS; b: SS/PAA/CS; c: SS/PAA/CS after eroded by HF; d: SS/PAA/CS whithout MBAM.

Transmission electron microscopy (TEM) was used to characterize the morphology and size of hybrid spheres. An intact spherical morphology with an average size about 50 nm is observed (Figure 2a). Ahn et al. (Ahn et al., 2001) had reported that acrylic acid could have undergone template polymerization in CS solution. In our case,we thought that the AA/CS nanoparticles were also prepared by template polymerization of acrylic acid in chitosan solution using chitosan as the template. We speculate that the hybrid spheres are composed of PAA-CS polyeletrolyte complex in the inner and PAA on the exterior. This may be due to the fact that there is excessive AA in the solution, and that some AA neutralized by NaOH is negatively charged. Some of the negatively charged PAA molecules were absorbed onto the surface of PAA-CS nanoparticals. In Figure 2b,the size of hybrid spheres has significant increase, it is about 200 nm. In order to confirm the structure of the hybrid spheres, the microscopy of SS/AA/CS after eroded by HF solution for 48 h at ambient temperature was investigated (Figure 2c). One can see some hollow nanospheres. A reasonable speculation is that addition of SS does not change the formation of AA/CS hybrid spheres. Since there is an interaction between –OH of SS after hydrolysis and –COOH of PAA, silica beads should be incorporated into PAA/CS hybrid spheres. These results indicate that the SS/PAA/CS hybrid spheres with cores of silica beads and shells of PAA/CS composite. In addition, we have confirmed the outer layer is PAA by TEM (Figure 2d). Compared to Figure 2c the average diameter of microspheres was significantly decreased, when there was no MBAM was introduced(Figure 2d). Just like the reference(Hu et al., 2002), in which the author stated that when the CS-PAA nanoparticals were dried to the TEM characterization, the water, which swelled the PAA cores,was removed off and formed some cavities in the cores. In the region, electron beams could easily pass though the CS-PAA nanoparticals, which resulted in a light region in the TEM photograph. So, In our paper, we speculate the outer layer is PAA according to the decrease of average diameter of the micropheres. Base on this, the formation process proposed is shown in Scheme 1. The silica precursors were hydrolyzed into silanols under the existence of AA after stirring for 24 h. Silanols can interact with –COOH of AA to form H-bonding, in addition, some carboxylic groups of AA are dissociated into COO- groups which complex with protonated amino grpups in CS through electrostatic interaction to form the polyelectrolyte complex as one part of the shell. Some AA neutralized by NaOH is negatively, some of the negatively charged AA molecules were absorbed onto the surface of PAA-CS nanoparticals. During aging the silanols condensed gradually to form a Si-O-Si inorganic network, just as an inorganic silica sphere to be the core, meanwhile, AA was polymerized to construct a organic netwok cover on the polyelectrolyte of PAA-CS as the other part of the shell.



Scheme. 1. Proposed formation process of SS/PAA/CS hydrogel with core-shell structure

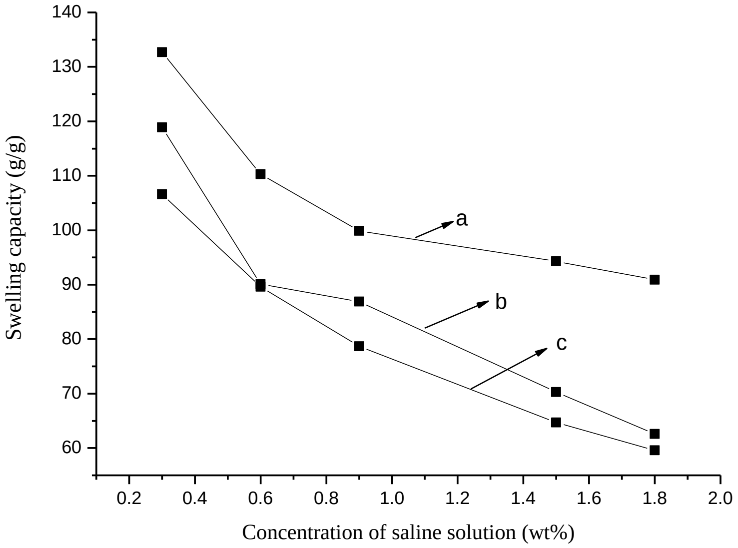


Fig. 3. The swelling behavior of SS/PAA/CS hydrogel under different salt concentrations. CS/AA (w/w) ,a=0.03; b=0.06; c=0.09.

The swelling behavior of SS/PAA/CS hydrogel under different salt concentrations was investigated. As shown in Figure 3, the hydrogel has certain salt-resistant ability under low mass ratio of CS/AA, for example, when the mass ratio of CS/AA is 0.03, the salt tolerance experiments showed only 10.0% decrease. But the swelling ratios of SS/PAA/CS hydrogels gradually decrease with increasing the contents of CS. The most possible reason is that with the increase of CS more and more NH_3^+ combined with COO^- to form interpolyelectrolyte complex between CS and PAA. The polyelectrolyte complex is hydrophobic, so it confine the swelling of hydrogels. Just because of this, the compressive strength of SS/PAA/CS hydrogels increase with increasing the contents of CS.

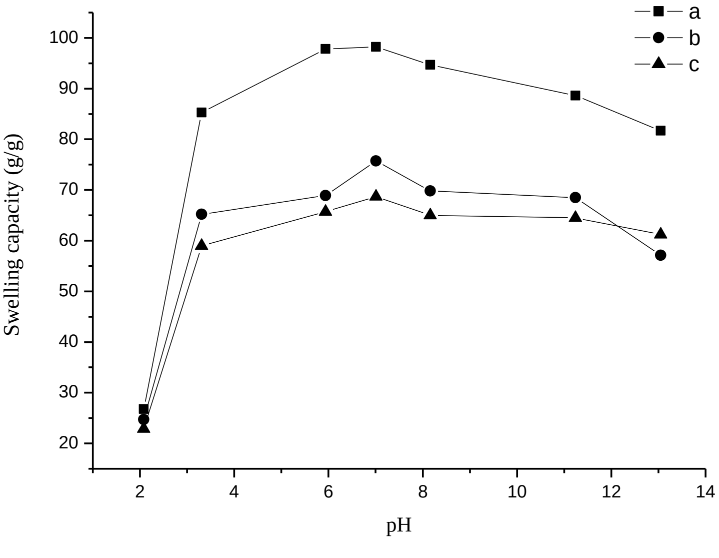


Fig. 4. The swelling behavior of SS/PAA/CS hydrogel under different pH. CS/AA (w/w) ,a=0.03; b=0.06; c=0.09.

In order to investigate the effect of pH values on SS/PAA/CS nanocomposite a series of experiments were carried out. It is found that the swelling ratios under stronger acidic conditions, such as pH<3.3, most carboxylic groups of PAA are in the form if –COOH. The interacton between NH_3^+ and COO^- could be disrupted by the acid of small molecules,but the hydrogen-bonding interaction between carboxylic groups of PAA and –OH on the surface of silica cores was enhanced. So the swelling ability was limited to some extent. As the increase of pH from 3.3 to 5.9 CS and PAA are partly ionized, the interacton between NH_3^+ and COO^- generated, meanwhile the hydrogen-bonding interaction between carboxylic groups of PAA and –OH on the surface of silica cores was weakened. Under the two effects made the swelling ability has little increase. At pH 7.0, the situation is quite different, as the PAA is highly ionized while CS is ionized minimally. Thus, the electrostatic repulsion between COO^- groups of PAA becomes dominant inside nanospheres, which causes a swelling of whole structure. Beyond this value, a screening effect of the counter ions, i.e., Na^+, shielding the charge of the carboxylate anions may prevents from an efficient repulsion. As a result, a remarkable decrease in equilibrium swelling is observed.

Table 1. Compress tests of SS/PAA/CS hydrogels.

Mass ratio of SS/AA	Mass ratio of CS/AA	Hydrogel strength	
		Compressive Strength (KPa)	Water Content (%)
0.23	0.015	39.7	99.6
0.23	0.03	40.8	99.6
0.23	0.06	50.5	99.4
0.23	0.09	57.9	99.1

Crosslinker content=0.03 wt%, initiator=2.5 wt%, neutralization degree=65%

The mechanical properity of SS/PAA/CS hydrogels with different mass ratios of CS/AA were measured by using compressive tests(Table 1). The hydrogels showed high compressive strength even under high water content of more than 99% while traditional organic superabsorbent hydrogels are relatively fragile. In comparison, the compressive strength of a poly(acrylamide-co-acrylic acid)/polyethylenimine hydrogel only reached 29 KPa, with a maximum swelling ratio of less than 250 g/g(Kim and Park, 2004). The form of the core-shell nano-microspheres was favorable to improve the mechanical properties of hydrogels.

4. Conclusion

A core-shell organic-inorganic composite nano-hydrogel was synthesized by sol-gel process and AA polymerization. The hydrogel has certain salt-resistant ability under low mass ratio of CS/AA. The hydrogels are pH-sensitive: their swelling capacity first increase and then decrease as pH value increases. A good compressive strength was obtained when the mass ratios of SS/AA and CS/AA were 0.23 and 0.09, respectively. In addition, CS is non-toxic and biodegradable. On the basis of those merits, this hybrid hydrogel could be used to make bioactive scaffold for biomaterials. Furthermore, due to their pH-Sensitive behavior, these SS/PAA/CS core-shell organic-inorganic composite nano-hydrogels have potential application in drug delivery.

Acknowledgments

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