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ORIGINAL PAPER

Effects of silica sol content on the properties of poly(acrylamide)/silica composite hydrogel

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Abstract Silica sol was first used as an inorganic component to form poly (acrylamide) (PAM)/silica composite hydrogels via in situ free-radical polymerization. The gelation reaction of the composite materials was monitored on a rheometer, indicating that the gelling induction time becomes longer with the increasing content of silica sol. Compression strength and elastic modulus of the composite hydrogels were significantly improved by adding silica sol compared with pure PAM hydrogels. Silica particles formed by silica sol were dispersed on the surface of PAM polymer network in nanosize, promoting high degree of attachment to the polymer chain and enhancing the interfacial interaction between these two components. TGA analysis showed that the silica stiffens the hydrogel network by creating additional physical cross-linking point, but the breakable nature of the bonds and a broad distribution of distances between crosslinks may creates most likely a wide dissipative zone.

Keywords Silica sol · Composite hydrogel · Induction time · Nanosize · Compression strength

Introduction

Composite hydrogels which composed of organic(polymer)/inorganic network have received a great deal of attention as a new type of polymer gel [1–5]. It contains the advantages of organic and inorganic component. Thus, they are of interest for a number of applications, such as in agriculture, medical and health, construction, petroleum chemical industry, daily chemical, food, environmental protection and

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other areas, and it is still in the wider application areas, especially in biomedical applications [6, 7].

PAM hydrogel is prepared by AM monomer, initiator, cross-linking agent through free-radical polymerization in solution. Usually, such PAM hydrogel has good water-soluble, high reactivity and in vitro low toxicity, can be endowed with different performance has been widely applied in efficient catalyst, biological engineering, drug release, etc. [8]. But the mechanical properties of ordinary polymer gel were weak, fragile, lower toughness. To increase the mechanical strength of the PAM hydrogel, in previous work, many used clay [2, 3], silica gel [4], and silica precursor [5] as the inorganic component in previous polymer/inorganic system to improve the mechanical properties of them. But an avenue of research about PAM hydrogel complex with silica sol has been far neglected.

Silica sol is a dispersion system of amorphous silica particles in water, which can be divided into acid and basic sol according to the pH value. Due to the strong surface activity of hydrogen groups on the surface of silica particles, it can mix and react with organic polymer. Thus, it was widely applied in organic and inorganic composites. Because of the presence of hydroxyl group, when on standing, silica particles could form hydrogen bonds to construct a space stereo 3D mesh structure in the system [6]. Silica particles would precipitate from the solution system with the variations of environment. For more, different application of silica sol requires different property index, but whatever the purpose, the particle size distribution and dispersion of silica sol is the most important index. Although silica sol has not previously been used in PAM hydrogel, it has been approved for use in organic and inorganic composites. Suo et al. [9] synthesized multilayered poly(vinyl alcohol) (PVA)/silica composites through silica colloid solution which the particle size is about 80 nm. It achieved a significant enhancement in tensile strength and ductility. The results showed that extensive plastic tearing took place in monolayered composites with low-silica contents and in all multilayered ones, whereas the monolayered composites with high-silica contents were dominated by brittle fracture. The enhanced properties of the multilayered composites also can be attributed to the interaction between silica and PVA by chemical bonds. And Creton et al. [10] have shown that the adsorption of PDMA chains on silica nanoparticles leads to the formation of a physical network, implying that the strength of the adsorption will be important for the mechanical properties even in the case where both physical adsorption and chemical covalent bonds are present. Such chemically cross-linked gels containing physically adsorbed polymers on silica nanoparticles materials provide a very general route for improving the properties of hydrogels. This type of architecture is widely used for filled rubbers where the chemically cross-linked rubber structure coexists with a physically interacting network of filler particles [11]. It indicated the inorganic particles deriving from silica sol played an important role in strengthening and toughening these materials.

On the basis of this idea, we aim to prepare a series of PAM composite hydrogels containing different contents of silica sol using in situ free-radical polymerization. The specific objective was to investigate the potential reinforcement and mechanism of the silica in PAM hydrogels, thereby the system has efficient, economic and practical value. We first monitored the gelation reactions of acrylamide (AM), *N*,*N*′-methylenebisacrylamide (MBAM) and silica sol in aqueous solutions using rheology tests. The gelation reactions were carried out with silica content varied between 0 and 10% in relation to the whole system. Microstructure of dry composite gels was also studied. Additionally, the mechanical properties and thermal behavior of the composite hydrogel were also considered. Detailed results are then discussed.

Experimental section

Materials and measurements

Silica sol was supplied from the Jiangyin Chemical Co., Ltd (CH83-125, 25.24 wt% SiO_2, mean grain size: 8–10 nm, pH 9.82, the density ρ is 1.17 g/cm^3). MBAM and ammonium persulfate (APS) were purchased by SCRC. AM was supplied by Tianjin Kermel chemical reagent Co., Ltd. All other chemicals were of analytical grade and used as received.

Rheological measurements were carried out using a rheometer (TA instruments Rheology Division, AR 2000) with parallel plate geometry. The mixture solution was heated to the desired temperature (65 °C) directly in the rheometer and then covered with mineral oil to prevent evaporation during the measurement. In each measurement, storage modulus was recorded at the frequency of 1.0 rad/s. The morphologies of the as-prepared samples were observed by a Hitachi S-4800 field emission-scanning electron microscope (FE-SEM), at an acceleration voltage of 10.0 kV. The thermal property of the samples were measured by Perkin-Elmer thermal gravimetric analysis (TGA) from 50 to 1000 °C at a heating rate of 25 °C/min^{-1} in N_2 atmosphere. The prepared composite hydrogel were allowed to dry under vacuum to constant weight and the resultant dried hydrogels were then coated with a thin layer of gold. The compression tests were carried out using Microcomputer Control Electronic Universal Testing: VMT4204. The loading speed is 2 mm/min. During the compression test, hydrogel samples are shaped in the PTFT cylindrical molds (8 cmφ × 6 cm).

Preparation of PAM/silica composite hydrogels

Standard techniques were used to prepare the hydrogel. A mixture of AM, MBAM, silica sol, and distilled water was stirred vigorously to produce a homogeneous and transparent solution. Then APS was added into the solution as the initiator and heated in a constant temperature water bath at 65 °C for reaction. The reaction time was at least 24 h till AM monomer was completely polymerized. The fixed mass ratios of [AM]:[MBAM]:[APS] at 100:5:1 were used for all the gels. The mass function of AM used in these systems was 10%. Similarly, the silica contents used in these systems were under various concentrations of 0, 2.5, 5.0, 7.5, 10, and 15%. And the related nomenclatures were Si0, Si2.5, Si5.0, Si7.5, Si10, and Si15.

Results and discussion

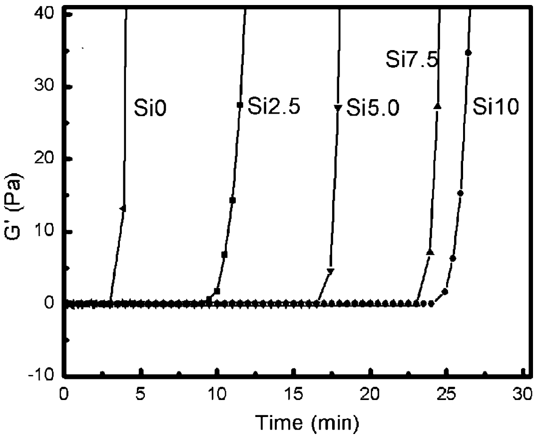
Gelation process

Figure 1 represented the storage modulus G', against the inverse of the time. From hydrogels gelation process, a certain induction period (Stage 2, a final reaction period during which G' are negligible) between 4 and 23 min was observed (Fig. 1). Interestingly, the induction time of PAM/silica composite hydrogel gradually increased with the increasing content of silica (Fig. 1). After a certain period of induction time t_0, G' started to increase abruptly, because of the formation of local clusters by cross-linking reaction. Gelation process always lasts for several hours and the critical sol–gel transition point can be observed on the time course of storage modulus G' [8, 12]. Therefore, the gelling kinetics of the PAM/silica composite gels were described by G'. It implied that it needed time to spread to touch and interact well when the macromolecular chains cross, so the longer induction time indicated increasing content of silica hinder the gelation process of the organic/inorganic system. It was confirmed that the composite hydrogels have been proposed to from both a high degree of heterogeneity in their network, due to the delocalized fracture of the bonds of the network in a large volume. On a more molecular level, it can be speculated that the dissipation occurs as a result of the interactions between the polymer chains and the silica particles in the network. In addition, the introduction of silica particles played an important role in the PAM chain relaxation.

Compression strength and modulus analysis

As depicted in Fig. 2, when the strain ratio between 0 and 2.5%, the stress–stain curve was linear relationship, according with Hooke's law. Thus, we can get the elastic modulus of sample Si0, Si2.5, Si 5.0, Si7.5 from these lines. Under compression stress, the trend of the PAM/silica composite hydrogels have been documented in cross-linked PAM–clay system [13]. As shown by our experiments, the amount of energy required for fracture increased under compression when

Fig. 1 The storage modulus G' of composite hydrogels as a function of polymerization time for different silica content



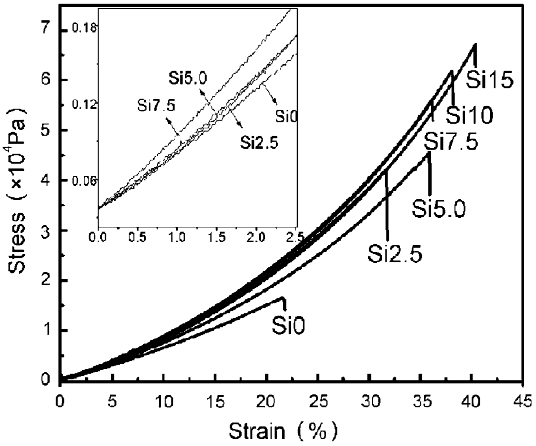


Fig. 2 Reduce stress of the composite hydrogel each curve is calculated from the loading cycle of the hydrogels that undergoes fracture under uniaxial compression

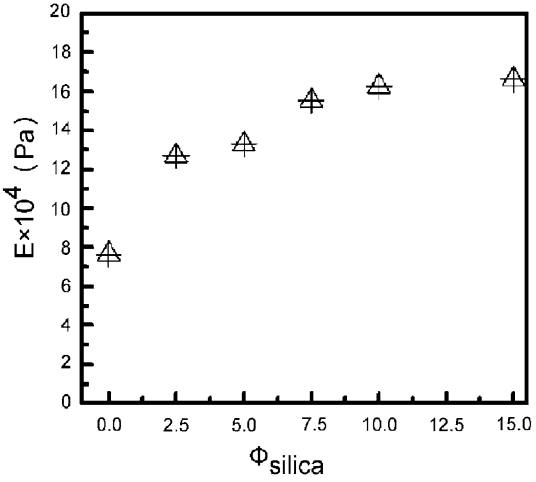


Fig. 3 Modulus *E* versus mass fraction of silica (Φ_{silica}) from compression experiment of the hydrogels undergoes fracture under uniaxial compression

greater amounts of silica were incorporated in the PAM network (Fig. 2). The elastic modulus, *E*, for each of the composite hydrogels was determined from the linear elastic loading portion of the compression and fracture tests [14] (Fig. 3). When the silica content was 15%, its maximum elastic modulus *E* was 1.61×10^5 Pa. It increased with the increasing of the silica mass fraction. The incorporation of the silica nanoparticles in the hydrogels has a notable effect on their compressive strengths and elastic modulus. The material deformed under the action of stress which represents the material's resistance to deformation, the higher modulus of the material is, the greater toughness of the materials. So the PAM/silica composite hydrogels are tough materials. Consequently, the introduction of silica particles was beneficial to strengthen mechanical strength. This was due to the non-covalent or physically crosslink interaction between polymer chains and nano fillers, which is reversible and available to the improved toughness of hydrogels based on the energy dissipation mechanism compared to the pure chemically cross-linked interaction.

The mechanical behavior was more similar to that well characterized physically cross-linked organic/inorganic system of PDMA filled with silica nanoparticles [9].

Structure of dry gels

To observe the distribution of silica particles, the PAM/silica composite hydrogels were allowed to dry under vacuum to constant weight. In Fig. 4a, the pure PAM gels had smooth surface with loose structure because the cross-section had relatively high density to form “island” structure or mesh structure. And this was in accordance with previous report about PAM gel [15]. As shown in Fig. 4b, silica particles appeared in nano degree and the Si5.0 composite gel had the largest aperture (about 300 nm). However, both Fig. 4c and d images showed the silica particles tended to form clusters and the aggregation phenomenon of silica was obvious. At the same resolution, the silica particles did not aggregate in large area when the silica mass function was lower and most of them absorbed on the surface of PAM polymer network. It seemed that the dry PAM/silica composite gels were the porous structure, which reduced precipitation and aggregation. Due to the strong interaction between organic and inorganic phase, the silica had both physical and chemical interaction on the PAM network. Such chemically cross-linked gels containing physically adsorbed polymers with silica nanoparticles materials provide a general route for improving the properties of hydrogels.

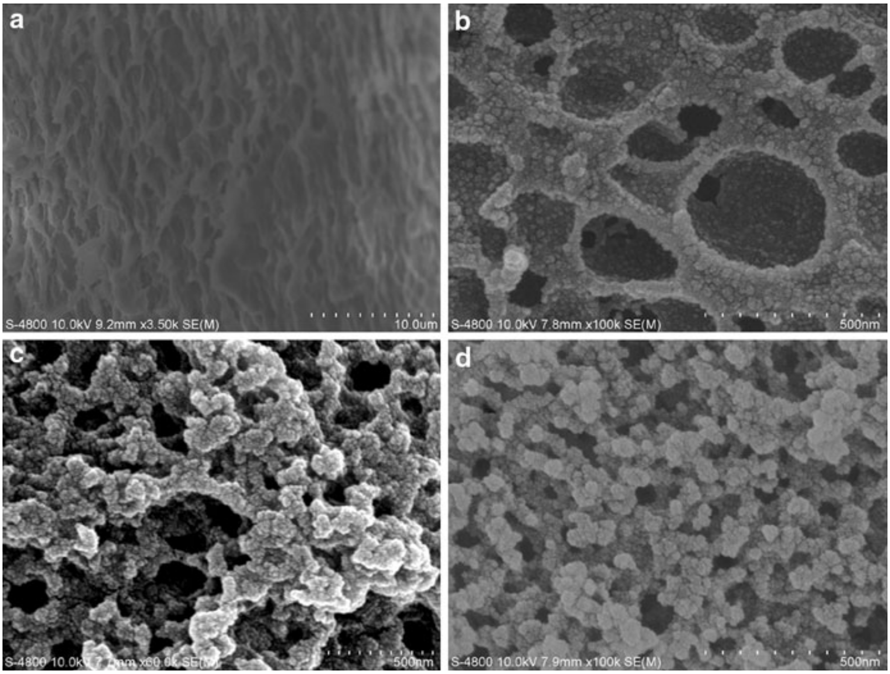


Fig. 4 SEM images of the fracture surfaces of dry PAM/silica sol composite gels Si0 (**a**), Si5.0 (**b**), Si7.5 (**c**), Si10 (**d**) (drying at 40 °C in vacuum)

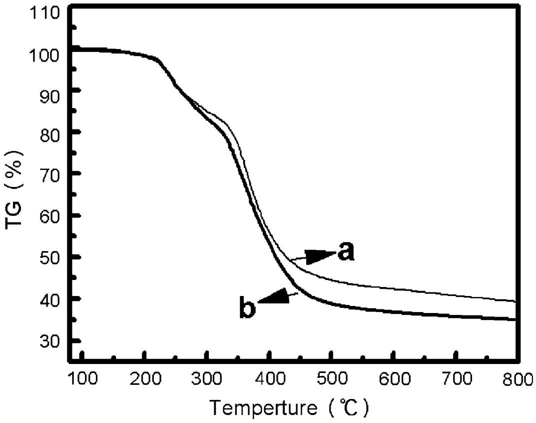


Fig. 5 TGA curves of (*a*) primitive dried sample Si5.0, (*b*) dried sample Si5.0 after swelling in distilled water

TGA analysis

To evaluate the thermostabilty of PAM/silica composite gel and the effect of silica, thermo gravimetric analysis (TGA) was used (Fig. 5). It was evident that the degradation of dry composite gel was affected by the presence of silica. Around 120 °C, this weight loss was assigned to the removal of water in the sample [16]. The weight of PAM/silica dry gel lost at three steps at 245, 358, and 495 °C (T_{max}). These peaks were attributed to possible degradation of AM and different molecular weights of PAM. Moreover, the multistage decomposition also indicated AM monomer was not completely polymerized. The silica particles were bind up by the PAM chain just like using the sol–gel method for the process of nano-particles. Thus, the last weight of the sample was inorganic silica. Additionally, polymer PAM may has H-bonding with the silica strengthen its T_g, compared with the previous reports [17].

As shown in Fig. 5, the total weight loss of Si5.0 was about 58.13%. While the total weight loss of Si5.0 was higher if the dried composite gel swelled again, it was about 62.49%. It showed that the porous structure of the composite gel let the silica particles out if the dry gel was immersed into the distilled water for a few hours. This phenomenon can be explained by the SEM images showing, the dry gel was the porous structure and dry gel moisture-absorbing and swelling with the osmotic pressure. The silica particles separate out because of the opened network structure. Meanwhile, the immersing solution of the gel appears milky floe. At the same time with PAM, pore size was concerned. From the different phenomenon of the samples (Si0, Si2.5, Si5, Si7.5, Si10) immersing solution, the larger porous structure makes more chances for silica separating from the composite hydrogel and more consistent aperture increases the chance of silica particles exhalation. This also coincided with SEM illustration.

Conclusions

In this article, a high toughness of PAM/silica composite hydrogel has been successfully prepared through adding silica sol as the inorganic system. The investigation on the gelation reaction of PAM/silica composite hydrogels demonstrated the fact that increasing mass function of silica hindered the PAM chains relaxation. The PAM/silica composite hydrogels exhibited the absorption of the silica particles onto cross-linked PAM network. And silica particles played an important role in the mechanical properties of the composite hydrogels. Meanwhile, the composite hydrogels showed improved compress strength, which can expand its application as value-added product.

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