

Rheological behaviors and secondary networks of polyacrylamide hydrogel filled with silica

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Abstract Polyacrylamide (PAM) hydrogel filled with different types and contents of hydrophilic silica was synthesized by in situ polymerization. Rheological behaviors of the hydrogels were measured with an oscillation rheometer. The results indicated that the addition of silica efficiently improved the mechanical properties of the hydrogel, both for the uncrosslinked system and crosslinked system; simultaneously, the storage modulus (G'), loss tangent ($\tan\delta$) and viscosity (η) of the hydrogel were obtained. These results suggest that a nonbonded complexation existed between the silica and the molecular chains of PAM that endowed the hydrogel with special behaviors. Results from Fourier Transform infrared spectroscopy (FTIR) showed that the action of the nonbonded complexation was derived from hydrogen bonds between hydroxyl groups of silica and amide groups of PAM. The formed secondary networks endowed the hydrogels with high mechanical properties.

Keywords Hydrogel · Rheological behaviors · Secondary network · Silica · Polyacrylamide

Introduction

Chemical flood is one of the most important enhanced oil recovery (EOR) techniques for oil production and super-absorbent polymers, such as polyacrylamide is widely used

in EOR. Super absorbent polymers (SAPs) are three-dimensional crosslinked networks of hydrophilic functional groups of polyelectrolytes; they can absorb a large amount of water that is much heavier than their masses because of their ionic nature and interconnected structural features (Buchholz 1996; Wan et al. 2008; Chen et al. 2010). Due to this unique characteristic, SAPs have been extensively used in many fields, such as personal care products, agriculture and horticulture, bioengineering, pharmaceutical, drug-delivery systems, food industry, enhanced oil recovery and other advanced technologies (Hua and Wang 2009; Lokhande and Varadarajan 1992; Raju et al. 2003, 2004; Guo et al. 2005; Liang et al. 2007; Sakiyama et al. 1993; Shiga et al. 1992; Yoshida et al. 1989; Hassan and Peppas 2000; Zohuriaan-Mehr et al. 2010; Pourjavadi and Kurdtabar 2010). In many application cases, the SAPs hydrogels are often broken down if they undergo large shear deformation; thus it is important to study and improve their elasticity to resist the shear destroy (Guo et al. 2005; Gosavi et al. 1999; Lee and Huang 2007; Yilmaz et al. 2007).

To improve the elasticity of the hydrogel, SAPs filled with different inorganic fillers have been studied. Santiago et al. (2007) prepared SAP/bentonite composites and studied the effect of the bentonite. Zhang et al. (2006) studied the swelling behaviors of poly(acrylic acid)/organo-attapulgite composite hydrogels in aqueous electrolyte solution. Wang et al. studied the swelling behaviors, and slow-release properties of a poly(acrylic acid-co-acrylamide)/sodium humate superabsorbent composite (Zhang et al. 2006). From the above research, it was found that filling an inorganic filler in a hydrogel is an effective way to improve the mechanical properties of hydrogel, especially their elasticity and anti-shear property.

Silica is a common filler which has a huge specific surface area. Abundant groups on the surface of silica make them

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easily form nonbonded complexations with polymer matrices. Therefore, silica has been widely used in the modification of rubber and plastic. However, only a few works have reported the use of silica in SAPs (Chinthamanipeta et al. 2008; Achilias et al. 2008; Meissner and Matějka 2008).

In the study, different types and contents of silica were novelly introduced into the polymerization system to improve the elasticity of the hydrogel. Both crosslinked and uncrosslinked polyacrylamide hydrogels containing silica were synthesized by in situ solution polymerization. FTIR was conducted to determine the structure of association between the silica and the polymer chains. Oscillation rheometer was performed to measure the rheological behaviors of the hydrogel SAPs. Effect comparisons among the different polyacrylamide hydrogels were made and the mechanism of silica improving polyacrylamide hydrogel with high mechanical properties was proposed.

Experiment

Materials

Acrylamide (AM, Chengdu Kelong Chemical Reagent Factory, China), and polymerizations were initiated by potassium persulfate (KPS, Tianjin Bodi Chemical Industry Ltd, China). Polyethylene glycol diacrylate-600 (PEGDA-600) as the crosslink agent was purchased from Aldrich and sodium chloride was purchased from Kermel Chemical Regent Ltd (China). Silica (H-T40, O-T40, H2000, QS20) was supplied by China BlueStar Chengrand Research and Design Institute of Chemical Industry. All these reagents were analytical grade and used as received. Water used in this study was deionized water unless otherwise mentioned.

Synthesis of silica/acrylamide polymer

The hydrogel was synthesized by free radical in situ polymerization in aqueous solution. The procedure was as follows: AM was dissolved in deionized water and added to a three-necked round-bottom flask equipped with a mechanical stirrer and a nitrogen gas inlet/outlet. Then silica dispersed in the water was also poured into the flask and the reaction solution was stirred under 300 rad min^{-1} to make sure the silica was completely dispersed. The flask was then put into a water bath at $60 \text{ }^\circ\text{C}$ and the polymerization mixture was flushed with nitrogen gas for 30 min, and a mechanical stirrer to exclude oxygen from the system. An aqueous solution of initiator was then added into the reactor. The reaction was carried out at $60 \text{ }^\circ\text{C}$ for 5 h with purging nitrogen. At the end of the reaction, the gel was granulated and dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ for 10 h. Then a white powdered sample was obtained by pulverizing.

Table 1 The specific area and methanol value of the silica used in the paper

Silica	Specific area ($\text{m}^2 \text{g}^{-1}$)	Methanol value (ml g^{-1})
H-T40	400	\
O-T40	400	35.1
H2000	200	23.9
QS20	200	\

Different hydrogels were prepared by changing the silica types (H-T40, O-T40, H2000 and QS20) and content (0, 1%, 2 %, 3 %, 4 % wt). The difference of the four kinds of silica was illustrated in Table 1 and they will be discussed in detail later.

Measurement of properties

FTIR tests

Crosslinked polyacrylamide (CPAM) samples were extracted by Soxhlet extraction using distilled water at $60 \text{ }^\circ\text{C}$ for 72 h, and then the extracted sample was dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ for 10 h. The dried CPAM powder was characterized by Nicolet 560 Fourier transform infrared spectra (FTIR).

Rheological measurements

1 g polymer powder was added to 29 g NaCl saline solution with the mineralization of $50,000 \text{ mg l}^{-1}$ by gentle magnetic stir for 30 min to obtain the hydrogel.

The viscoelastic properties of the hydrogel were investigated by oscillatory measurements on a Bohlin VOR Rheometer (Bohlin Gemini 200, Malvern Instruments Ltd, UK). Samples were squeezed between stainless steel parallel plates (diameter 40 mm, gap 1 mm) and subjected to oscillating rotational deformations at frequencies from 0.01 to 10 Hz at a constant stress (0.1 Pa). Steady-state shear viscosity measurements were performed using the same instrument at shear rates ranging from 0.01 to 10 s^{-1} .

Results and discussion

Rheological properties of linear polyacrylamide (LPAM) hydrogel and crosslinked polyacrylamide (CPAM) hydrogel filled with different contents of hydrophilic H-T40 silica

The elasticity and viscosity are important properties to water-soluble polymer. The change of the polymeric structure will cause the difference of the properties. The

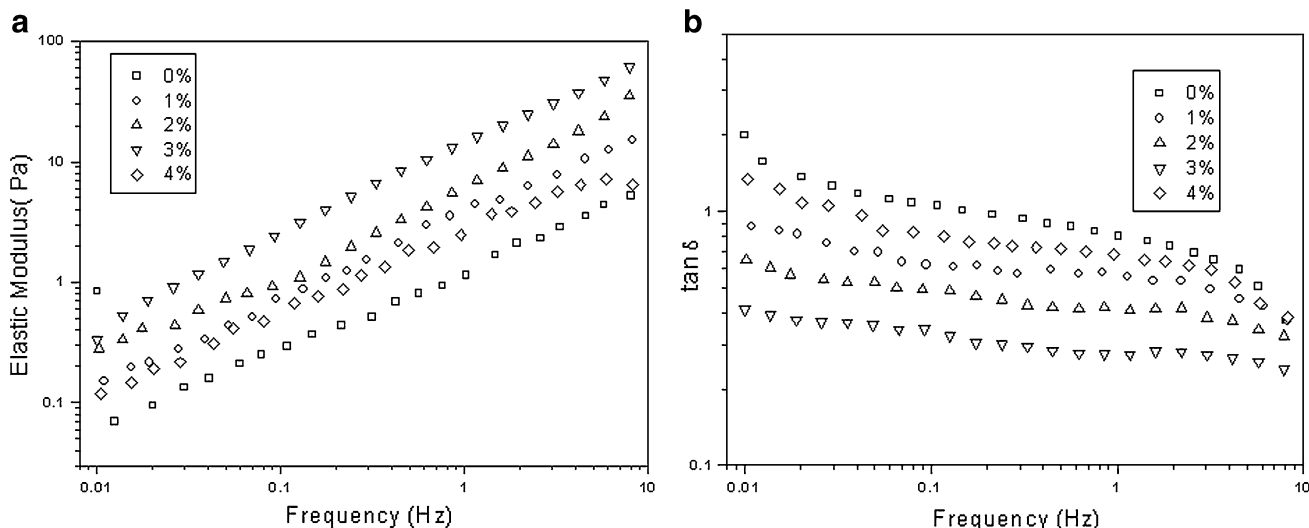


Fig. 1 Rheological properties of LPAM hydrogel filled with different amounts of silica (**a** G' curve vs frequency and **b** $\tan\delta$ curve vs frequency)

rheological behaviors of the hydrogel were measured to study the differences.

Figure 1 showed the rheological curves of the LPAM hydrogel (uncrosslinked), which was filled with different contents of hydrophilic H-T40 silica. It is clear that the G' increases when the silica content rises from 0 to 3 % and decreases when the silica content rises to 4 %. The $\tan\delta$ curves of LPAM are shown in Fig. 1b. When the silica content is 3 %, the $\tan\delta$ reaches the smallest. It has been proved that $\tan\delta$ can reflect the crosslink degree of the CPAM hydrogel (Rubinstein and Colby 2003; Wu and Wu 2002). The smaller the $\tan\delta$ is the bigger crosslink degree of the network is. So, from Fig. 1b it can be deduced that silica can act as the crosslink points in the secondary networks generated from the hydrogen bond between polyacrylamide and silica, and the secondary networks improved the elasticity of the hydrogel. However, when the silica content increased further, the excessive silica might play a role as the polymerization inhibitor, which caused the crosslink reaction incomplete and the network incomplete. The inhibited reaction had also been found during the polymerization. When the content of silica was 4 % wt, after reaction there was some dilute solution in the three-necked flask, which did not react and the phenomenon was not found when the content was 0–3 %.

The steady-state viscosity (η) curves of silica-filled LPAM hydrogel are showed in Fig. 2. It can be seen that with the increase of silica from 0 to 3 %, the η continues to increase; however, with the further increase of the silica content, the η goes down. The reason is consistent with that of the increase in G' . From the results above, it can be concluded that the silica could improve the G' and viscosity of the hydrogel indeed, which could also be an

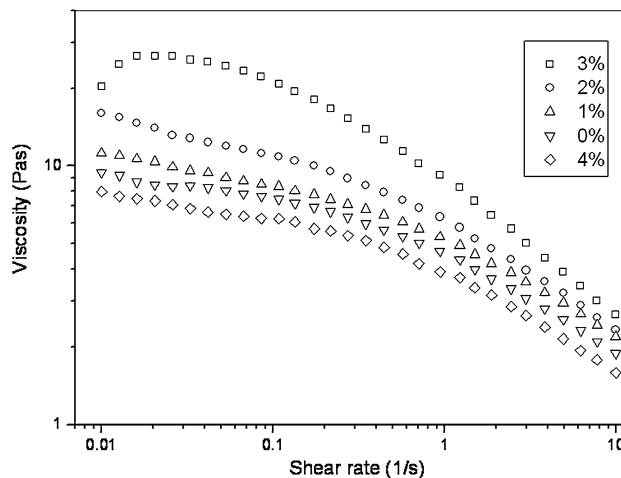


Fig. 2 Steady-state viscosity of silica-filled LPAM hydrogel

evidence for that the increase of silica would be effective to the improvement of elasticity of the hydrogel.

Figure 3 showed rheological curves of CPAM hydrogel crosslinked with PEGDA-400 filled with different contents of silica. The change trend of G' and $\tan\delta$ is similar as that of hydrogel without crosslink one, which means that the addition of silica can improve the crosslink network no matter there is chemical crosslinking points or not.

Rheological properties of LPAM hydrogel and CPAM hydrogel filled with different kinds of silica

The difference of specific area and methanol value of the four silica is shown in Table 1. The content of –OH of the hydrophobic silica can be represented by the methanol value, which is the possessive volume of 1 g hydrophobic

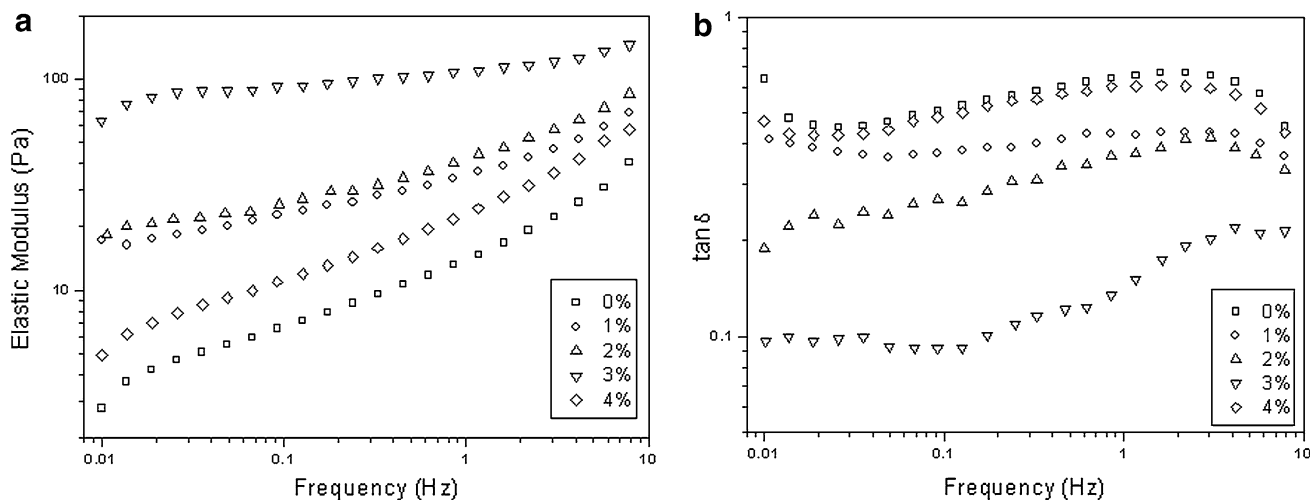


Fig. 3 Rheological properties of CPAM hydrogel filled with different amounts of silica (**a** G' curve vs frequency and **b** $\tan\delta$ curve vs frequency)

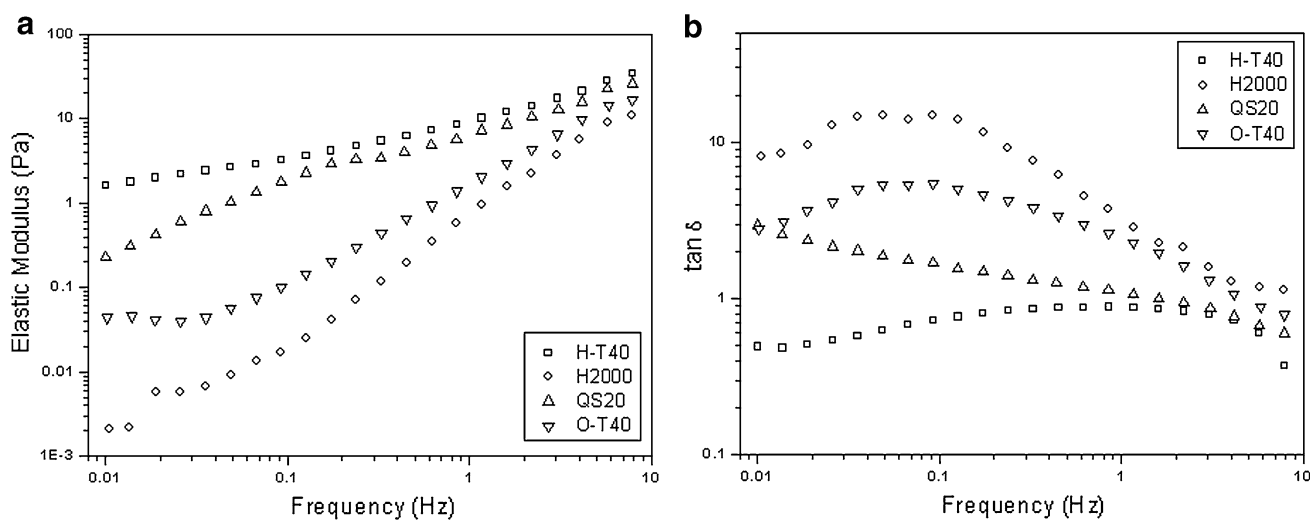


Fig. 4 Rheological properties of LPAM hydrogel filled with different types of silica (**a** G' curve vs frequency and **b** $\tan\delta$ curve vs frequency)

silica dispersed in water. H-T40 and QS20 are hydrophilic, and the other two are hydrophobic.

Figure 4 showed rheological curves of LPAM hydrogel filled with different types of silica. It is obvious that the more hydrophilic the silica is, the larger the G' is, i.e., G' of hydrogel filled with H-T40 or QS20 is larger than that with H2000 or O-T40. The reason can be attributed that the hydrophilic silica has more $-\text{OH}$ and they could combine with the polymer matrix better than the hydrophobic silica with less $-\text{OH}$ does, so the crosslink networks formed more completely, resulting in a larger G' . It also can be found from Fig. 4a that G' of hydrogel with H-T40 and O-T40 is larger than that with QS20 and H2000, respectively, which indicates the specific area of silica plays another important role in forming secondary network. That is, the silica with larger specific area has more $-\text{OH}$ and stronger capability

to combine with the polyacrylamide matrix, so the network becomes more complete and the G' larger.

The effects of different types of silica on the CPAM hydrogel are similar as those of LPAM hydrogel, which is shown in Fig. 5. It could be concluded that the hydrophilic silica with larger specific area can effectively form secondary crosslink network and improve the mechanical properties of the hydrogel for both chemical crosslinked and uncrosslinked system of polyacrylamide.

The zero-shear viscosity and flow index of the CPAM hydrogel filled with different contents of H-T40

To study the effect of incorporation silica on the behaviors of the hydrogel, the viscosity–shear rate curves are

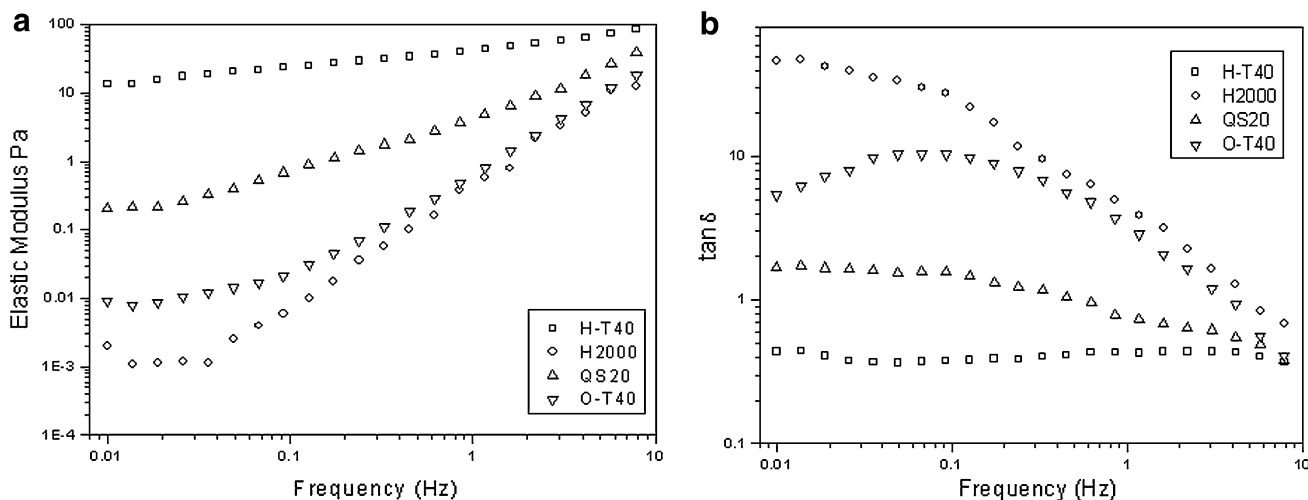


Fig. 5 Rheological properties of CPAM hydrogel filled with different types of silica (**a** G' curve vs frequency and **b** $\tan \delta$ curve vs frequency)

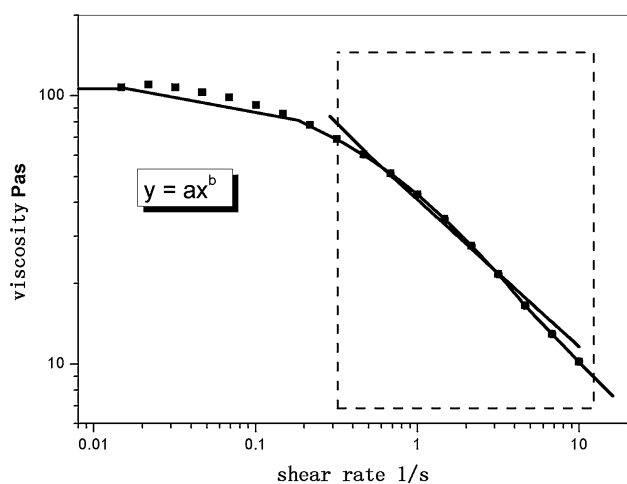


Fig. 6 Extrapolation and fit of rheological curves of CPAM hydrogel filled with 1 % H-T40 and absorbed 20 times water

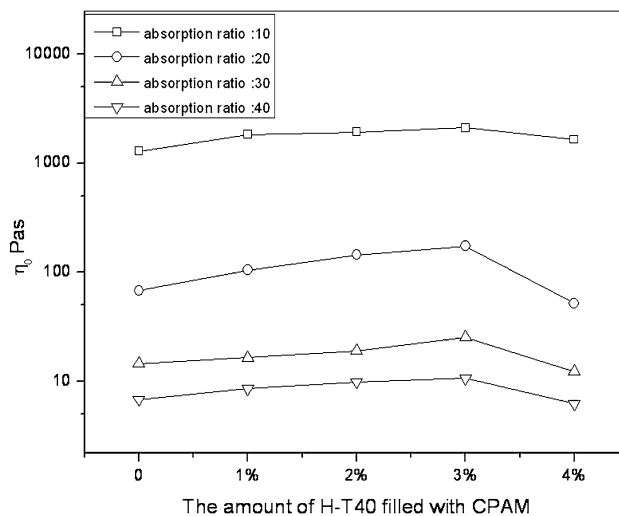


Fig. 7 η_0 of CPAM hydrogel filled with H-T40 silica of different water absorbency

measured. The rheological behaviors of the hydrogel could be express by $\tau = f(\dot{\gamma})$. And the viscosity–shear rate curve could be fit by Ostwald–de Waele power-law equation (Han 1976).

$$\eta = k\dot{\gamma}^{n-1}$$

Here η is viscosity, k a constant and n the flow index. When the shear rate of the curve $\eta = f(\dot{\gamma})$ is extrapolated to zero, η_0 was obtained. η_0 was the zero-shear viscosity value, which is not affected by the shear rate but by the molecular structure and conformation. So the η_0 can be an evidence of the molecular weight and the molecular interaction. While it is Newton flow, the value of n is 1. The more the departure of the value of n from 1, the more the trend towards the non-Newton flow. So the value of n can be an evidence of the degree

of nonbonded complexation between silica and polyacrylamide.

According to the test method above (Fig. 6), the η_0 and n of the CPAM hydrogel filled with H-T40 silica of different water absorbency ratio was shown in Figs. 7 and 8. Obviously, with the increasing content of H-T40 from 0 to 3 %, η_0 increases and n decreases, indicating the storage modulus of the hydrogel increase. When the content of H-T40 arrives to 4 %, the value of n increases, the reason is similar to that of G' . It is also found in Figs. 7 and 8 that with the increase of water absorbency, η_0 decreases and n increases. It is a result of the competition complex between polyacrylamide–silica and polyacrylamide–water. Obviously the secondary network between polyacrylamide and silica is stronger than the interaction between polyacrylamide and water.

FTIR evidence and model of nonbonded complex

From the results of rheological measurements of LPAM and CPAM hydrogel filled with silica, the nonbonded secondary complexation between silica and molecular

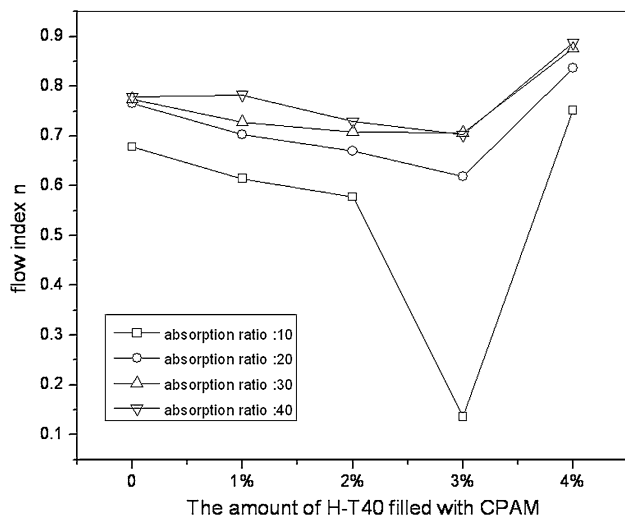


Fig. 8 n of CPAM hydrogel filled with H-T40 silica of different water absorbency

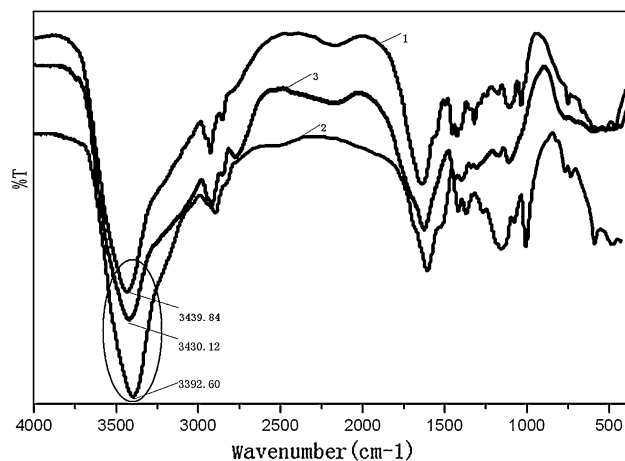
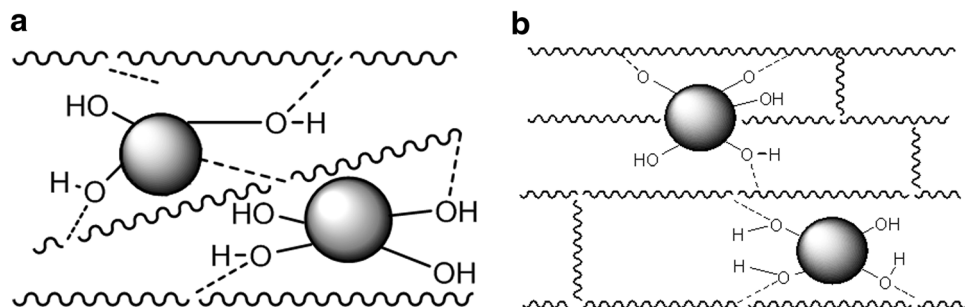


Fig. 9 FTIR spectrum of CPAM samples with different contents of silica (1 silica content: 0, 2 silica content: 1 %, and 3 silica content: 3 %)

Fig. 10 Sketch of the association between silica and polymer chain for LPAM hydrogel (a) and CPAM hydrogel (b)



chains of polyacrylamide is put forward and proved indirectly. To directly prove existence of the nonbonded complexation, the FTIR was used to test the CPAM hydrogel filled with silica. As can be seen in Fig. 9, for the sample without silica, the stretching vibration of $-\text{NH}_2$ appears at 3439.84 cm^{-1} . The stretching vibration of $-\text{NH}_2$ can be found at 3392.60 cm^{-1} for the samples filled with silica which indicates a phenomenon of red shift. Simultaneously, in the same FTIR spectra the symmetric and asymmetric vibration of Si-O groups appear at about 1050 and 1180 cm^{-1} , respectively. It is evident that more the content of silica, the bigger the red shift, which implies that some associations must be generated, i.e., one kind of nonbonded complex network, between the $-\text{NH}_2$ groups on the polyacrylamide molecular chain and the $-\text{OH}$ on the surface of silica. Based on the conclusion above, a sketch for explaining association between polyacrylamide chain and silica particles was illustrated in Fig. 10. With the increase of the silica content, more silica combines with the polyacrylamide matrix which makes the polyacrylamide network become more complete, resulting in G' increase. However, when the silica content goes up further, the excessive silica might play a role as the polymerization inhibitor, which makes the crosslink reaction incomplete and the network imperfect, so the G' decreases. From the FTIR results, we have known that the silica has strong association with the polyacrylamide matrix.

Conclusions

Hydrogel of polyacrylamide filled with different types and contents of silica was successfully prepared by aqueous polymerization. The results of rheological measurements indicated that with the increase of silica content, the secondary network forms more completely. But the excessive silica might play a role as the polymerization inhibitor, which caused the crosslink reaction incomplete and the network incomplete. And the hydrophilic silica with larger specific area can effectively form secondary crosslink network and improve the mechanical properties of the hydrogel for both chemical crosslinked and uncrosslinked

system of polyacrylamide. The above conclusions were proved by FTIR tests.

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