



## Technical Note

## Improved mechanical and swelling behavior of the composite hydrogels prepared by ionic monomer and acid-activated Laponite

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## ABSTRACT

A composite hydrogel (CH) with much improved mechanical and swelling properties was prepared using an ionic monomer and acid-activated Laponite XLS which was used as a cross-linking agent. Addition of acid-activated clay solved the gelation problem when ionic monomers were added to clay mineral dispersions. Reaction of Laponite XLS with sulfuric acid yielded amorphous silica. A dispersion of the acid-activated Laponite and the monomers was used to synthesize composite hydrogels by in-situ polymerization. The FT-IR spectra and rheological results of the composite hydrogels demonstrated the formation of a network. The equilibrium swelling ratios of composite hydrogels (>6000 g/g) were more than 18 times larger than traditional organic cross-linked hydrogels. The moduli  $G'$  and  $G''$  in the observed frequency range were about 4 and 10 times larger than those of organic cross-linked hydrogel (OR gel). The improvement in both the equilibrium swelling ratio and mechanical strength was attributed to the homogeneous cross-linked network structure.

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## 1. Introduction

Hydrogels consisting of three-dimensional polymer networks filled with water have attracted considerable attention as functional soft materials. Hydrogels were used in many fields, such as contact lenses, superabsorbent polymeric gels, carriers for proteins and nucleic acids in gel electrophoresis, amendments in greening and agriculture, medical and food products, etc. (Matsumoto et al., 2004; Akashi et al., 2002; Hellweg et al., 2000). Most conventional hydrogels are cross-linked by organic compounds. However, an inhomogeneous randomly cross-linked network often makes the hydrogel weak and fragile, which limit its application seriously (Kim et al., 1995).

Several attempts were made to design hydrogels with improved mechanical properties (Okumurs and Ito, 2001; Gong et al., 2003). Recently, three new hydrogels with excellent mechanical properties (Tanaka et al., 2005) were prepared: a 'topological gel (TP gel)' using figure-of-eight cross-linkers (Okumurs and Ito, 2001), a 'nanocomposite gel (NC gel)' using a Hectorite as cross-linker (Haraguchi and Takehisa, 2002), and a 'double network gel (DN gel)' by interpenetrating polymer networks (IPN) (Gong et al., 2003). Compared with the other two gels, the NC gel had the advantage of simplicity of

synthesis. However, it is very difficult to prepare NC hydrogels containing ionic groups. When ionic monomers are added, the viscosity of the clay mineral dispersion increases significantly due to the aggregation of the clay mineral particles which inhibits polymerization. Application of ionic monomers in hydrogels limited the weak mechanical stability. It is a challenge to prepare NC hydrogels with ionic monomers.

In order to solve the problem, quaternary ammonium ions containing two double bonds were added as co-monomers or intercalating agents (Zhang et al., 2005; Xu et al., 2007). However, anionic NC gels cannot be prepared in this way.

Reaction of Laponite with acids yields amorphous silica with high specific surface area, pore volume and surface charge density (Van Rompaey et al., 2002; Madejova, 2003; Komadel and Madejová, 2006). Another possibility is to prepare hydrogels by cross-linking with acid-activated clay minerals. Due to the large specific surface area and high surface charge density, sufficient amounts of the initiator can be adsorbed so that a network structure forms without an organic cross-linker.

## 2. Experimental

## 2.1. Materials

Acrylic acid (AA) (TCI, Japan), N,N'-methylene-bis-acrylamide (Sigma, reagent grade), N,N,N',N'-tetramethylethylenediamine (TEMED)

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(TCI, Japan), potassium persulfate (KPS, TCI, Japan), potassium hydroxide (KOH) (Junsei Chemical, Japan), and concentrated  $\text{H}_2\text{SO}_4$  (98% assay, Duksan Pure Chemicals, Korea) were used as received. Synthetic Laponite XLS (92.32 mass%  $\text{Mg}_{5.34}\text{Li}_{0.66}\text{Si}_8\text{O}_{20}(\text{OH})_4\text{Na}_{0.66}$  and 7.68 mass%  $\text{Na}_4\text{P}_2\text{O}_7$ ) was provided by Rockwood Co., USA. Distilled water was used in all experiments.

## 2.2. Acid-activation of Laponite

Amounts of 2 g Laponite XLS were dispersed in sulfuric acid solutions of different concentrations. After stirring for 10 h at room temperature, the sample was washed with distilled water on an aspirator until the washings showed no acidity (Table 1).

## 2.3. Synthesis of the hydrogels

The acid-activated Laponite was dispersed in 50 ml water, which was followed by the addition of 16.7 ml AA and 4.15 g KOH. The dispersion was ultrasonicated for 30 min, then stirred for 12 h. After standing for 10 min, a part of the activated Laponite settled on the bottom and the supernatant (40 ml) was separated to remove  $\text{O}_2$  from the dispersion,  $\text{N}_2$  gas was bubbled for 3 h. Finally, 0.06 g KPS and 48  $\mu\text{L}$  TEMED were added. Polymerization was performed in airtight glass tubes in a water bath at 30 °C for 24 h.

The same amounts of AA, KOH,  $\text{H}_2\text{O}$  and 0.06 g NMBA solution were used to prepare the organic cross-linked poly(potassium acrylate) gel (OR gel). After bubbling  $\text{N}_2$  gas, the initiator KPS (0.06 g) and catalyst TEMED (48  $\mu\text{L}$ ) were added, polymerization was carried out under the same conditions described above.

## 2.4. Characterization

The Fourier transform infrared (FT-IR) spectra of KBr pellets were recorded on a Nicolet 6700 spectrometer at 4000–400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  over 40 scans.

The X-ray diffraction (XRD) patterns of the Laponite and dried gel were recorded on a Rigaku D/max 2500 Diffractometer, Tokyo, Japan at 40 kV, 30 mA,  $\text{Cu-K}\alpha$ . The samples were scanned in the  $2\theta$  2–50° range at a scanning speed of 4°/min.

## 2.5. Swelling behavior of the hydrogels

A gravimetric procedure was used to monitor the swelling behavior of the composite hydrogels in distilled water. Briefly, a known mass of the hydrogel (0.1 g) was immersed in a large amount of distilled water (800 ml) at 20 °C. The hydrogel was separated by filtration at regular intervals to measure the mass change. The measurements were continued until a constant mass was reached. The swelling degree (water uptake) ( $Q$ ) was calculated from the mass changes related to the dried hydrogel.

## 2.6. Rheological characterization

The rheological measurements (storage modulus  $G'$  and loss modulus  $G''$ ) were performed with a HAAKE RheoStress 1 Rotational Rheometer. The specimens for rheological testing were cut by hand into a disk shape with the approximate thickness and diameter of

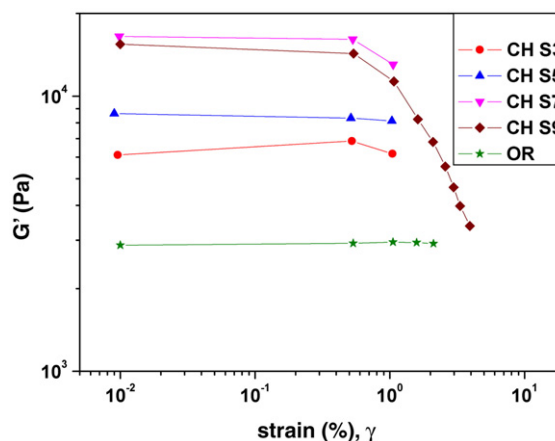


Fig. 1. Strain sweeps of the hydrogels.

2.5 mm and 20 mm. The samples were measured between two horizontal parallel stainless steel plates of 20 mm diameter. Each test was repeated 7 times, and the average values were reported.

Fig. 1 reveals the linear viscoelastic range of  $G'$  at  $\omega = 0.1$  rad/s. Based on Fig. 1,  $\gamma = 0.1$  was chosen for the subsequent frequency sweeps.

## 3. Results and discussion

### 3.1. Formation of the network structure

As expected (Komadel and Madejová, 2006, pp. 263–281), the dispersion of Laponite in sulfuric acid solutions transforms the clay mineral into an amorphous product (Fig. 2). In the FT-IR spectra, the band at 1008  $\text{cm}^{-1}$ , assigned to Si–O vibrations of the tetrahedral sheet, disappeared by acid-activation. The new band at 1070  $\text{cm}^{-1}$  indicated the Si–O vibrations of amorphous silica. Another characteristic band of amorphous silica appeared at 794  $\text{cm}^{-1}$  (Komadel et al., 1996). The band at 649  $\text{cm}^{-1}$ , assigned to the  $\text{Mg}_3\text{OH}$  bending vibration of Laponite, also disappeared after the acid-activation (Fig. 3).

Fig. 4 shows the FT-IR spectra of composite hydrogels and the pure polymer hydrogel, and Table 2 lists the band assignments for the hydrogels. The spectra of the composite hydrogels contained all bands of the pure polymer. The disappearance of the band at around 1070  $\text{cm}^{-1}$  in the spectra of composites, corresponding to the stretching vibration of the Si–O bond, indicated reactions between the  $-\text{COO}-$  and the  $-\text{OH}$  groups on the silica surface. This was also

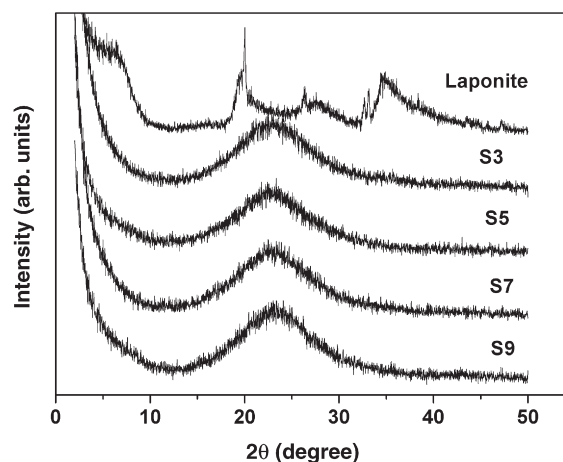


Fig. 2. XRD pattern of Laponite and acid-activated Laponite.

Table 1  
Sulfuric acid concentrations for acid-activation of Laponite.

	S3	S5	S7	S9
$\text{H}_2\text{O}$ (mL)	47	45	43	41
$\text{H}_2\text{SO}_4$ (mL)	3	5	7	9
Clay (g)	2	2	2	2

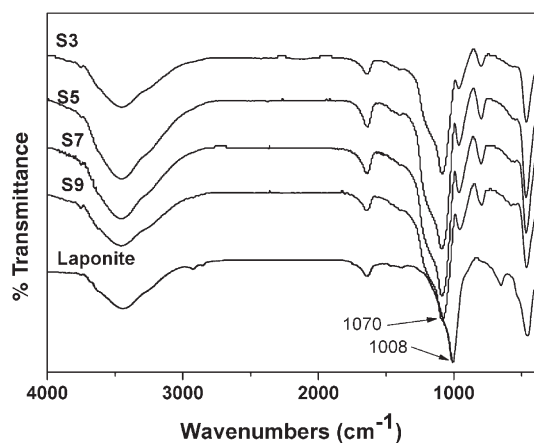


Fig. 3. FT-IR spectra of Laponite with and without the acid-treatment.

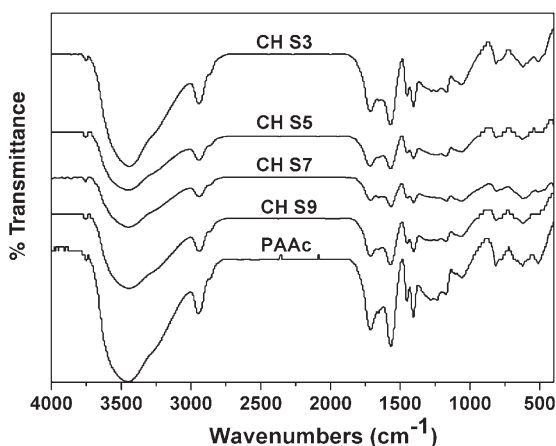


Fig. 4. FT-IR spectra of the hydrogels.

demonstrated by the decrease in the vibrations of the  $-\text{COO}$  groups at  $1711$ ,  $1557$  and  $1403\text{ cm}^{-1}$ . The intensity of the peaks decreased with increasing silica content. Therefore, according to the intensity of the bands, the silica content in the composite hydrogels decreased as:  $\text{CH S7} > \text{CH S5} > \text{CH S9} > \text{CH S3}$ .

Fig. 5 shows plots of  $G'$  ( $f$ ) and  $G''$  ( $f$ ) for the hydrogels.  $G'$  was always higher than  $G''$  in the observed frequency range, and  $G'$  appeared as a plateau in the low frequency range for all composite hydrogels. This suggests that the cross-linked network was formed without an organic cross-linking agent (Xiong et al., 2008). As CH S7 had the highest values of  $G'$  and  $G''$ , the content should be highest in CH S7 in agreement with the FT-IR results.

Based on FT-IR and rheological measurements, we concluded that the polymer network was cross-linked by the silica particles (acid-activated Laponite).

**Table 2**  
FT-IR band assignments for the composite hydrogels.

Maxima ( $\text{cm}^{-1}$ )	Assignments
3456	$-\text{OH}$ and $-\text{NH}$ stretching
2938	$-\text{CH}$ stretching of acrylate
1711	$-\text{CO}$ stretching of acrylate
1557	$-\text{CO}$ stretching of $\text{COO}-$
1403	$-\text{CO}$ stretching of $\text{COO}-$
1070	$\text{Si}-\text{O}$ stretching

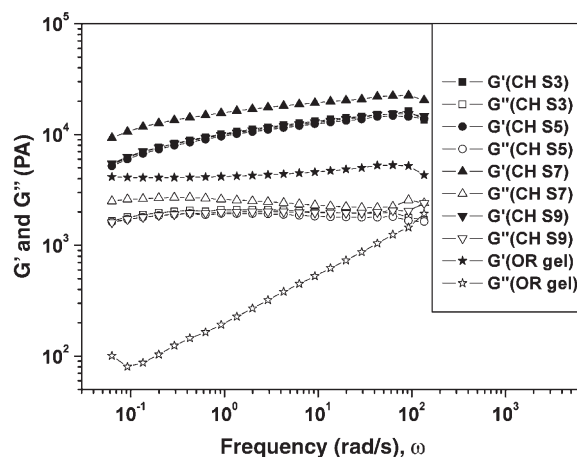


Fig. 5. Frequency sweeps of  $G'$  and  $G''$ .

### 3.2. Swelling behavior of the hydrogels

The equilibrium swelling ratio of the composite hydrogels was much larger than that of the OR gel (Fig. 6). Even the smallest swelling ratio of CH S7 (6000 g/g) was approximately 18 times higher than that of the OR hydrogel. As the silica particles were dispersed uniformly in the monomer solution, the network formed after polymerization was homogeneous compared to the OR hydrogel, and the chains between the particles were mobile. This structure was similar to that of NC gels. The osmotic pressure of the composite hydrogel was also increased due to the increased charge density of the activated Laponite particles, which is another factor for improving the equilibrium swelling ratio. The equilibrium swelling ratios of all CH hydrogels were similar, and only that of CH S7 was slightly smaller. The degree of cross-linking was highest in CH S7 due to the highest silica content.

### 3.3. Mechanical properties

Fig. 7 shows the shape of the CH S5 (Fig. 7(a)) and OR gel (Fig. 7(c)) before and after rolling by a small bottle. CH S5 sample recovered after rolling (Fig. 7(b)), while the OR gel sample was broken (Fig. 7(d)). The magnitude of  $G'$  indicates the impressive strength (or "stiffness") of these materials, while the  $G''$  indicates the mechanical energy-damping ability (Guo et al., 1999). Due to the highest  $G'$  and  $G''$  values (Fig. 5) of CH S7, the mechanical strength was also highest for CH S7. All composite hydrogels showed a higher mechanical strength (expressed by the moduli) than the OR gel.

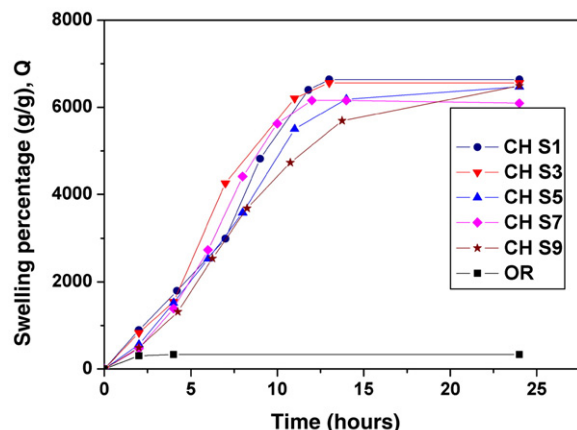


Fig. 6. Time-dependent swelling profiles of the hydrogels.

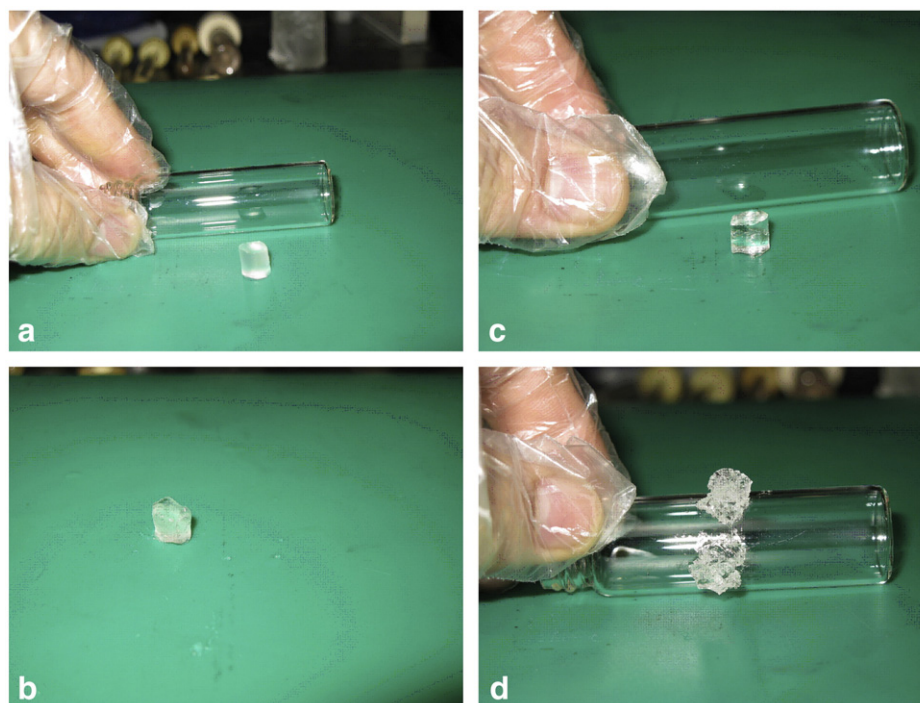


Fig. 7. Photographs of the CH S5 and OR gel before and after rolling; (a) CH S5 (before rolling), (b) CH S5 (after rolling), (c) OR gel (before rolling), and (d) OR gel (after rolling).

#### 4. Conclusions

The composite hydrogels cross-linked with acid-activated Lapo-nite particles were prepared. The FT-IR spectra and rheological measurements indicated the formation of a network structure. Due to this homogeneous network formation, the equilibrium swelling ratio of the composite hydrogels was distinctly higher than that of the conventional gels cross-linked by organic molecules (OR gels). The higher  $G'$  and  $G''$  values of the composite hydrogels indicated higher mechanical strength compared to the OR gels.

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